Handbook of Inorganic Chemicals

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Preface

This handbook is an encyclopedic treatment of chemical elements and their most important compounds intended for professionals and students in many areas of chemistry throughout the manufacturing, academic, and consulting communities. Chemicals are presented in alphabetical order in a descriptive format highlighting pertinent information on physical, chemical, and thermodynamic properties of chemicals, methods of preparation, industrial applications, chemical analyses, and toxic and hazardous properties. Synonyms, CAS Registry Numbers, brief history of discovery and natural occurrence are provided for many entries. The objective is to provide readers a single source for instant information about important aspects each substance. In this sense it should serve as a combination handbook and encyclopedia.

Readers may note three unique features in this text. First, there is a substantial discussion of chemical reactions of all elements and many of their compounds, a practice abandoned nowadays by most modern reference and handbooks. Second, analytical methods are presented for identification and measurement of practically all entries. In many instances, the method is based on my own research and experience. Third, a preparation method is given for all entries. For most compounds, more than one preparative method is presented, covering both laboratory and commercial production. Also, a brief history of the discovery and early production of selected elements is presented to serve as background against which modern methods may be judged and historical perspective maintained.

It has been a hard task indeed to select a limited number of compounds from among over one hundred thousand inorganic chemicals used in industry. Because of space limitations, only a small number have been selected as main entries, but many more have been cited under each entry.

I hope that you find this book useful, and that you will let the publisher and me know how we may make it more useful to you.

Pradyot Patnaik,
Burlington, NJ.
November, 2001

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Introduction

All of the elements and many important compounds are presented in this reference. Substances are arranged in alphabetical order. Each entry topic is discussed briefly below.

Elements

Chemical names are followed by Chemical Abstract Service (CAS) registry numbers. This is followed by symbols, atomic numbers, atomic weights, group numbers in the Periodic Table (the older but more common CAS system and the present IUPAC Group numbers given in parentheses), electron configuration, valence states, most stable oxidation states, and atomic and ionic radii. Naturally occurring stable isotopes, abundance, artificial radioactive isotopes and longest- and shortest-lived radioisotopes with half-lives are presented for all elements. Additionally for many elements, electronegativity and standard electrode potential data are presented.

The next section under "Elements" is subtitled "History, Occurrence and Uses." This includes a brief history of chemical discoveries and the origin of their names and symbols, natural occurrence, principal minerals, abundance in the earth's crust and in sea water and principal uses. Uses include commercial applications, preparative reactions, analytical applications and other laboratory reactions. More general information is provided in this section.

The "Physical Properties" are listed next. Under this loose term a wide range of properties, including mechanical, electrical and magnetic properties of elements are presented. Such properties include color, odor, taste, refractive index, crystal structure, allotropic forms (if any), hardness, density, melting point, boiling point, vapor pressure, critical constants (temperature, pressure and volume/density), electrical resistivity, viscosity, surface tension, Young's modulus, shear modulus, Poisson's ratio, magnetic susceptibility and the thermal neutron cross section data for many elements. Also, solubilities in water, acids, alkalies, and salt solutions (in certain cases) are presented in this section.

Under the title "Thermochemical Properties," both thermodynamic and thermal properties appear. These include thermodynamic properties, enthalpies of formation, Gibbs free energy of formation, entropies and heat capacities, and thermal properties such as thermal conductivities, coefficient of linear expansion, heat of fusion, and the heat of vaporization.

Under the "Recovery" or "Production" mining of ores, ore opening, separation, and isolation into pure elements are touched upon briefly.

The "Reactions" section highlights only important reactions that include formation of binary compounds, oxo salts, and complexes.

The "Analysis" section includes qualitative identification and quantitative measurement of the element in free elemental form or its compounds and alloys.

"Toxicity" or "Hazard" sections are presented last to illustrate dangerous properties of elements and compounds that are toxic, flammable, explosive, or otherwise harmful.

Compounds

Compounds of the elements are also presented in similar format. This includes CAS Registry Numbers, formulas, molecular weights and the hydrates they form (if any). This is followed by occurrence (for naturally occurring compounds) and industrial applications. The section on "Physical Properties" covers the color, crystal structure, density, melting and boiling points and solubilities of the compounds in water, acids, alkalies and organic solvents.

"Thermochemical Properties" mostly covers heats of formation, Gibbs free energy, entropies, and heat capacities. For many compounds, heats of fusion and vaporization are included.

Under the heading "Preparation" or "Production," preparative processes are described briefly. Chemical equations are shown wherever applicable. While "Preparation" refers to laboratory method or a general preparative method, the term "Production" refers to commercial manufacturing processes. For many compounds both historical preparative methods and those in common use are described.

The section "Analysis" starts with elemental composition of the compound. Thus the composition of any compound can be determined from its elemental analysis, particularly the metal content. For practically all metal salts, atomic absorption and emission spectrophotometric methods are favored in this text for measuring metal content. Also, some other instrumental techniques such as x-ray fluorescence, x-ray diffraction, and neutron activation analyses are suggested. Many refractory substances and also a number of salts can be characterized nondestructively by x-ray methods. Anions can be measured in aqueous solutions by ion chromatography, ion-selective electrodes, titration, and colorimetric reactions. Water of crystallization can be measured by simple gravimetry or thermogravimetric analysis.

A section on "Toxicity" is presented in many entries for poisonous and carcinogenic substances. If a substance is flammable or explosive or toxic, the section is subtitled "Hazard." Only substances that manifest poisoning effects even at small doses or are highly corrosive, or highly flammable or reactive are mentioned in this section, although most substances can be hazardous at high doses or under unusual conditions.

Definitions

General and Physical Properties

Electron configuration of an atom indicates its extranuclear structure; that is, arrangement of electrons in shells and subshells. Chemical properties of elements (their valence states and reactivity) can be predicted from electron configuration.

Valence state of an atom indicates its power to combine to form compounds. It also determines chemical properties.

Electronegativity refers to tendency of an atom to pull electrons towards itself in a chemical bond. Nonmetals have high electronegativity, fluorine being the most electronegative while alkali metals possess least electronegativity. Electronegativity difference indicates polarity in the molecule.

Ionization potential is the energy required to remove a given electron from its atomic orbital. Its values are given in electron volts (eV).

Isotopes are atoms of the same elements having different mass numbers. Radioisotopes are the isotopes of an element that are radioactive or emit ionizing radiation. All elements are known to form artificial radioactive isotopes by nuclear bombardment.

Half-life of a radioactive isotope is the average time required for one-half the atoms in a sample of radioactive element to decay. It is expressed as $t_{1/2}$ and is equal to:

$t_{1/2} = \ln 2/\lambda$, where λ is a decay constant.

Atomic radius refers to relative size of an atom. Among the main group of elements, atomic radii mostly decrease from left to right across rows in the Periodic Table. Going down in each group, atoms get bigger. Ionic radius is a measure of ion size in a crystal lattice for a given coordination number (CN). Metal ions are smaller than their neutral atoms, and nonmetallic anions are larger than the atoms from which they are formed. Ionic radii depend on the element, its charge, and its coordination number in the crystal lattice. Atomic and ionic radii are expressed in angstrom units of length (Å).

Standard electrode potential is an important concept in electrochemistry. Standard potentials for many half-reactions have been measured or calculated. It is designated as Eϒ and expressed in volts (V). From the values of E° one can predict if a species will be oxidized or reduced in solution (under acidic or basic conditions) and whether any oxidation-reduction reaction will take place.

Solubility data are presented for practically all entries. Quantitative data are also given for some compounds at different temperatures. In general, ionic substances are soluble in water and other polar solvents while the non-polar, covalent compounds are more soluble in the non-polar solvents. In sparingly soluble, slightly soluble or practically insoluble salts, degree of solubility in water and occurrence of any precipitation process may be determined from the solubility product, Ksp, of the salt. The smaller the Ksp value, the less its solubility in water.

Hardness measures ability of substances to abrade or indent one another. Several arbitrary scales have been developed to compare hardness of substances. Mohs hardness is based on a scale from 1 to 10 units in which diamond, the hardest substance, is given a value of 10 Mohs and talc given a value of 0.5.

Vapor pressure is exerted by a solid or liquid in equilibrium with its own vapor. All liquids have vapor pressures. Vapor pressure depends on temperature and is characteristic of each substance. The higher the vapor pressure at ambient temperature, the more volatile the substance. Vapor pressure of water at 20ºC is 17.535 torr.

Refractive index or index of refraction is the ratio of wavelength or phase velocity of an electromagnetic wave in a vacuum to that in the substance. It measures the amount of refraction a ray of light undergoes as it passes through a refraction interface. Refractive index is a useful physical property to identify a pure compound.

Temperature at the critical point (end of the vapor pressure curve in phase diagram) is termed critical temperature. At temperatures above critical temperature, a substance cannot be liquefied, no matter how great the pressure. Pressure at the critical point is called critical pressure. It is the minimum pressure required to condense gas to liquid at the critical temperature. A substance is still a fluid above the critical point, neither a gas nor a liquid, and is referred to as a supercritical fluid. The critical temperature and pressure are expressed in this text in ºC and atm, respectively.

Viscosity is a property of a fluid indicating its resistance to change of form (or resistance to flow). It is expressed as g/cm sec or Poise; 1 Poise = 100 centipoise.

Surface tension occurs when two fluids are in contact with each other. This is caused by molecular attractions between the molecules of two liquids at the surface of separation. It is expressed as dynes/cm or ergs/cm^2.

Modulus of elasticity is the stress required to produce unit strain to cause a change of length (Young's modulus), or a twist or shear (shear modulus), or a change of volume (bulk modulus). It is expressed as dynes/cm^2.

Thermochemical and Thermal Properties

The enthalpy of formation, ΔH_f°, is the energy change or the heat of reaction in which a compound is formed from its elements. Two examples are shown below:

$$Ca(s) + O_2(g) + H_2(g) \rightarrow Ca(OH)_2(s) \qquad \Delta H_{rxn} = -235.68 \text{ kcal}$$

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \Delta H_{rxn} = -22.04 \text{ kcal}$$

The ΔH_f° in the above reactions are –235.68 and –11.02 kcal/mol, respectively. In the second case, the value of ΔH_f° is one-half of ΔH_{rxn} since two moles of NH_3 are produced in the reaction. Also note that ΔH_f° refers to the formation of a compound from its elements only at the standard state (25°C and 1 atm), and not the formation from other compound(s).

The term ΔG_f° refers to the standard free energies of formation of compounds at 25°C and 1 atm. Its relation with enthalpy change, ΔH, and entropy change, ΔS, at a temperature T (in °K) can be expressed as:

$$\Delta G = \Delta H - T\Delta S$$

The value of ΔG_f° can be calculated from the above equation and from other equations also.

Entropy is a thermodynamic quantity that is a measure of disorder or randomness in a system. When a crystalline structure breaks down and a less ordered liquid structure results, entropy increases. For example, the entropy (disorder) increases when ice melts to water. The total entropy of a system and its surroundings always increases for a spontaneous process. The standard entropies, S° are entropy values for the standard states of substances.

Heat capacity, C_ρ is defined as the quantity of thermal energy needed to raise the temperature of an object by 1°C. Thus, the heat capacity is the product of mass of the object and its specific heat:

$$C_\rho = \text{mass} \times \text{specific heat}$$

Specific heat is the amount of heat required to raise the temperature of one gram of a substance by 1°C. The specific heat of water is 1 calorie or 4.184 Joule.

The heat of fusion, ΔH_{fus} is the amount of thermal energy required to melt one mole of the substance at the melting point. It is also termed as latent heat of fusion and expressed in kcal/mol or kJ/mol.

The heat of vaporization, $\Delta H_{vap,}$ is the amount of thermal energy needed to convert one mole of a substance to vapor at boiling point. It is also known as latent heat of vaporization and expressed kcal/mol or kJ/mol.

Thermal conductivity measures the rate of transfer of heat by conduction through unit thickness, across unit area for unit difference of temperature. It is measured as calories per second per square centimeter for a thickness of one centimeter and a temperature difference of 1°C. Its units are cal/cm sec.°K or W/cm°K.

The coefficient of linear thermal expansion is the ratio of the change in length per degree C to the length at 0°C.

Analysis

All metals at trace concentration, or in trace quantities, can be analyzed by atomic absorption (AA) spectrophotometry in flame or graphite furnace (electrothermal reduction) mode. A rapid, multi-element analysis may use advanced instruments available commercially. Also, Inductively Coupled Plasma Atomic Emission Spectrophotometric methods (ICP-AES) are rapid, versatile, and multi-element analytical methods. They offer certain advantages over flame or furnace AA. ICP/MS (mass spectrometry) is the most sensitive technique because it provides a detection level over one hundred times lower than AA or ICP. For all such analyses, solid compounds must be dissolved in water by acid digestion or alkali fusion. Other instrumental techniques for metal analyses include x-ray fluorescence, x-ray diffraction, neutron activation analysis, and ion-specific electrode methods. Also, colorimetric methods that are prone to interference effects may be applied to identify metals in their pure salts.

Anions may be measured best by ion chromatography, using appropriate anion exchange resin columns that are available commercially. Salts may be diluted for such measurements. Ion-selective electrode methods also yield satisfactory results at trace concentrations. Numerous colorimetric methods are reported in literature. They are susceptible to erroneous results when impurities are present. Many titration methods are available in analytical chemistry. They may be applied successfully to measure certain anions, oxidizing and reducing substances, acids, and bases.

Thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) may be used to measure the water of crystallization of a salt and the thermal decomposition of hydrates.

Substances also can be identified from physical properties such as density, melting and boiling points, and refractive index. Elemental analysis can confirm the identity of a compound.

Hazard

Toxicity of many entries are expressed quantitatively as LD_{50} (median lethal dose) or LC_{50} (median lethal concentration in air). The latter refers to inhalation toxicity of gaseous substances in air. Both these terms refer to the calculated concentration of a chemical that can kill 50% of test animals when administered.

A substance is usually termed “flammable” if its flash point is below 100°F (38°C).

Some Physical Constants

Velocity of light, $c = 2.9979 \times 10^{8}$ m/s (in vacuum)
Planck's constant, $h = 1.05457 \times 10^{-34}$ J.s
Rydberg constant, $R_H = 2.17991 \times 10^{-18}$ J
Boltzmann constant, $k = 1.3807 \times 10^{-16}$ erg/K
Acceleration of gravity, $g = 980.6$ cm/s
Electron mass, $me = 9.1094 \times 10^{-31}$ kg
Proton mass, $m_r = 1.6726 \times 10^{-27}$ kg
Neutron mass, $mn = 1.6749 \times 10^{-27}$kg
Proton-electron mass ratio = 1836
Atomic mass unit (amu) = 1.6605×10^{-27} kg
Electron charge, $e = 1.60219 \times 10^{-19}$ C
Faraday constant, $F = 9.648456 \times 10^{4}$ C
Avogadro constant = 6.022×10^{23}/mol
Molar volume at STP = 22.41384 L
Molar gas constant, R = 0.08026 L. atm/mol. K
= 8.3145 J/mol. K
= 1.9872 cal/mol. K

Units and Conversion

Temperature

°C = (°F –32)/1.8
°F = 1.8°C + 32
°K = °C + 273.15

Pressure

1 atm = 101.365 KPa
= 101,365 Pa
= 0.101365 MPa
1 MPa = 9.87 atm
1 atm = 760 torr = 760 mm Hg
1 atm = 14.696 psi
1 KPa = 7.50 torr

Volume

1 L = 1,000 mL
1 mL = 1 cubic centimeter (cc)
1 m^3 = 1000 L
1 gal (US) = 3.784 L
1 quart (qt) = 946.4 mL
1 tablespoon = 14.79 mL
1 teaspoon = 4.93 mL

Energy

1 cal = 4.184 J
1 kcal = 1,000 cal
1 kJ = 1,000 J
1 eV = 1.602×10^{-19} J
1 MeV = 1.602×10^{-13} J

Distance, Bond Length and Atomic Radii

1 km = 1,000 m
1 m = 100 cm or 1,000 mm
1 mm = 1,000 µm
1 µm = 1,000 mm
1 nm = 1,000 pm
1 m = 10^6 mm or 10^9 nm
1 mho = 1 siemen (S)
1 Å = 10^{-10} m
1 Å = 10pm
1 micron = 1 micorometer (µm)

Density

Solid = g/cm^3
Liquid = g/mL
Gas = g/L
Density of gas/vapor at STP = molecular wt(g)/22.4 L
Vapor density (times heavier than air) = molecular wt/29

Concentration

1ppm (w/w) = 1mg/L (in aqueous solution)
1M = mol/L
1N = gram equivalent weight/L
1 m = mol/kg solvent

Miscellaneous

1dyne/cm^2 = 0.10 Pa
1 erg = 10^{-7} J
1 erg/s = 10^{-7}watt (W)
1 Faraday = 96,495 coulomb (C)
1 inch = 2.54 cm
1 mho = 1 siemen (S)
1 ohm.cm = 10^{-2} ohm.cm
1 ohm.cm = 10^6 microhm.cm
1 centipoise = 0.001 Pascal-second
1 centistoke = 1×10^{-6} m^2/sec

Bibliography

Some general bibliographic references follow. Additional references from journals and historical literature have been cited in the text.

1. *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., Vol 1-23, 1970-86; New York: John Wiley & Sons
2. *The Encyclopedia of Chemical Elements*, ed. Clifford A. Hempel, 1968, New York: Reinhold Book Corporation
3. *CRC Handbook of Chemistry and Physics*, 77th ed., edited. David R. Lide, 1999, Boca Raton: CRC Press
4. Cotton, F.A., Wilkinson, G., Murillo, C.A. and M. Bochmann. 1999. *Advanced Inorganic Chemistry*, 6th ed., New York: John Wiley & Sons
5. Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons
6. Lewis(Sr.), R.J. 1996 *Sax's Dangerous Properties of Industrial Materials*, 9th ed. New York: Van Nostrand Reinhold
7. *The Merck Index*, 12thed, edited. Susan Budavery, 1995 Rahway, NJ: The Merk and Company, Inc.
8. American Public Health Association, American Water Works Association and Water Environment Federation. 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Edited Arnold E. Greenberg, Lenore S. Clesceri, and Andrew D. Easton. Washington, DC: American Public Health Association.
9. *The Merck Index*, 12th ed, edited. Susan Budavery, 1995 Rahway, NJ: The Merck and Company, Inc.
10. American Public Health Association, American Water Works Association and Water Environment Federation. 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Edited Arnold E. Greenberg, Lenore S. Clesceri and Andrew D. Easton. Washington, DC: American Public Health Association
11. Patnaik, P. 1997. *Handbook of Environmental Analysis*, Boca Raton: CRC Press
12. Skoog, D.A. West, D.M. and F. James Holler. 1992. *Fundamentals of Analytical Chemistry*, 6th ed. 1992. New York: Saunders College Publishing
13. Silberberg, M. 1996. *Chemistry, The Molecular Nature of Matter and Change*, St. Louis: Mosby
14. H. Remy. 1956. *Treatise on Theoretical and Inorganic Chemistry*, Amsterdam: Elsevier Publishing Company

ABBREVIATIONS AND STANDARD LETTER SYMBOLS

Absorbance (decaidic)	A
Absorption coefficient, linear decaidic	a
Activation energy	E_a
Activity (radioactive)	A
Adjusted retention time	t'_R
Adjusted retention volume	V'_R
Alcohol	alc
Alkaline	alk
Alpha particle	α
Alternating current	ac
Amorphous	am
Amount concentration	c
Amount of substance	n
Ampere	A
Angle of optical rotation	α
Angstrom	Å
Angular dispersion	$d\theta/d\lambda$
Angular velocity	ω
Anhydrous	anhyd
Approximate	ca.
Aqueous solution phase	aq
Area	A
Atmosphere, unit of pressure	atm
Atomic mass unit	amu
Atomic percent	at.%
Atomic weight	at. wt.
Average	av
Average linear gas velocity	μ
Band width	σ^2
Bar, unit of pressure	bar
Barn, cross section (radioactivity)	b
Base of natural logarithms	e
Becquerel	Bq
Bed volume	V_g
Beta particle	β
Bohr magneton	μ_B
Boiling point	bp
Boltzmann constant	k_B
Bragg angle	θ
Butyl	Bu
Calorie, unit of energy	cal
Capacitance	C
Celsius temperature	t
Charge number of an ion	z
Chemical shift	δ
Citrate	Cit
Compare (confer)	cf.
Concentration at peak maximum	$C_{\max}$
Concentration of solute in mobile phase	C_M
Concentration of solute in stationary phase	C_S
Conductance	G
Conductivity	κ
Coulomb	C
Critical temperature	t_c
Cross section	σ
Curie	Ci
Cycles per second	Hz
Dalton (atomic mass unit)	Da
Decay constant (radioactive)	λ
Decompose	dec
Degree of dissociation	α
Degrees Celsius	°C
Density, critical	d_c
Detect, determine(d)	det(d)
Diffusion coefficient	D
Diffusion coefficient, mobile phase	D_M
Diffusion coefficient, stationary phase	D_S
Diffusion current	i_d
Dilute	dil
Direct current	dc
Disintegration per minute	dpm
Distribution ratio	D
Dropping mercury electrode	dme
Electric current	I
Electric potential	V
Electrical resistance	R
Electromotive force	E, emf
Electron	e^-, e
Electronvolt	eV
Equivalent weight	equiv wt, eq wt
et alii (and others)	et al.
et cetera (and so forth)	etc.
Ethyl	Et
Ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid	EDTA

ABBREVIATIONS AND STANDARD LETTER SYMBOLS (*Continued*)

Exempli gratia	e.g.
Exponential	exp
Faraday constant	F
Flowrate, column chromatography	F_c
Freezing point	fp
Gamma radiation	γ
Gas (physical state)	g
Gas constant	R
Gauss	G
Gram	g
Half-life	$t_{1/2}$
Half-wave potential	$E_{1/2}$
Hertz	Hz
Hour	h
Hygroscopic	hygr
ibidem (in the same place)	ibid.
id est (that is)	i.e.
Inch	in*
Inorganic	inorg
Inside diameter	i.d.
Insoluble	insol
In the same place	ibid.
In the work cited	op. cit.
Joule	J
Kelvin	K
Kilo-	k-
Liter	L
Logarithm, common	log
Logarithm, base *e*	ln
Mass absorption coefficient	$\mu/\rho, \mu_m$
Maximum	max
Melting point	mp
Meter	m
Milliequivalent	meq
Millimeters of mercury, pressure unit	mmHg
Millimole	mM
Minute	m, min
Molar	M
Mole	mol
Mole percent	mol %
Molecular weight	mol wt
Neutron	n
Nuclear magnetic resonance	NMR
Ohm	Ω
Organic	org
Outer diameter	o.d.
Oxalate	Ox
Oxidant	ox
Page(s)	p. (pp.)
Partition ratio	k'
Parts per billion, volume	ng/mL
Parts per billion, weight	ng/g
Parts per million, volume	μg/mL
Parts per million, weight	μg/g
Pascal	Pa
Peak resolution	Rs
pH, expressed in activity	paH
expressed in molarity	pH
Phenyl	Ph
Plate number, effective	N_{eff}
Pounds per square inch	psi
Pressure, critical	p_c
Propyl	Pr
Pyridine	py
Radiofrequency	rf
Reductant	red
Retardation factor	R_f
Retention time	t_R
Retention volume	V_R
Saturated	satd
Saturated calomel electrode	SCE
Second	s
Signal-to-noise ratio	S/N
Slightly	sl
Solid	c, s
Soluble	sol
Solution	soln
Solvent	solv
Standard	std
Tartrate	tart
Transit time of nonretained solute	t_M, t_0
Ultraviolet	uv
Vacuum	vac
Velocity	u, w
Versus	vs
Volt	V
Volume	V, v
Volume mobile phase in volume	V_M
Volume per volume	v/v
Weight	W
Weight percent	wt %
Weight per volume	w/v
Zone width at base	W_b
Zone width at one-half peak height	$W_{1/2}$

About the Author

Pradyot Patnaik, Ph.D., is Director of the Laboratory of the Interstate Environmental Commission at Staten Island, NY. He also teaches as an Adjunct Professor at the New Jersey Institute of Technology in Newark, NJ, and Community College of Philadelphia and does his research in the Center for Environmental Science at the City University of New York on Staten Island. His diverse interests include chemical processing, product development, catalysis, reaction mechanisms, environmental pollutants, and mass spectrometry.

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Dr. Patnaik has written two other books, *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, and *Handbook of Environmental Analysis*.

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ACTINIUM

[7440-34-8]
Symbol: Ac; a radioactive element; atomic number 89; atomic weight 227.028; electronic config. $[\mathrm{Rn}]6d^17s^2$; oxidation state +3; the principal isotope is ^{227}Ac, $t_{1/2}$ 21.77 y; emits beta rays forming thorium-227, radium-223 and several short-lived isotopes of radon, polonium, bismuth and lead; a minor isotope is ^{228}Ac, $t_{1/2}$ 6.15 hr, a beta-emitter producing thorium-228; also several other minor isotopes are known which include: ^{225}Ac ($t_{1/2}$ 10 ± 0.1 d), ^{226}Ac ($t_{1/2}$ 1.224 d), ^{224}Ac ($t_{1/2}$ 2.7 hr), ^{229}Ac ($t_{1/2}$ 1.04 hr), ^{231}Ac ($t_{1/2}$ 7.5 min), ^{233}Ac ($t_{1/2}$ 2.4 min), ^{223}Ac ($t_{1/2}$ 2.1 min), ^{230}Ac ($t_{1/2}$ 2.03 min), and ^{232}Ac ($t_{1/2}$ 2.0 min).

Occurrence, Preparation and Uses

Actinium-227 occurs in uranium ore and is a decay product of uranium-235. It is found in equilibrium with its decay products. It is prepared by bombarding radium atoms with neutrons. Chemically, the metal is produced by reducing actinium fluoride with lithium vapor at 1,100°C to 1,300°C.

$$AcF_3 + 3Li \xrightarrow{1{,}100^\circ\ \text{to}\ 1{,}300^\circ C} Ac + 3LiF$$

The element was discovered independently by A. Debierne and F. Giesel in 1899 and 1902, respectively. It is used in nuclear reactors as a source of neutrons.

Physical Properties

Silvery metal; cubic crystal; melts at 1,051°C; vaporizes at 3,198°C; density 10.0 g/cm^3

Chemical Reactions

Actinium behaves like lanthanum forming mostly the trivalent salts of the metal. It is strongly electropositive, the first ionization potential being 5.17eV. Reacts with HCl forming $AcCl_3$; also reacts with organic acids forming corresponding salts; combustion in air can produce oxide and nitride; susceptible to react with CO_2 forming carbonate.

Analysis

The radioactivity can be measured by a beta counter. The metal at trace concentrations can be determined by an atomic absorption or emission spectrophotometer.

Toxicity

Exposure to radiation can cause cancer.

ALUMINUM

[7429-90-5]
Symbol Al; atomic number 13; atomic wt. 26.982; a Group III A (Group 13) metal; principal natural isotope ^{27}Al; electronic config. $[Ne]3s^23p^1$; valence +3

Occurrence and Uses

Aluminum is the third most abundant element in the crust of the earth, accounting for 8.13% by weight. It does not occur in free elemental form in nature, but is found in combined forms such as oxides or silicates. It occurs in many minerals including bauxite, cryolite, feldspar and granite. Aluminum alloys have innumerable application; used extensively in electrical transmission lines, coated mirrors, utensils, packages, toys and in construction of aircraft and rockets.

Physical Properties

Silvery-white malleable metal, cubic crystal; melts at 660°C; b. p. 2520°C; density 2.70 g/cm^3; insoluble in water, soluble in acids and alkalies.

Thermal, Electrochemical, and Thermochemical Properties

Specific heat 0.215 cal/g.°C (0.900 J/g.°C); heat capacity 5.81 cal/mol.°C (24.3 J/mol.°C); ΔH_{fus} (2.54 kcal/mol (10.6 kJ/mol); ΔH_{vap} 67.9 kcal/mol (284 kJ/mol); E° in aqueous soln. (acidic) at 25°C for the reaction
$Al^{3+} + 3e^- \longrightarrow Al_{(s)}$, –1.66V; $S°_{298}$ 6.77 cal/degree mol. K (28.3 J/degree mol.K)

Production

Most aluminum is produced from its ore, bauxite, which contains between 40 to 60% alumina either as the trihydrate, gibbsite, or as the monohydrate, boehmite, and diaspore. Bauxite is refined first for the removal of silica and other impurities. It is done by the Bayer process. Ground bauxite is digested with NaOH solution under pressure, which dissolves alumina and silica, forming sodium aluminate and sodium aluminum silicate. Insoluble residues containing most impurities are filtered out. The clear liquor is then allowed to settle and starch is added to precipitate. The residue, so-called “red-mud”, is filtered out. After this “desilication,” the clear liquor is diluted and cooled. It is then seeded with alumina trihydrate (from a previous run) which promotes hydrolysis of the sodium aluminate to produce trihydrate crystals. The crystals are filtered out, washed, and calcined above 1,100°C to produce anhydrous alumina. The Bayer process, however, is not suitable for extracting bauxite that has high silica content (>10%). In the Alcoa process, which is suitable for highly silicious bauxite, the “red mud” is mixed with limestone and soda ash and calcined at 1,300°C. This produces “lime-soda sinter” which is cooled and treated with water. This leaches out water-soluble sodium alumnate, leaving behind calcium silicate and other impurites.

Alumina may be obtained from other minerals, such as nepheline, sodium potassium aluminum silicate, by similar soda lime sintering process.

Metal aluminum is obtained from the pure alumina at 950 to 1000°C electrolysis (Hall-Heroult process). Although the basic process has not changed since its discovery, there have been many modifications. Aluminum is also produced by electrolysis of anhydrous $AlCl_3$.

Also, the metal can be obtained by nonelectrolytic reduction processes. In carbothermic process, alumina is heated with carbon in a furnace at 2000 to 2500°C. Similarly, in "Subhalide" process, an Al alloy, Al-Fe-Si-, (obtained by carbothermic reduction of bauxite) is heated at 1250°C with AlCl vapor. This forms the subchloride (AlCl), the vapor of which decomposes when cooled to 800°C.

Chemical Reactions

Reacts in moist air forming a coating of Al_2O_3; reacts with dilute mineral acids liberating H_2,

$$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2\uparrow$$

also reacts with steam to form H_2; reduces a number of metals that are less active (in activity series), these include Fe, Mn, Cr, Zn, Co, Ni, Cu, Sn, Pb, etc.,

$$Al(s) + 3Ag^+(aq) \longrightarrow Al^{3+}(aq) + 3Ag(s)$$

Reactions, e.g., with alkyl halides in ether using Ziegler-Natta catalyst form alkyl aluminum halides, $R_3Al_2X_3$, $[R_2AlX]_2$ and $[RAlX]_2$; with bromine vapor forms anhydrous aluminum bromide,

$$2Al + 3Br_2 \longrightarrow Al_2Br_6$$

Combines with iodine vapor forming aluminum iodide, AlI_3; heating with HCl gas produces $AlCl_3$,

$$2Al + 6HCl \xrightarrow{heat} 2AlCl_3 + 3H_2$$

Heating with Cl_2 at 100°C also yields $AlCl_3$,

$$2Al + 3Cl_2 \xrightarrow{heat} 2AlCl_3$$

When the metal is heated with $AlCl_3$ at 1000°C it forms monovalent aluminum chloride, AlCl.

Produces aluminum carbide when the powder metal is heated with carbon at 2000°C or at 1000°C in presence of cryolite,

$$4Al + 3C \xrightarrow{heat} Al_4C_3$$

Heating the metal powder over 1000°C with sulfur, phosphorus, or selenium forms aluminum sulfide Al_2S_3, aluminum phosphide, AlP and aluminum selenide, Al_2Se_3, respectively,

$$2Al + 3S \xrightarrow{heat} Al_2 S_3$$

Heating over 1100°C with N_2 produces nitride, AlN; alkoxides are formed when the metal powder is treated with anhydrous alcohol, catalyzed by $HgCl_2$

$$Al + C_2H_5OH \xrightarrow[xylene]{HgCl_2/I_2} Al(OC_2H_5)_3$$

Reaction with CO at 1000°C produces the oxide Al_2O_3 and the carbide Al_4C_3.

Chemical Analysis

The metal may be analyzed by atomic absorption or emission spectrophotometry (at trace levels). Other techniques include X-ray diffraction, neutron activation analysis, and various colorimetric methods. Aluminum digested with nitric acid reacts with pyrocatechol violet or Eriochrome cyanide R dye to form a colored complex, the absorbance of which may be measured by a spectrophotometer at 535 nm.

Hazard

Finely divided aluminum dust is moderately flammable and explodes by heat or contact with strong oxidizing chemicals. Chronic inhalation of the powder can cause aluminosis, a type of pulmonary fibrosis. It is almost nontoxic by ingestion.

ALUMINUM BROMIDE

[7727-15-3]
Formula $AlBr_3$; MW 266.72; Structure: anhydrous $AlBr_3$ is body-centered crystal, exists in dimeric form as Al_2Br_6 in crystal and also in liquid phases; partially dissociates to monomeric form $AlBr_3$ in gaseous state; mass spectra show the presence of di-, tetra-, and hexameric forms, Al_2Br_6, Al_4Br_{12}, Al_6Br_{18}, respectively.

Uses

The anhydrous form is used as a catalyst for the Friedel-Crafts alkylation reaction. Its catalytic activity is similar to anhydrous $AlCl_3$. Commercial applications, however, are few.

Physical Properties

Colorless crystalline solid in anhydrous form; melts at 97.5°C; boils at 256°C;

density 3.01 g/cm^3 at 25°C; moisture sensitive, fumes in air; soluble in water (reacts violently in cold water, and decomposes in hot water, alcohols, acetone, hexane, benzene, nitrobenzene, carbon disulfide and many other organic solvents).

Preparation

Prepared from bromine and metallic aluminum.

$$2Al + 3Br_2 \longrightarrow Al_2Br_6 \text{ (anhydrous)}$$

Thermochemical Properties

$AlBr_3$ (cry)	$\Delta Hf°$	–126.0 kcal/mc
	Cp	24.3 cal/degree
$AlBr_3$ (gas)	$\Delta Hf°$	–101.6 kcal/mc
$AlBr_3$ (aq)	$\Delta Hf°$	–214.0 kcal/mc
Al_2Br_6 (gas)	$\Delta Hf°$	–232.0 kcal/mc
$AlBr_3$ (aq)	S°	–17.8 cal/degre
Al_2Br_6 (gas)	H_{fusion}	10.1 cal/g

Chemical Reactions

Decomposes upon heating in air to bromine and metallic aluminum.

$$2\,AlBr_3 \xrightarrow{heat} 2Al + 3Br_2$$

Reacts with carbon tetrachloride at 100°C to form carbon tetrabromide;

$$4AlBr_3 + 3CCl_4 \longrightarrow 4AlCl_3 + 3Br_4$$

Reaction with phosgene yields carbonyl bromide and aluminum chlorobromide;

$$AlBr_3 + COCl_2 \longrightarrow COBr_2 + AlCl_2Br$$

Reacts violently with water; absorbs moisture forming hexahydrate, $AlBr_3{\cdot}6H_2O$ [7784-27-2]

Chemical Analysis

Elemental composition, Al 10.11% and Br 89.89%; Al analyzed by AA spectrophotometry or colorimetric methods; Br^- analyzed by iodometric titration or ion chromatography and then calculated stoichiometrically; solid may be dissolved in an organic solvent and determined by GC/MS, identified by mass ions $(AlBr_3)_n$ where n is 2, 4 and 6.

Toxicity

Skin contact can cause tissue burn. It is moderately toxic by all routes of exposure. LD_{50} oral (rat and mouse): ~1600 mg/kg.

ALUMINUM CHLORIDE

[7446-70-0]
Formula: $AlCl_3$; MW 133.31; Structure and bonding: an electron-deficient compound, a Lewis acid, occurs as dimer Al_2Cl_6 in hexagonal crystal form. Above 300 °C, dissociation to monomer $AlCl_3$ begins; completely dissociates to $AlCl_3$ at 1,100°C.

Uses

Aluminum chloride has extensive commercial applications. It is used primarily in the electrolytic production of aluminum. Another major use involves its catalytic applications in many organic reactions, including Friedel-Crafts alkylation, polymerization, isomerization, hydrocracking, oxidation, decarboxylation, and dehydrogenation. It is also used in the production of rare earth chlorides, electroplating of aluminum and in many metal finishing and metallurgical operations.

Physical Properties

White or light-yellow crystalline solid (or amorphous solid depending on the method of production); odor of HCl; hygroscopic; melts at 190°C at 2.5 atm; sublimes at 181.2°C; density 2.44 g/cm^3 at 25°C; decomposes in water evolving heat; soluble in HCl; soluble in many organic solvents, including absolute ethanol, chloroform, carbon tetrachloride and ether; slightly soluble in benzene.

Thermochemical Data

$\Delta H°f(s)$	–168.3 kcal/mol
$\Delta G°f(s)$	–150.3 kcal/mol
$S°$	26.45 cal/deg mol
$H_{soln.}$	–77.7 kcal/mol
H_{fus}	8.45 kcal/mol

Preparation

Aluminum chloride is made by chlorination of molten aluminum at temperatures between 650 to 750°C;

$$2\,Al + 3Cl_2 \xrightarrow{650\text{–}750^\circ C} 2AlCl_3$$

or by chlorination of alumina (bauxite or clay) at 800°C in the presence of a reducing agent, such as carbon or CO. It can be prepared by similar high temperature chlorination of bauxite in the presence of a chlorinated organic reductant such as CCl_4.

A pelletized mixture of clay, lignite and a small amount of NaCl is chlorinated at 900°C, producing gaseous $AlCl_3$ (Toth process). Alternatively, alumina is mixed with about 20% by weight carbon and a small amount of sodium salt. The mixture is chlorinated at 600°C (Bayer process).

In the laboratory, anhydrous $AlCl_3$ can be prepared by heating the metal with dry HCl gas at 150°C. The product sublimes and deposits in the cool air condenser. Unreacted HCl is vented out.

Reactions

Reacts with calcium and magnesium hydrides in tetrahydrofuran forming tetrahydro aluminates, $Ca(AlH_4)_2$; reacts with hydrides of alkali metals in ether forming aluminum hydride;

$$AlCl_3 + 3LiH \xrightarrow{ether} AlH_3 + 3LiCl$$

Hydrolyzes in chilled, dilute HCl forming aluminum chloride hexahydrate, $AlCl_3{\cdot}6H_2O$; reacts violently with water, evolving HCl,

$$AlCl_3 + H_2O \longrightarrow Al(OH)_3 + HCl\uparrow$$

Hazard

Violent exothermic reactions can occur when mixed with water or alkene. Corrosive to skin.

ALUMINUM CHLORIDE HEXAHYDRATE

[7784-13-6]
Formula: $AlCl_3{\cdot}6H_2O$; MW 241.31

Uses

The hexahydrate is used in the preparation of deodorant and antiperspirant. Also, it is applied in textile finishing to improve the antistatic characteristics and flammability ratings of various textile materials. Commercially, it is sold as crystalline powder or as a 28% solution in water.

Physical Properties

White or yellowish deliquescent powder; faint odor of HCl; density 2.40 g/cm^3; soluble in water and polar organic solvents such as alcohol; aqueous solution acidic.

Preparation

Aluminum chloride hexahydrate is prepared by dissolving $Al(OH)_3$ in conc. HCl and passing gaseous HCl through the solution at 0°C. The precipitate is washed with diethyl ether and dried. Alternatively, it is prepared by hydrolyzing anhydrous $AlCl_3$ in cold dilute HCl.

Reactions

Decomposes to alumina when heated at 300°C;

$$2AlCl_3 \bullet 6H_2O \xrightarrow{\text{heat}} 2Al_2O_3 + 6HCl + 9H_2O$$

Reacts with caustic soda solution forming gelatinous precipitate of aluminum hydroxide (hydrous aluminum oxide); yields aluminum monobasic stearate, $Al(OH)_2[OOC(CH_2)_{16}CH_3]$ when its solution is mixed with a solution of sodium stearate.

ALUMINUM HYDRIDE

[7784-21-6]
Formula AlH_3; MW 30.005; Structure: polymeric, containing residual ether;

Uses

It is used as a reducing agent, and also as a catalyst for polymerization reaction.

Physical and Thermochemical Properties

Colorless cubic crystal; very unstable; decomposes in water; $\Delta H°f$ –11.0 kcal/mol (-46.0kJ/mol)

Preparation

Aluminum hydride is prepared by the reaction of lithium hydride with aluminum chloride in diethyl ether

$$3LiH + AlCl_3 \xrightarrow{ether} AlH_3 + 3LiCl$$

Chemical Reactions

Aluminum hydride decomposes in air and water. Violent reactions occur with both. It forms a complex, aluminum diethyl etherate with diethyl ether. The product decomposes in water releasing heat.

$$AlH_3 + (C_2H_5)_2O \longrightarrow H_3Al \cdot O(C_2H_5)_2$$

Similar complexes are likely to form with other lower aliphatic ethers. It also forms a 1:1 complex with trimethyl amine, $H_3Al \cdot N(CH_3)_3$ which reacts explosively with water (Ruff 1967).

Aluminum hydride reduces CO_2 to methane under heating:

$$4\ AlH_3 + 3CO_2 \xrightarrow{heat} 3CH_4 + 2Al_2O_3$$

Reaction with lithium hydride in ether produces lithium aluminum hydride,

$$AlH_3 + LiH \xrightarrow{ether} LiAlH_4$$

Safety

Many reactions of aluminum hydride or its complexes may proceed with explosive violence, especially with water or moist air.

ALUMINUM NITRATE

[13473-90-0]
Formula: $Al(NO_3)_3$; MW 213.00; the anhydrous salt is covalent; also occurs as hydrated salts, $Al(OH)(NO_3)_2$, $Al(OH)_2NO_3$, and the more stable nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$ [7784-27-2]

Uses

The nonahydrate and other hydrated aluminum nitrates have many applications. These salts are used to produce alumina for preparation of insulating papers, in cathode tube heating elements, and on transformer core laminates. The hydrated salts are also used for extraction of actinide elements.

Physical Properties

White or colorless crystalline solid (nonahydrate – rhombic crystal); deliquescent; refractive index 1.54; melts at 73.5°C; decomposes at 150°C; highly soluble in cold water (63.7% at 25°C), decomposes in hot water, soluble in polar organic solvents.

Preparation

The nonahydrate is prepared by treating aluminum, aluminum hydroxide, aluminum oxide, or aluminous mineral with nitric acid. The nitrate is crystallized from the solution.

Reactions

Since $Al(NO_3)_3$ or its salt hydrates dissociates to Al^{3+} and NO_3^- ions in the aqueous solution, its reactions in solutions are those of Al^{3+}. It is partially hydrolyzed, producing H_3O^+ and thus accounting for the acidity of its solution in water. The products constitute a complex mixture of mono- and polynuclear hydroxo species.

Aluminum nitrate is soluble in bases, forming aluminates, $[Al(OH)_4(H_2O)_2]^-$. It decomposes to Al_2O_3 when heated at elevated temperatures.

Chemical Analysis

Elemental composition: Al 12.67%, N 19.73%, O 67.60%. Al may be analyzed by various instrumental techniques, including atomic absorption or emission spectroscopy, or colorimetry (see under Aluminum). The nitrate anion in aqueous phase may be measured by the NO_3^- ion selective electrode, ion chromatography, or reduction with cadmium or hydrazine, followed by colorimetric tests.

ALUMINUM NITRIDE

[24304-00-5]
Formula: AlN; MW 40.99

Uses

Aluminum nitride is used in manufacturing of steel and in semiconductors.

Physical Properties

White crystalline solid, hexagonal; odor of ammonia in moist air; sublimes at 2000°C; melts in N_2 atmosphere over 2200°C; density 3.26 g/cm^3 ; decomposes in water, alkalies and acids

Thermochemical Properties

$\Delta H°f(s)$	–76.0 kcal/mol
$\Delta G°f(s)$	–68.6 kcal/mol
S°	4.82 cal/degree mol
C_ρ	7.20 cal/degree mol

Preparation

Aluminum nitride may be prepared in the laboratory by heating powdered aluminum metal with nitrogen.

$$2Al + N_2 \xrightarrow{heat} 2AlN$$

Commercially, it is made by heating an aluminous mineral, such as, bauxite with coal in a stream of nitrogen.

Chemical Reactions

The nitride reacts with water forming aluminum hydroxide and ammonia.

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

The compound decomposes in alkalies and acids forming products of complex stoichiometry.

Analysis

Elemental composition: Al 65.82%, N 34.18%, the metal is determined by wet analysis or AA spectroscopy. NH_3 liberated on hydrolysis may be determined by titration or colorimetry (see under Ammonia).

ALUMINUM OXIDE

[1344-28-1]

Formula: Al_2O_3; MW 101.96; available or prepared in several forms for various commercial applications. Some of these are (i) α–alumina (corundum), (ii) activated aluminas, such as, γ-alumina, η-alumina and ρ–alumina, (iii) hydrated aluminas including aluminum oxide monohydrate, $Al_2O_3 \cdot H_2O$ and aluminum oxide trihydrate, $Al_2O_3 \cdot 3H_2O$ (natural gibbsite) and, (iv) acidic, neutral and basic aluminas (no definite chemical compositions; made by adding varying amounts of water to activated aluminas)

Occurrence and Uses

Occurs in nature in abundance; the principal forms are bauxites and laterites. The mineral corundum is used to produce precious gems, such as ruby and sapphire. Activated aluminas are used extensively as adsorbents because of their affinity for water and other polar molecules; and as catalysts because of their large surface area and appropriate pore sturcture. As adsorbents, they are used for drying gases and liquids; and in adsorption chromatography. Catalytic properties may be attributed to the presence of surface active sites (primarily OH^-, O^{2-}, and Al^{3+} ions). Such catalytic applications include sulfur recovery from H_2S (Clauss catalysis); dehydration of alcohols, isomerization of olefins; and as a catalyst support in petroleum refining.

Physical Properties

Al_2O_3	Colorless hexagonal crystal; refractive index 1.768; density 3.965 g/cm^3 (at 25°C); mp 2072°C; bp 2980°C; insoluble in water
α-Al_2O_3	Colorless rhombic crystal; mp between 2005 to 2025°C ; density 4.022 g/m^3; hardness 9Moh
γ-Al_2O_3	white microscopic crystal
$Al_2O_3 \bullet H_2O$	colorless rhombic crystal; refractive index 1.624; density 3.014 g/cm^3
$Al_2O_3 \bullet 3H_2O$	white monoclinic crystal; refractive index 1.577; density 2.420 g/cm^3

All forms are insoluble in water.

Thermochemical Properties

ΔH°*f*	– 400.5 kcal/mol (α-alumina)
	– 395.0 kcal/mol (γ-alumina crystal)
	– 390.0 kcal/mol (γ-alumina amorphous)
	– 472.0 kcal/mol ($Al_2O_3 \bullet H_2O$)
	– 612.5 kcal/mol ($Al_2O_3 \bullet 3H_2O$)
ΔG°*f*	– 378.2 kcal/mol (α-alumina)
	– 436.3 kcal/mol ($Al_2O_3 \bullet H_2O$)
	– 546.7 kcal/mol ($Al_2O_3 \bullet 3H_2O$)
S°	12.17 cal/deg mol (α-alumina)
	3.15 cal/deg mol ($Al_2O_3 \bullet H_2O$ (boehmite))
	16.86 cal/deg mol ($Al_2O_3 \bullet H_2O$ (diaspore))
	33.51 cal/deg mol ($Al_2O_3 \bullet 3H_2O$(gibbsite))
C_ρ	18.89 cal/deg mol (α-alumina)
	31.37 cal/deg mol ($Al_2O_3 \bullet H_2O$ (boehmite))
	25.22 cal/deg mol ($Al_2O_3 \bullet H_2O$ (diaspore))
	44.49 cal/deg mol ($Al_2O_3 \bullet 3H_2O$(gibbsite))

Preparation

Pure alumina, needed to produce aluminum by the Hall process, is made by the Bayer process. The starting material is bauxite ($Al_2O_3 \cdot nH_2O$). The ore contains impurities, such as, SiO_2, Fe_2O_3, TiO_2, and Na_2O. Most impurities are removed following treatment with caustic soda solution. Bauxite is dissolved in NaOH solution. Silica, iron oxides and other impurities are filtered out of the solution. CO_2 is then bubbled through this solution. This precipitates out hydrated alumina, which is heated to remove water and produce Al_2O_3. These impurities are removed. Calcinations of bauxite produce alumina of abrasive and refractory grades. Activated aluminas of amorphous type, as well as the transition aluminas of γ, η, χ, and ρ forms, are obtained from various aluminum hydroxides, such as, α- and β-trihydrates, α-monohydrate and alumina gel. Such chemicals are obtained from bauxite by the Bayer process also.

Chemical Reactions

Alumina exhibits amphoteric behavior. It is soluble both in acids and bases. With acids, it produces their corresponding salts. It froms $Al_2(SO_4)_3$, $Al(NO_3)_3$ and $AlCl_3$ upon reactions with H_2SO_4, HNO_3, and HCl, respectively. In acid medium, it exists as a solvated aluminum ion, in which water molecules are hexacoordinated to trivalent Al^{3+}, as shown below:

$$Al_2O_3 + 6H_3O^+ + 3H_2O \longrightarrow 2[Al(H_2O)_6]^{3+}$$

(Rollinson, C. L., 1978., *Aluminum Compounds*. In *Kirk-Othmer Encyclopedia of Chemical Technology,* 3rd ed. Vol 2, pp 188-97. NY,: Wiley Interscience)

Alumina forms hydroxide in aqueous alkaline solution. The reaction is slow. The products, aluminum hydroxides (hydrated aluminas), contain hexacoordinated aluminohydroxide anion:

$$Al_2O_3 + 2OH^- + 7H_2O \rightarrow 2[Al(OH)_4(H_2O)_2]^-$$

In its dry state, alumina exhibiting basicity reacts with silica, forming aluminum silicate

$$Al_2O_3 + 3SiO_2 \rightarrow Al_2(SiO_3)_3$$

Similarly, with basic CaO or MgO aluminate salts are formed

$$MgO + Al_2O_3 \rightarrow Mg(AlO_2)_2$$

$$CaO + Al_2O_3 \rightarrow Ca(AlO_2)_2$$

It forms aluminum nitride, AlN when heated with coal in a stream of nitrogen; and aluminum borate, $Al_2O_3 \cdot B_2O_3$ when heated with B_2O_3 at 1000°C.

Analysis

Elemental composition: Al 52.91%, O 47.08%. Al may be anlayzed by atomic absorption or emission spectrophotometry or by colorimetric methods after acid digestion. Different forms of alumina may be identified by x-ray diffraction analysis. The X-ray crystallogaphic data for the mineral corundum are as follows:

crystal system:	rhombohedral symmetry
space group	R3c
αo	4.7591
χo	12.9894
z	6
x-ray density	3.9869 g/cm^3

Toxicity

Chronic inhalation of Al_2O_3 dusts may cause lung damage.

ALUMINUM PHOSPHATE

[7784-30-7]
Formula: $AlPO_4$; MW 121.95
Synonym: Aluminum orthophosphate

Occurrence and Uses

The compound occurs in nature as the mineral, berlinite. Also, it occurs in nature in minerals, amblygonite, [$NaAl(PO_4)(OH)$]; augelite, [$Al_2(PO_4)(OH)_3$]; lazulite, [$(Mg,Fe)Al_2(PO_4)_2(OH)_2$]; variscite [$(Al,Fe^{3+})(PO_4)\cdot 2H_2O$]; and wavellite, [$Al_3(OH)_3\cdot(PO_4)_2\cdot 5H_2O$]. It is used as flux for ceramics; as cement in combination with calcium sulfate and sodium silicate; and in the manufacture of special glasses. It is also used in dried gel and therapeutically as an antacid.

Physical Properties

White powdery solid (rhombic plate); the mineral berlinite ($AlPO_4$) has hexagonal quartz-like structure; refractive index 1.546; mp > 1,500°C; density 2.566 g/cu^3; insoluble in water and alcohol; K_{sp} 9.83x10^{-10} very slightly soluble in HCl or HNO_3.

Thermochemical Properties

$\Delta H°f(s)$	–414.4 kcal/mol
$\Delta G°f(s)$	–368.7 kcal/mol
S°	166.6 cal/degree mol
C_ρ	22.27 cal/degree mol

Preparation

It is prepared by treating sodium aluminate with phosphoric acid.

$$NaAlO_2 + H_3PO_4 \longrightarrow AlPO_4 + NaOH + H_2O$$

It may be prepared by slowly adding (with stirring) ammonium phosphate (0.2*M*) to a solution of aluminum sulfate (0.1*M*).

$$Al_2(SO_4)_3 + 2(NH_4)_3PO_4 \longrightarrow 2AlPO_4 + 3(NH_4)_2SO_4$$

The compound may, alternatively, be prepared by the reaction of aluminum sulfate with sodium phosphate.

$$Al_2(SO_4)_3 + 2Na_3PO_4 \longrightarrow 2AlPO_4 + 3Na_2SO_4$$

ALUMINUM SULFATE

[10043-01-3]
Formula: $Al_2(SO_4)_3$; MW 342.14

Occurrence and Uses

It occurs in nature in minerals; alunite, $KAl_3(SO_4)_2(OH)_6$ and natroalunite, $NaAl_3(SO_4)_2(OH)_6$. The anhydrous salt is used in food applications.

Physical Properties

White powder; refractive index 1.47; density 2.71 g/cm^3; mp 770°C (decomposes); hygroscopic; readily soluble in water (31% at 0°C; solubility increases with temperature 98% in boiling water); soluble in dilute mineral acids; slightly soluble in alcohol.

Preparation

The anhydrous salt may be obtained by slow and progressive heating of commercial hydrated salt, $Al_2(SO_4)_3 \cdot 18H_2O$. Most water molecules are lost at heating between 250 to 420°C. The last three water molecules are lost between 250 to 420°C at a heating rate of 10°C/min.

Chemical Reactions

The compound decomposes to γ–alumina and SO_3 when heated between 580 and 900°C. It combines with water forming hydrated salts of various compositions.

Produces calcium aluminate with evolution of SO_3 when calcined with $CaCO_4$, (Bayliss, N. S. 1945. *J and Proc. Austral. Chem. Inst.,* 12, 127)

$$Al_2(SO_4)_3 + CaSO_4 \longrightarrow Ca(AlO_2)_2 + 4SO_3$$

Reacts with $NaHCO_3$ in aqueous solution, forming fire-extinguishing foams, producing CO_2, (Albert K. 1937. French Pat. 820,492, November 12, 1937)

$$Al_2(SO_4)_3 + 6NaHCO_3 \longrightarrow 2\,Al(OH)_3 + 3Na_2\,SO_4 + 6CO_2$$

Reaction with ammonium phosphate yields $AlPO_4$ (see Aluminum phosphate, preparation)

Analysis

Elemental analysis: Al 15.77%; O 56.12%; S 28.11%. Al may be determined by colorimetric method or by atomic absorption or emission spectrophotometry; sulfate may be determined by $BaCl_2$ precipitation method in the aqueous solution of the salt.

ALUMINUM SULFATE OCTADECAHYDRATE

[7784-31-8]
Formula: $Al_2(SO_4)_3\ 18H_2O$; MW 648.41
Synonyms: alum, cake alum (the term alum also refers to aqueous solutions of this substance, as well as other hydrate salts containing varying number of waters of crystallization; also the term alum applies to a whole class of sulfate double salts, such as potassium aluminum sulfate or ammonium aluminum sulfate.)

Uses

The compound is used heavily in the paper industry. In its acidic solution form, which contains a slight excess of H_2SO_4, it is used for pH control of pulp slurries, treatment of process waters, setting of dyes and also for precipitating dissolved resin for setting the size on the fibers. In slight basic form (containing a slight excess of Al_2O_3), it is used for treatment of drinking and waste waters (e.g., for reducing phosphorus content). Other major applications include dyeing, tanning, catalysts, modification of concrete, and in the manufacture of various chemicals and pharmaceutical products.

Physical Properties

White crystal; sweet taste; density 1.62 $g/cm^{3:}$ decomposes at 86.5°C; soluble in water.

Preparation

Prepared from bauxite, kaolin or aluminum compounds on reaction with H_2SO_4. The insoluble silicic acid is filtered out; the hydrate salt forms on crystallization.

AMERICIUM

[7440-35-9]
Symbol: Am; Atomic Number 95; Atomic Weight 243.0614; an inner-transition, actinide series, radioactive man-made element; electron configuration:

[Rn]^{86} $5f^66d^17s^2$, partially filled *f*-orbitals; valence 2, 3, 4, 5 or 6

Isotopes	**Half-life**	**Decay Mode**
Am-237	1.22 hr.	Orbital electron emission
Am-238	1.63 hr.	Orbital electron emission
Am-239	11.90 hr.	Orbital electron emission
Am-240	50.90 hr.	Orbital electron emissionAlpha emission
Am-241	432.2 yr.	Alpha emission
Am-242	16.01 hr.	Beta emission (83%) Orbital electron emission (17%)
Am-242	~141 yr.	Isomeric transition (isomer)
Am-243	7,370 yr.	Alpha emission
Am-244	10.1 hr.	Beta emission
Am-244	26 min.	Beta emission (isomer)
Am-245	2.05 hr.	Beta emission
Am-246	39 min.	Beta emission
Am-246	25 min.	Beta emission (isomer)
Am-247	~22 min.	Beta emission

Occurrence

Americium does not occur in nature. It is a man-made element produced in nuclear reactors.

Uses

One of its isotopes, Am-241, is a portable source for gamma radiography; also a source of ionization for smoke detectors. In the glass industry, it is used as a radioactive glass thickness gage. Other isotopes do not have much commercial application.

Physical Properties

White lustrous metal when freshly prepared; turns silvery; exists in two forms: as a double hexagonal closed-packed alpha form, and a closed-packed cubic structure known as beta form; melts at 994°C; more volatile than its neighbor elements, plutonium or curium; vaporizes at 2,607°C; density 13.67 g/cm^3; soluble in dilute acids.

Production

Am-241 may be prepared in a nuclear reactor as a result of successive neutron capture reactions by plutonium isotopes:

$$^{239}_{94}\mathrm{Pu} + ^{1}_{0}n \rightarrow ^{240}_{94}\mathrm{Pu} + \gamma$$

$$^{240}_{94}\mathrm{Pu} + ^{1}_{0}n \rightarrow ^{241}_{94}\mathrm{Pu} + \gamma$$

Pu-241 isotope undergoes β-decay forming Am-241:

$$^{241}_{94}\mathrm{Pu} \xrightarrow{\beta^-} ^{241}_{95}\mathrm{Am} \qquad t_{1/2}\ 13.2\ \mathrm{yr}$$

Am-241 obtained as a decay product in the above nuclear reaction (over a period of years), can be separated by extraction. Am-242 and Am-243 isotopes can be prepared from Am-241 by neutron bombardments:

$$^{241}_{95}\text{Am} + {}^{1}_{0}n \rightarrow {}^{242}_{95}\text{Am} + \gamma$$

$$^{242}_{95}\text{Am} + {}^{1}_{0}n \rightarrow {}^{243}_{95}\text{Am} + \gamma$$

Also, Am-243 can be made from Pu-242, which can be prepared either by very intense neutron irradiation of Pu-239, or from Am-241; resulting from successive neutron-capture reactions.

$$^{241}_{95}\text{Am} + {}^{1}_{0}n \rightarrow {}^{242}_{95}\text{Am} + \gamma$$

$$^{242}_{95}\text{Am} \rightarrow {}^{242}_{94}\text{Pu} + \text{e}^{+}$$

$$^{242}_{94}\text{Pu} + {}^{1}_{0}n \rightarrow {}^{243}_{94}\text{Pu} + \gamma$$

$$^{243}_{94}\text{Pu} \xrightarrow{\beta^{-}decay} {}^{243}_{95}\text{Am} + \text{e}^{-}$$

The Pu-242 obtained in the nuclear reaction is separated by chemical extraction. Americium metal can be prepared from its dioxide by reducing with lanthanum metal at high temperature in a vacuum.

$$\text{AmO}_2 + \text{La} \xrightarrow{\text{elevated temp}} \text{Am} + \text{LaO}_2$$

or from its fluoride by reducing the latter with Ba vapors at 1,100°C to 1,200°C:

$$2\text{AmF}_3 + 3\text{Ba} \xrightarrow{1200^\circ C} 2\text{Am} + 3\text{BaF}_2$$

The metal is soluble in a melt of its trihalide salts.

Americium may be separated from other elements, particularly from the lanthanides or other actinide elements, by techniques involving oxidation, ion exchange and solvent extraction. One oxidation method involves precipitation of the metal in its trivalent state as oxalate (controlled precipitation). Alternatively, it may be separated by precipitating out lanthanide elements as fluorosilicates leaving americium in the solution. Americium may also be oxidized from trivalent to pentavalent state by hypochlorite in potassium carbonate solution. The product potassium americium (V) carbonate precipitates out. Curium and rare earth metals remain in the solution. An alternative approach is to oxidize Am^{3+} to AmO_2^{2+} in dilute acid using peroxydisulfate. AmO_2^{2+} is soluble in fluoride solution, while trivalent curium and lanthanides are insoluble.

Ion exchange techniques have been widely applied in the separation process. In the large-scale ammonium thiocyanate process, the metal is retained on strong base anion exchanger; thus, separating it from the lighter lanthanide elements which are not strongly absorbed on the resin.

Americium and other actinide elements may be separated from lanthanides by solvent extraction. Lithium chloride solution and an eight to nine carbon tertiary amine are used in the process. Americium is then separated from curium by the above methods.

Chemical Reactions

The metal forms its oxide, AmO on its surface in contact with air or oxygen. Similarly, reaction with hydrogen forms the hydride, AmH_2.

Divalent Am^{2+} is less stable than the corresponding divalent lanthanide elements. It has not been found in aqueous solutions, even after treatment with strong reducing agents.

Am^{3+} is the most stable oxidation state of the metal. In trivalent state, its properties are similar to europium. Am^{3+} reacts with soluble fluoride, hydroxide, phosphate, oxalate, iodate and sulfate of many metals forming precipitates of these anions; e.g., $Am(OH)_3$, $Am(IO_3)_3$, etc.

No stable divalent salt is known. However, Am^{2+} has been detected in CaF_2 matrix (0.1% Am) by paramagnetic resonance spectrum at low temperature. Its formation is attributed to the reduction of Am^{3+} by electrons in the lattice set free by the effects of alpha particle emission.

Trivalent Am^{3+} ions occur in aqueous acid solution. The solution has a pink color and the ion exists as a hydrated species. Reactions with halide salts or the acids produce trihalides.

In solution Am^{4+} ion is not so stable, slowly reducing to trivalent Am^{3+}. However, simple and also complex tetravalent compounds of americium are known. Some examples are $Am(OH)_4$, AmF_4, $LiAmF_8$, and K_2AmF_4. $Am(OH)_4$ is stable in basic solution and results from the oxidation of $Am(OH)_3$ by hypochlorite ion.

All pentavalent americium compounds are complex salts. Examples are $KAmO_2CO_3$, $KAmO_2F_2$ and Li_3AmO_4. These are formed upon oxidation of Am^{3+} . For example, Am^{3+} reacts with hypochlorite ion in hot K_2CO_3, precipitating $KAmO_2CO_3$ as a crystalline solid.

No simple hexavalent americium compound is known. All Am^{6+} compounds are complex salts containing oxygen. Examples are Li_6AmO_6, $NaAmO_2AC_3$ (Ac is acetate ion), AmO_2F_2 and Ba_3AmO_6. Hexavalent americium ion is a strong oxidizing agent and is reduced to AmO^{+2} in oxidation-reduction reactions. Am ion in higher oxidation states is reduced to Am^{3+} by Am-241 alpha radiation.

Safety Precautions

Am emits alpha and gamma radiation. The alpha decay of the isotope Am-241 is three times as active as radium and is associated with 59 KeV gamma radiation, which is a serious health hazard. The alpha energies of Am-241 and Am-243, the two longest lived isotopes, are 5.48 and 5.27 MeV, respectively, accompanied with gamma rays. Therefore, a totally enclosed storage system using x-ray glass should be used, maintaining a slight negative pressure.

AMMONIA

[7664-41-7]
Formula; NH_3; MW 17.03; tetrahedral planar geometry, H—N—H bond angle 107.3°; N—H bond distance 1.016Å; dipole moment of the gas 1.46×10^{-18} esu; a Lewis base.

Occurrence and Uses

Ammonia occurs in nature, being constantly formed by putrefaction of the protein of dead animals and plants. While some of it is washed away by the rain into rivers and oceans where it is recycled and converted into proteins by microorganisms, much of it is rapidly absorbed from the earth by living plants making new proteins. Ammonia occurs in urine from which it was produced earlier by chemists and alchemists for use as a soluble base. It occurs in gas liquor obtained from coal gas and producer gas plants and coke ovens. Gas liquor was a major source for producing ammonia before Haber-Bosch process was developed. Combustion of coal, fuel oil, wood and natural gas, as well as forest fires produce ammonia in small amounts in the range 1 to 10 lb per ton. It occurs in many industrial effluents, wastewaters, and groundwaters at trace concentrations. It is also found at trace levels in varying concentrations in the air in most metropolitan cities.

The single largest use of ammonia is its direct application as fertilizer, and in the manufacture of ammonium fertilizers that have increased world food production dramatically. Such ammonia-based fertilizers are now the primary source of nitrogen in farm soils. Ammonia also is used in the manufacture of nitric acid, synthetic fibers, plastics, explosives and miscellaneous ammonium salts. Liquid ammonia is used as a solvent for many inorganic reactions in non-aqueous phase. Other applications include synthesis of amines and imines; as a fluid for supercritical fluid extraction and chromatography; and as a reference standard in ^{15}N–NMR.

Physical Properties

Colorless gas; pungent suffocating odor; human odor perception 0.5 mg/m^3; liquefies by compression at 9.8 atm at 25°C, or without compression at –33.35°C (at 1 atm); solidifies at –77.7°C; critical temperature and pressure, 133°C and 112.5 atm, respectively; vapor density 0.59 (air=1); density of liquid ammonia 0.677 g/mL at –34°C; dielectric constant at –34°C is about 22; extremely soluble in water; solution alkaline; pKa 9.25 in dilute aqueous solution at 25°C; the gas does not support ordinary combustion, but burns with a yellow flame when mixed in air at 16—27% composition.

Thermochemical Properties

$\Delta H^\circ f$ (g)	–11.02 kcal/mol
$\Delta H^\circ f$ (aq)	–19.19 kcal/mol
$\Delta H^\circ f$ [NH_4^+(aq)]	–31.67 kcal/mol
$\Delta G^\circ f$ (g)	–3.94 kcal/mol

G°*f* (aq)	–6.35kcal/mol
ΔG°*f* [NH_4^+(aq)]	–18.97 kcal/mol
S°(g)	45.97 cal/degree mol
S°(aq)	26.6 cal/degree mol
S° [NH_4^+(aq)]	27.1 cal/degree mol
C_ρ° (g)	8.38 cal/degree mol
C_ρ° [NH_4^+(aq)]	19.1 cal/degree mol
ΔH_{vap}	5.57 kcal/mol

Synthesis

Ammonia is produced from nitrogen and hydrogen at elevated temperature (500 to 550°C) and pressure (200–350 atm) (Haber–Bosch process), using a promoted iron catalyst

$$N_2 + 3H_2 \xrightarrow[\textit{catalyst}]{\substack{500\text{–}550^\circ C \\ 200\text{-}350\ atm}} 2NH_3 + heat$$

In the above process, finely divided iron oxide combined with sodium oxide and silica or alumina is used as the catalyst. The reaction is favored (as per Le Chatelier's principle) by high pressure and low temperature. However, a temperature of 500 to 550°C is employed to enhance the reaction rate and prevent catalyst deactivation. Although at 200°C and 250 atm the equilibrium may yield up to 90% ammonia, the product yield is too slow. The sources of hydrogen in commercial processes include natural gas, refinery gas, water gas, coal gas, water (electrolysis) and fuel oil, and the nitrogen source is liquefied air.

Most other synthetic processes are modifications of the Haber–Bosch process, using different pressures, temperatures, gas velocities, and catalysts.

Ammonia may be obtained by decomposition of ammonium carbonate or bicarbonate. Such reactions, however, are not applied in commercial production.

$$(NH_4)_2CO_3 \xrightarrow[\textit{60C}]{\textit{heat}} 2NH_3 + CO_2 + H_2O$$

$$NH_4HCO_3 \longrightarrow NH_3 + CO_2 + H_2O$$

Ammonia also may be produced as a by-product from gas liquor obtained from coal, gas, and coke ovens. Organic nitrogen in the coal converts to ammonium compounds which are separated from tar and distilled with an aqueous suspension of $Ca(OH)_2$ to produce ammonia.

$$(NH_4)_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O + 2\ NH_3$$

Reactions

Ammonia is stable at ordinary temperatures but begins to decompose to H_2 and N_2 at 450°C. Decomposition is catalyzed by porcelain, pumice and metal surfaces (but not glass) in presence of which the dissociation starts at 300°C and completes around 500 to 600°C.

Ammonia reacts with water producing NH_4OH. The reaction is reversible; NH_4OH dissociates into NH_4^+ and OH^- ions in solution;

$$NH_3 + H_2O \rightarrow [NH_4OH] \rightarrow NH_4^+ + OH^-$$

NH_4OH is probably unstable in the molecular form, dissociating into ions. There is evidence of existence of $NH_3 \cdot H_2O$ and $2NH_3 \cdot H_2O$ species in aqueous solution (J.R. LeBlanc, (Jr), Madhavan, S. and R.E. Porter. 1978. Ammonia. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., Vol. 2 p. 474, New York: Wiley Interscience). Formation of such adducts may be attributed to hydrogen bonding.

Gaseous NH_3 and its aqueous solution is weakly basic, undergoing neutralization reactions with acids. It reacts with HCl, H_2SO_4, HNO_3 to form corresponding ammonium salts (after the loss of water from evaporation):

$$NH_3 \cdot H_2O + HCl \rightarrow NH_4Cl + H_2O$$

$$2NH_3 \cdot H_2O + H_2SO_4 \rightarrow (NH_4)_2SO_4 + H_2O$$

Similar neutralization reactions occur with phosphoric, acetic and other acids. Liquid ammonia reacts with alkali metals forming amides and liberating H_2. The reaction occurs in presence of a catalyst (e.g., Pt black). Alternatively, heating alkali metals in a stream of ammonia yields their amides.

$$2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$$

Reacts with Mg to form magnesium nitride, Mg_3N_2 liberating H_2:

$$3Mg + 2\,NH_3 \rightarrow Mg_3N_2 + 3H_2$$

Aqueous ammonia reacts with solutions of many metal salts forming precipitates of metal hydroxides:

$$2NH_3 \cdot H_2O + ZnSO_4 \rightarrow Zn(OH)_2 + (NH_4)_2SO_4$$

Forms cupric hydroxide, $Cu(OH)_2$ with $CuSO_4$; the precipitate, however, dissolves in excess ammonia, forming a tetrammine copper (II) complex ion.

$$Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$$

Reacts with chlorine forming chloramines: monochloramine, dichloramine and nitrogen trichloride:

$$NH_3 + Cl_2 \rightarrow NH_2Cl + HCl$$

$$NH_2Cl + Cl_2 \rightarrow NHCl_2 + HCl$$

$$NHCl_2 + Cl_2 \rightarrow NCl_3 + HCl$$

Such chloramines may occur in trace quantities in many chlorine-treated wastewaters that also contain trace ammonia. NCl_3 combines with ammonia to form an unstable adduct, $NCl_3 \cdot NH_3$ which reacts with excess NH_3 producing NH_4Cl and liberating N_2.

$$NCl_3 \cdot NH_3 + 3NH_3 \rightarrow 3NH_4Cl + N_2$$

Chloramine is also formed when chlorine is passed into liquid ammonia; further reaction with ammonia produces hydrazine:

$$NH_2Cl + NH_3 \rightarrow N_2H_4 + HCl$$

However, with excess ammonia, chlorine and bromine form ammonium chloride and bromide, respectively, liberating N_2:

$$8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$$

Reaction with hypochlorite solution also produces chloramine. Ammonia reacts with iodine to form nitrogen triiodide, which further combines with a molecule of NH_3 to form an adduct $NI_3 \cdot NH_3$, an insoluble brown-black solid which decomposes upon exposure to light in the presence of NH_3:

$$NH_3 + 3I_2 \rightarrow NI_3 + 3HI$$

$$NI_3 + NH_3 \rightarrow NI_3 \cdot NH_3$$

Reacts with carbon at red heat to give ammonium cyanide, NH_4CN; forms phosphine and nitrogen upon reaction with phosphorus vapor at red heat:

$$2NH_3 + 2P \xrightarrow{\text{red heat}} 2PH_3 + N_2$$

Liquid ammonia reacts with sulfur forming nitrogen sulfide and H_2S:

$$10S + 4NH_3 \longrightarrow N_4S_4 + 6H_2S$$

whereas gaseous ammonia and sulfur vapor react to form ammonium sulfide and N_2:

$$8NH_3 + 3S \rightarrow 3(NH_4)_2S + N_2$$

Heating with oxygen or air produces nitrogen and water:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

However, reaction at 750°C to 900°C in presence of platinum or platinum-rhodium catalyst produces nitric oxide and water:

$$4NH_3 + 5O_2 \xrightarrow[750-900^\circ C]{Pt} 4NO + 6H_2O$$

Reacts with oxides of copper, zinc, silver and many metals other than those of Group 1A and Mg at high temperatures, decomposing to N_2 and water. At ambient temperatures strong oxidants oxidize ammonia:

$$2\,NH_3 + 2\,KMnO_4 \rightarrow 2\,KOH + 2\,MnO_2 + 2H_2O + N_2$$

$$K_2S_2O_8 + 2NH_3 \rightarrow 2KOH + 2SO_2 + 2K_2O + N_2$$

Reactions with H_2S at different stoichiometric ratios may produce ammonium sulfide, hydrosulfide, NH_4HS and polysulfide $(NH_4)_2S_3$ having varying S contents, depending on temperature and stoichiometric ratios.

Forms ammonium carbamate, $NH_2{\bullet}COO{\bullet}NH_4$ with CO_2 and ammonium dithiocarbamate, $NH_2{\bullet}CSS{\bullet}NH_4$ with CS_2:

$$2NH_3 + CO_2 \rightarrow NH_2{\bullet}COO{\bullet}NH_4$$

$$2NH_3 + CS_2 \rightarrow NH_2{\bullet}CSS{\bullet}NH_4$$

The carbamate decomposes to urea and water when heated. Reaction with chromic acid forms ammonium dichromate, $(NH_4)_2Cr_2O_7$:

$$2NH_3 + 2CrO_3 + H_2O \rightarrow (NH_4)_2Cr_2O_7$$

Reactions with organic acids such as formic, acetic, benzoic, oxalic, and salicylic acids produce their corresponding ammonium salts; concentrated ammonia solution in excess forms ammonium stearate, $CH_3{\bullet}(CH_2)_{16}{\bullet}COONH_4$ with stearic acid.

Forms a red-colored double salt, ammonium ferric chromate, $NH_4Fe(CrO_4)_2$ when added to an aqueous solution of $Fe(NO_3)_3{\bullet}6H_2O$ and CrO_3.

Forms a number of coordination compounds (ammonia complex) with several metals; adds to AgCl forming soluble complex $[Ag(NH_3)_2]Cl$; forms tetraamine complex $[Cu(NH_3)_4]SO_4$ with $CuSO_4$; and forms many hexaamine complexes with cobalt, chromium, palladium, platinum and other metals.

Ammonia undergoes “ammonolysis” reactions with many classes of organics including alcohols, ketones, aldehydes, phenols, and halogenated hydrocarbons. Addition and substitution reactions of ammonia are utilized in many organic syntheses. Reactions of liquid ammonia with ethanol, or gaseous ammonia with ethyl iodide, produce diethylamine, monoethylamine, and tri–ethylamine in lesser amounts. Many organic amines and imines are synthesized using ammonia. For example, reaction with ethylene dichloride gives ethylenediamine.

Analysis

Ammonia may be readily identified from its odor. It may be measured by titrimetry. It is absorbed in an excess amount of a standard solution of dilute sulfuric acid and the excess unreacted acid is back titrated against a standard solution of caustic soda using methyl orange indicator. Alternatively, potentiometric titration may be used to find the end point. Concentrations at trace levels in wastewaters, groundwaters, drinking waters, and air may be measured by various colorimetric techniques or by the ammonia–selective electrode method (APHA, AWWA and WEF, 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington, DC, American Public Health Association). Ammonia reacts with Nessler reagent under alkaline conditions, forming a yellow color. The intensity of color is measured by spectrophotometer, absorbance being proportional to concentration of ammonia in the solution. Alternatively, it may be analyzed by the indophenol blue method. Ammonia reacts with hypochlorite to form monochloramine which reacts with phenol in the presence of manganous sulfate catalyst to produce blue indophenol (Patnaik, P. 1997. *Handbook of Environmental Analysis*. Boca Raton, FL, Lewis Publishers). Solutions at high concentrations may be appropriately diluted to measure ammonia within the calibration range in colorimetric and electrode methods.

Hazard

Ammonia causes intense irritation of eyes, nose and respiratory tract which can lead to tears, respiratory distress, chest pain, and pulmonary edema. A few minutes exposure to 3,000 ppm can cause severe blistering of skin, lung edema, and asphyxia which can lead to death (Patnaik, P. 1992. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, p. 304. New York, Van Nostrand Reinhold). Contact with liquid ammonia can cause serious blistering and destruction of skin tissues. LC_{50} inhalation (mouse): 4,200 ppm/hr.

Fire or explosion hazard may arise from the following ammonia reactions: Reaction with halogens produces nitrogen trihalides which explode on heating; its mixture with fluorine bursts into flame; reacts with gold, silver, or mercury to form unstable fulminate-type shock-sensitive compounds; similarly, shock-sensitive nitrides are formed when ammonia reacts with sulfur or certain metal chlorides, such as mercuric, or silver chloride; liquid ammonia reacts violently with alkali metal chlorates and ferricyanides.

AMMONIUM ACETATE

[631–61–8]
Formula: CH_3COONH_4; MW 77.08

Uses

Ammonium acetate is used for preserving meats; as a mordant in the dyeing of wool; in analytical chemistry for standardization of electrodes, and in titrations; also as a therapeutic diuretic and diaphoretic.

Physical Properties

White crystalline solid; deliquescent; melts at 114°C; decomposes at elevated temperatures; density 1.17 g/cm^3 at 20°C, density of a 10% solution 1.022 g/mL, and a 50% solution 1.092 g/mL; very soluble in cold water (1,480 g/L at 4°C); also soluble in cold alcohol and acetone (78.9 g/L in methanol at 15°C); solution loses ammonia on standing and becomes acidic.

Preparation

Ammonium acetate is made by exact neutralization of acetic acid with ammonia to neutral pH (pH 7):

$$CH_3COOH + NH_3 \rightarrow CH_3COONH_4$$

Instead of aqueous solutions, hot glacial acetic acid and anhydrous ammonia may be used. Ammonium acetate also is prepared by reaction of acetic acid with ammonium carbonate:

$$CH_3COOH + (NH_4)_2CO_3 \rightarrow 2CH_3COONH_4 + CO_2 + H_2O$$

Reactions

Ammonium acetate forms an acid salt, ammonium acetate double salt, with hot acetic acid:

$$CH_3COONH_4 + CH_3COOH \rightarrow CH_3COONH_4 \cdot CH_3COOH$$

The acid salt readily dissolves in water and melts at 66°C.
Water-insoluble lead iodide dissolves in ammonium acetate solution, lead acetate and ammonium iodide are formed:

$$PbI_2 + 2CH_3COONH_4 \rightarrow (CH_3COO)_2Pb + 2NH_4I$$

AMMONIUM BICARBONATE

[1066–33–7]
Formula: NH_4HCO_3; MW 79.06
Synonyms: ammonium hydrogen carbonate; ammonium acid carbonate

Uses

Ammonium bicarbonate is used in preparing baking dough; in the production of ammonium salts; in heat-exchanger tubes as a scale-removing compound; in fire-extinguishing compositions; in cooling baths; in the manufacture of porous plastics and ceramics; and as a “smelling salt,” mixed with oil of lavender.

Physical Properties

White crystalline solid; prismatic crystal; faint odor of ammonia; stable at ambient temperature but decomposes on heating at 60°C; melts at 107.5°C on very rapid heating; density 1.586 g/cm^3; vapor pressure 435 torr at 25°C; readily dissolves in water (21.6g/100g at 20°C, and 36.6g/100g at 40°C).

Manufacture

Ammonium bicarbonate is made by passing carbon dioxide through an aqueous solution of ammonia in an absorption column or a packed tower:

$$NH_3 + H_2O + CO_2 \rightarrow NH_4HCO_3$$

In this process, ammonia solution flows countercurrent to the ascending stream of CO_2. Crystals of ammonium bicarbonate precipitate out when the solution becomes sufficiently saturated. The crystals are filtered or centrifuged out of the mother liquor, washed, and air-dried. Pure product may be obtained by using high purity CO_2. Alternatively, high purity ammonium bicarbonate may be obtained by subliming the product formed at relatively low temperatures.

Reactions

Ammonium bicarbonate decomposes to CO_2, ammonia, and water vapor on heating; it liberates CO_2 when treated with dilute mineral acids:

$$NH_4HCO_3 + HCl \rightarrow NH_4Cl + CO_2 + H_2O$$

It reacts with sulfates of alkaline-earth metals precipitating out their carbonates:

$$CaSO_4 + 2NH_4HCO_3 \rightarrow CaCO_3 + (NH_4)_2SO_4 + CO_2 + H_2O$$

The above reaction is applied in descaling calcium sulfate scale in heat-exchanger tubes.

Ammonium bicarbonate forms double salts with many other salts.

AMMONIUM BIFLUORIDE

[1341–49–7]
Formula: NH_4HF_2; MW 57.04
Synonym: ammonium hydrogen fluoride

Uses

NH_4HF_2 is used to solubilize silica and silicates in siliceous rocks of oil wells, thus to regenerate oil flow; as a neutralizer for alkalies in textile plants and commercial laundries; for removing stains from fabrics; for treating, polishing and rapid frosting of glass plates, window panes, picture frames, ampoules and optical lenses; to produce pure salts of metal fluorides; in treatment processes to prevent corrosion on magnesium and its alloys; in the preservation of wood; and in aluminum anodizing formulations.

Physical Properties

Orthorhombic or tetragonal crystals; etches glass; deliquescent; density 1.50 g/cm^3; refractive index 1.390; melts at 125.6°C; very soluble in water; slightly soluble in alcohol.

Preparation

Commercial grade salt containing 1% NH_4F is made by gas-phase reaction of one mole of anhydrous ammonia with two moles of hydrogen fluoride:

$$NH_3 + 2\ HF \rightarrow NH_4HF_2$$

It may also be prepared in the anhydrous form by dehydration of ammonium fluoride solution, followed by thermal decomposition of dry crystals.

Reactions

Thermal dissociation produces ammonium fluoride and ammonia; at elevated temperatures products contain ammonia and hydrogen fluoride. It forms a colorless double salt, ammonium iron fluoride $3NH_4F \cdot FeF_3$, with iron, a reaction of commercial application for removing stains from fabric. It reacts with many metal oxides at elevated temperatures forming double fluorides:

$$2NH_4HF_2 + BeO \xrightarrow{\text{heat}} (NH_4)_2BeF_4 + H_2O$$

$$6NH_4HF_2 + Al_2O_3 \xrightarrow{\text{heat}} 2(NH_4)_2AlF_6 + 3H_2O$$

On further heating, the double fluorides decompose to metal fluorides, liberating ammonia and hydrogen fluoride:

$$(NH_4)_2BeF_4 \xrightarrow{heat} BeF_2 + 2NH_3 + 2HF$$

$$(NH_4)_3AlF_6 \xrightarrow{heat} AlF_3 + 3NH_3 + 3HF$$

The above reactions are employed commercially for obtaining metal fluorides in high purity.

Similar reactions occur with many metal carbonates at elevated temperatures, producing double fluorides. The latter decompose to metal fluorides on further heating:

$$2NH_4HF_2 + MgCO_3 \xrightarrow{\text{heat}} (NH_4)_2MgF_4 + CO_2$$

$$(NH_4)_2MgF_4 \xrightarrow{heat} MgF_2 + 2NH_3 + 2HF$$

Analysis

Elemental composition: F 66.61%; H 8.83%; N 24.55%

A measured amount of salt is thermally decomposed to ammonia and hydrogen fluoride. These gases liberated in stoichiometric amounts are absorbed in excess standard sulfuric acid solution. Ammonia is measured by back titration of excess acid against a standard solution of caustic soda, using methyl orange indicator. Fluoride ion is measured with an ion-specific electrode. Ammonia may be collected and measured by alternative techniques (see Ammonia).

AMMONIUM BROMIDE

[12124–97–0]

Formula: NH_4Br; MW 97.94; ionic salt, cubic crystal

Uses

Ammonium bromide is used for photography in films, plates, and papers; in fireproofing of wood; in lithography and process engraving; in corrosion inhibitors; and in pharmaceutical preparations.

Physical Properties

White crystal or granule; strong saline taste; no odor; slightly hygroscopic; density 2.429 g/cm^3 at 25°C; refractive index 1.712; sublimes at elevated temperatures: vapor pressure 54.75 torr at 300°C and 758.2 torr at 395°C; highly soluble in water: 60.6 g and 75.5 g/100 mL at 0° and 20°C, respectively—solubility increasing approximately 16 to 18 g/100 mL for every 20°C increase in temperature.

Thermochemical Properties

$\Delta Hf°(s)$	–64.73 kcal/mol
$\Delta Gf°(s)$	–41.9 kcal/mol
S°	27 cal/degree mol
C_ρ	23 cal/degree mol

Preparation

Ammonium bromide is prepared by treating excess ammonia with bromine:

$$8NH_3 + 3Br_2 \rightarrow 6NH_4Br + N_2$$

It may be also prepared by the reaction of ammonia and hydrobromic acid:

$$NH_3 + HBr \rightarrow NH_4Br$$

NH_4Br is also made by the reaction of ammonia with ferrous and ferric bromide, which may be obtained by passing aqueous bromine solution over iron filings.

$$2NH_3 + FeBr_2 + H_2O \rightarrow 2NH_4Br + FeO$$

$$6NH_3 + 2FeBr_3 + 3H_2O \rightarrow 6NH_4Br + Fe_2O_3$$

Reactions

Ammonium bromide exhibits acid reaction in aqueous solution; acts as an excellent acid in liquid NH_3, undergoing neutralization reactions:

$$NH_4Br + NaNH_2 \xrightarrow{\text{liguid } NH_3} NaBr + 2NH_3$$

Contact with metal surfaces produces bromides of the metals; similarly reactions with metal hydroxide bases yield corresponding bromides:

$$2NH_4Br + Ca(OH)_2 \rightarrow CaBr_2 + 2NH_3 + 2H_2O$$

Ammonium bromide decomposes to ammonia and hydrogen bromide when heated at elevated temperatures:

$$NH_4Br \xrightarrow{\text{heat}} NH_3 + HBr$$

Chemical Analysis

Elemental composition: Br 81.58%, H 4.12%, N 14.30%

Mixed with NaOH solution and distilled; distillate analyzed for ammonia by titration, colorimetry, or electrode method (see Ammonia and Ammonium chloride). Bromide portion of NH_4Br in aqueous solution may be analyzed by ion chromatography, or by the colorimetry method in which red to violet color is produced upon treatment with chloramine–T, and phenol red at pH 4.5. The colorimetry test for bromide is subject to interference from oxidizing and reducing agents, chloride, and bicarbonate. NH_4Br may then be determined stoichiometrically.

AMMONIUM CARBAMATE

[1111–78–0]
Formula: NH_2COONH_4; MW 78.07;
Synonyms: ammonium aminoformate; ammonium carbonate anhydride

Uses

Ammonium carbamate is used as an ammoniating agent. It occurs as a mixed salt with ammonium bicarbonate and carbonate.

Physical Properties

Colorless rhombic crystal; odor of ammonia; sublimes at 60°C; very soluble in cold water; decomposes in hot water; slightly soluble in alcohol; insoluble in acetone.

Preparation

Ammonium carbamate is prepared from dry ice and liquid ammonia:

$$CO_2 + 2NH_3 \rightarrow NH_2COONH_4$$

Reactions

Decomposes on heating to ammonia and carbon dioxide; in contact with air at ambient temperatures, it loses ammonia, forming ammonium carbonate. In solution, it is partly hydrolyzed to carbonate.

$$NH_2COONH_4 + H_2O \rightarrow (NH_4)_2CO_3$$

The carbamate is decomposed by acids and their salts.

AMMONIUM CARBONATE

[506–87–6]
Formula: $(NH_4)_2CO_3 \cdot H_2O$; MW 114.10; not available in pure form; crystalline products consist of double salts of ammonium carbonate, ammonium bicarbonate, and ammonium carbamate.
Synonyms: salt of hartshorn; sal volatile

Uses

Applications of ammonium carbonate are similar to those of ammonium bicarbonate. It is used in baking powder; in fire extinguishers; as mordant in dyeing; for washing and defatting wools; in tanning; in manufacture of rubber products; as a "smelling salt"; as a source of ammonia, and as an expectorant.

Physical Properties

Colorless or translucent hard crystalline mass or white cubic crystals or powder; sharp taste; odor of ammonia; decomposes at 58°C; slow decomposition at ambient temperatures; readily dissolves in cold water; decomposes in hot water; insoluble in liquid ammonia, alcohol and carbon disulfide.

Preparation

Ammonium carbonate is obtained by passing carbon dioxide into aqueous ammonia solution in a column or tower. Ammonia, carbon dioxide and water vapor are distilled and the vapors condensed into a solid crystalline mass. It also may be prepared by subliming a mixture of ammonium sulfate and calcium carbonate.

Reactions

Ammonium carbonate slowly decomposes on exposure to air, or rapidly breaks down on heating to ammonia, CO_2, and water; liberates CO_2 on treatment with dilute mineral acids. It reacts with metals forming their carbonates. Reaction with hydriodic acid produces ammonium iodide; and forms ammonium oxalate with oxalic acid.

AMMONIUM CHLORIDE

[12125–02–9]
Formula: NH_4Cl; MW 53.49
Synonym: Sal ammoniac

Occurrence and Uses

Ammonium chloride occurs in nature in crevices near volcanoes. Also, it is found in smoke when burning dry camel or donkey dung as fuel. Important applications of this compound include the manufacture of dry cells for batteries; as a metal cleaner in soldering; as a flux in tin coating and galvanizing; in fertilizers; in pharmaceutical applications as a diuretic, or diaphoretic expectorant; and as an analytical standard in ammonia analysis. Also, it is used in freezing mixtures; washing powders; lustering cotton; in safety explosives and in dyeing and tanning.

Physical Properties

Colorless cubic crystals or white granular powder; saline taste; odorless; hygroscopic; does not melt but sublimes on heating at 340°C; vapor pressure 48.75 torr at 250°C and 251.2 torr at 300°C; density 1.5274 g/cm^3 at 25°C; refractive index 1.642; readily dissolves in water, solubility: 229 g and 271 g/L solution at O°C and 20°C, respectively; solubility lowered by alkali metal chlorides and HCl; dissolution lowers the temperature of the solution; sparingly soluble in alcohols (6 g/L at 19°C) and soluble in liquid NH_3; insoluble in acetone and ether.

Thermochemical Properties

$\Delta H°f(s)$	–75.15 kcal/mol
$\Delta H°f(s)$ [$NH_3(g) + HCl(g)$]	–41.9 kcal/mol
$\Delta G°f(s)$	–48.51 kcal/mol
S°	22.6 cal/degree mol
C_ρ	20.1 cal/degree mol
$\Delta H°_{subl}$ (1 atm)	39.6 kcal/mol

Manufacture

Ammonium chloride is produced as a by-product in the Solvay process for manufacture of sodium carbonate:

$$NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 + NH_4Cl$$

$NaHCO_3$ precipitate is filtered out of solution while NH_4Cl is obtained by crystallization followed by washing and drying. Ammonium chloride also is produced from spent calcium chloride liquor obtained in ammonia-soda process:

$$CaCl_2 + 2NH_3 + CO_2 + H_2O \rightarrow Na_2SO_4 + 2\ NH_4Cl$$

It also is made by heating a mixture of slight excess of NaCl solution with ammonium sulfate. The filtrate containing NH_4Cl is concentrated and cooled. NH_4Cl crystallizes:

$$(NH_4)_2SO_4 + 2NaCl \rightarrow Na_2SO_4 + 2\ NH_4Cl$$

It is produced by direct neutralization reaction of NH_3 and HCl combined as gaseous mixtures.

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

Reactions

NH_4Cl is acidic in aqueous solution: the pH of 1%, 3%, and 10% solution at 25°C are 5.5, 5.1 and 5.0, respectively. (Merck 1996. *The Merck Index*, 12th ed. Rahway, NJ: Merck & Co.) It loses ammonia and becomes more acidic on prolonged exposure or storage. It reacts with iron, copper, nickel and other metals and some of their alloys such as bronze and brass. It reacts with alkalies forming NH_3.

$$NH_4Cl + NaOH \rightarrow NH_3 + NaCl + H_2O$$

Ammonium chloride decomposes to ammonia and HCl when heated. The vapor resulting from sublimation consists of equal volume of NH_3 and HCl, and does not consist of molecular NH_4Cl. (Young, R. D. 1976. Ammonium Compounds. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd. ed. Vol. 2, p. 52l. New York: Wiley Interscience.)

Reacts with formaldehyde (neutralized with NaOH) forming hexamethylenetetramine and HCl.

$$NH_4Cl + 6\ HCHO \rightarrow C_6H_{12}N_4 + 4HCl + 6H_2O$$

Reaction with copper(II) chloride at 2:1 ratio produces yellow orthorhombic crystals of cupric ammonium chloride, which reacts with water to form blue dihydrate crystal, ammonium tetrachlorodiaquocuprate(II):

$$2NH_4Cl + CuCl_2 \xrightarrow[evaporation]{heat} (NH_4)_2 + CuCl_4$$

A similar complex formation occurs with mercuric chloride, zinc chloride, osmium chloride and platinum (II) and (VI) chlorides, forming mercuric ammonium chloride, $(NH_4)_2 \cdot HgCl_4$, zinc ammonium chloride $(NH_4)_3ZnCl_4$ or $ZnCl_2 \cdot 3NH_4Cl$, osmium ammonium chloride, $(NH_4)_2OsCl_6$, platinum ammonium chloride, $(NH_4)_2PtCl_4$ and platinic ammonium chloride $(NH_4)_2PtCl_6$, respectively. Similarly, it reacts with palladium chloride to form ammonium chloropalladate, $(NH_4)_2PdCl_4$. It precipitates out ammonium platinichloride from solution of chloroplatinic acid (Archibald, E. H. 1920. *J. Chem. Soc.*, 117, 1105):

$$H_2PtCl_6 + 2NH_4Cl \rightarrow (NH_4)_2PtCl_6 + 2HCl$$

Neutralization reaction occurs with amide, forming chloride salt and ammonia:

$$NH_4Cl + KNH_2 \rightarrow KCl + 2NH_3$$

Heating with zirconium chloride gives a tetraamine adduct:

$$4NH_4Cl + ZrCl_4 \xrightarrow{heat} ZrCl_4 \bullet 4NH_3 + 4HCl$$

Chemical Analysis

Elemental composition: Cl 66.28%, H 7.54%, N 26.18%

Ammonium chloride is analyzed by treatment with formaldehyde (neutralized with NaOH) and the product HCl formed is analyzed by titration using an acid-base color indicator such as phenolphthalein. Alternatively, it may be mixed with caustic soda solution and distilled. The distillate may be analyzed for NH_3 by titration with H_2SO_4; or by colorimetric Nesslerization; or with an ammonia-selective electrode (APHA, AWWA, WEF. 1995. *Standard Methods for the Examination of Water and Wastewater*. 19th ed. Washington, DC, American Public Health Association). The presence of ammonia or any other ammonium compound would interfere in the test. The moisture content in NH_4Cl may be determined by Karl–Fischer method.

AMMONIUM CYANIDE

[12211–52–8]
Formula: NH_4CN; MW 44.056

Uses

NH_4CN is used in organic synthesis. Unstable, it is not shipped or sold commercially.

Physical Properties

Colorless crystalline solid; cubic crystal; unstable; density 1.02 g/cm^3; decomposes at 36°C; sublimes at 40°C; very soluble in cold water and alcohol; decomposes in hot water.

Preparation

Ammonium cyanide is prepared in solution by bubbling hydrogen cyanide into aqueous ammonia at low temperature:

$$HCN + NH_3(aq) \rightarrow NH_4CN(aq)$$

It may be prepared in solution by the reaction of calcium cyanide and ammonium carbonate:

$$Ca(CN)_2 + (NH_4)_2CO_3 \rightarrow 2NH_4CN + CaCO_3$$

or barium cyanide and ammonium sulfate:

$$Ba(CN)_2 + (NH_4)_2SO_4 \rightarrow 2NH_4CN + BaSO_4$$

In dry state, NH_4CN is made by heating a mixture of potassium cyanide or potassium ferrocyanide with ammonium chloride and condensing the vapors into ammonium cyanide crystals:

$$KCN + NH_4Cl \rightarrow NH_4CN + KCl$$

Reactions

Ammonium cyanide decomposes to ammonia and hydrogen cyanide; often forming black polymer of HCN:

$$NH_4CN \rightarrow NH_3 + HCN$$

It undergoes double decomposition reactions in solution with a number of metal salts. It reacts with glyoxal producting glycine (aminoacetic acid)

$$NH_4CN + (CHO)_2 \rightarrow NH_2CH_2COOH + HCN$$

Reactions with ketones yield aminonitriles:

$$NH_4CN + CH_3COCH_3 \rightarrow NH_2CH_2CH_2CH_2CN + H_2O$$

Analysis

Elemental composition: H 9.15%, C 27.23%, N 63.55%.

NH_4CN may be analyzed by heating the salt and trapping the decomposed products HCN and ammonia in water at low temperatures. The aqueous solution is analyzed for cyanide ion by silver nitrate titrimetric method or an ion-selective electrode method; and ammonia is measured by titration or electrode technique (Patnaik, P. 1997. *Handbook of Environmental Analysis*, Boca Raton, FL: Lewis Publishers).

Toxicity

The solid or its solution is highly toxic. Ingestion can cause death. Exposure to the solid can be harmful as it decomposes to highly toxic hydrogen cyanide and ammonia.

AMMONIUM DICHROMATE

[7789–09–5]
Formula: $(NH_4)_2Cr_2O_7$; MW 252.10
Synonym: ammonium bichromate

Uses

Ammonium dichromate is used in pyrotechnics; in photoengraving and lithography; as a source of pure nitrogen in the laboratory; and as a catalyst.

Physical Properties

Bright orange-red monoclinic crystals; odorless; hygroscopic; decomposes at 180°C; density 2.115 g/cm^3 at 25°C; readily dissolves in water (26.67 g/100 g at 20°C).

Preparation

$(NH_4)_2Cr_2O_7$ may be prepared by the reaction of ammonia gas with chromic acid:

$$2NH_3 + 2CrO_3 + H_2O \rightarrow (NH_4)_2Cr_2O_7$$

or ammonium sulfate with sodium dichromate:

$$(NH_4)_2SO_4 + Na_2Cr_2O_7 \rightarrow (NH_4)_2Cr_2O_7 + Na_2SO_4$$

Reactions

$(NH_4)_2Cr_2O_7$ decomposes at 180°C. On further heating to 225° C it begins to swell and dissociates exothermically, liberating nitrogen and water vapor, leaving behind a residue of chromium(III) oxide:

$$(NH_4)_2Cr_2O_7 \xrightarrow{225^\circ C} N_2 + Cr_2O_3 + 4H_2O$$

As an acid salt, its solution is acidic (pH 3.45 and 3.95 for a 10% and 1% solution, respectively). It undergoes acid reactions. Also, it undergoes double decomposition reactions, forming metal dichromates:

$$(NH_4)_2Cr_2O_7 + Pb(NO_3)_2 \rightarrow PbCr_2O_7 + 2NH_4NO_3$$

As an oxidizing agent, it undergoes oxidation-reduction reactions with reducing agents at ambient and elevated temperatures.

Hazard

Ammonium dichromate is an irritant to skin. Inhalation of dusts can cause pulmonary irritation, perforation of the nasal septum and "chrome sores." Ingestion can cause ulceration. It is also a flammable salt.

AMMONIUM FLUORIDE

[12125–01–8]
Formula: NH_4F; MW 31.04

Synonyms: neutral ammonium fluoride; normal ammonium fluoride

Uses

NH_4F is used for etching glass; for preserving wood; as a mothproofing agent; in printing and dyeing textiles; and as an antiseptic in brewery

Physical Properties

White, deliquescent, crystalline solid; occurs in various forms, as granular powder (commercial products), needles or leaflets, or hexagonal prism (formed on sublimation and condensation); density 1.009 g/cm^3 at 25°C; decomposes on heating; highly soluble in cold water (100g/100g at 0°C); decomposes in hot water; slightly soluble in alcohol, insoluble in liquid ammonia

Thermochemical Properties

$\Delta H°f$	–110.89 kcal/mol
$\Delta G°f$	–83.36 kcal/mol
S°	17.20 cal/degree mol
C_ρ	15.60 cal/degree mol

Preparation

NH_4F is made by passing ammonia gas through a 40% aqueous solution of hydrofluoric acid (ice-cooled):

$$NH_3 + HF \rightarrow NH_4F$$

Alternatively, it may be prepared by heating ammonium chloride with excess sodium fluoride. Ammonium fluoride is obtained by sublimation.

$$NH_4Cl + NaF \rightarrow NH_4F + NaCl$$

Also, it may be prepared by mixing an equimolar amount of aqueous ammonia and ammonium bifluoride.

Reactions

Decomposes on heating to ammonia and hydrogen fluoride; also decomposes in hot water producing ammonia and ammonium bifluoride:

$$2NH_4F \rightarrow NH_3 + NH_4F{\cdot}HF$$

The solution is acidic; it reacts with weak bases forming double salts; i.e., ammonium hexafluoroaluminate, $(NH_4)_3AlF_6$; ammonium hexafluorophosphate, NH_4PF_6; ammonium hexafluorosilicate, $(NH_4)_2\,SiF_6$; ammonium hexafluorogallate, $(NH_4)_3GaF_6$:

$$6NH_4F + Al(OH)_3 \rightarrow (NH_4)_3AlF_6 + 3NH_3 + 3H_2O$$

Chemical Analysis

Elemental composition: F 51.30%, H 10.88%, N 37.82%. A measured amount is dissolved in water and the aqueous solution diluted appropriately and analyzed for fluoride by fluoride ion-selective electrode, or by ion chromatography. Ammonium ion (or liberated ammonia) is analyzed by titration or by ammonium ion-specific electrode (see Ammonia).

Toxicity

NH_4F is a highly toxic substance; ingestion can cause nausea, vomiting, abdominal pain, tremor, hemorrhage, muscular weakness, convulsions and vascular collapse. Ingestion of large quantity can cause death. Chronic effects include mottling of enamel, osteoclerosis and calcification in ligaments.

AMMONIUM FORMATE

[540–69–2]
Formula: $HCOONH_4$; MW 63.06;
Synonym: formic acid ammonium salt

Uses

Ammonium formate is used in chemical analysis to separate base metals from noble metal salts.

Physical Properties

White monoclinic deliquescent crystals or granules; density 1.280 g/cm^3; melts at 116°C; highly soluble in water (102 g/100 g at 0°C), solubility rapidly increasing with temperature (i.e., 531 g/100 g at 80°C); soluble in liquid ammonia, alcohol and ether.

Preparation

NH_4COOH is prepared by the reaction of ammonia with formic acid:

$$NH_3 + HCOOH \rightarrow HCOONH_4$$

or from methyl formate and ammonia:

$$HCOOCH_3 + 2NH_3 \rightarrow HCOONH_4 + CH_3NH_2$$

Reactions

Thermal dissociation produces ammonia, carbon dioxide, and water; reacts with metal salts forming their formates; oxidized by strong oxidants forming carbon dioxide, water, and oxides of nitrogen.

AMMONIUM HYDROSULFIDE

[12124-99–1]
Formula: NH_4HS; MW 51.113
Synonyms: ammonium sulfhydrate, ammonium bisulfide, ammonium hydrogen sulfide

Uses

Aqueous solutions of NH_4HS are used in various commercial applications including textile manufacture.

Physical Properties

White tetragonal or orthorhombic crystal; density 1.17g/cm^3; refractive index 1.74; unstable, sublimes readily at ordinary temperatures; vapor pressure 748 torr at 32°C; highly soluble in water, alcohol, liquid ammonia and liquid hydrogen sulfide; insoluble in benzene, hexane and ether.

Thermochemical Properties

$\Delta H°f$	–37.5 kcal/mol
$\Delta G°f$	–12.1 kcal/mol
S°	23.3 cal/degree mol

Preparation

NH_4HS is prepared by the reaction of an equimolar amount of ammonia and hydrogen sulfide:

$$NH_3 + H_2S \rightarrow NH_4HS$$

Reactions

When heated, the hydrosulfide dissociates into ammonia and hydrogen sulfide; addition of sulfur produces ammonium sulfide:

$$2NH_2HS + 2S \rightarrow (NH_4)_2S_3 + H_2S$$

AMMONIUM MOLYBDATE

[27546–07–2]
Formula: $(NH_4)_2MoO_4$; MW 196.01
Ammonium ion forms isopolymolybdates, such as di–, tri–, or heptamolybdates with the molybdate anion. Only the dimolybdate, $(NH_4)_2Mo_2O_7$, and ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ [12027–67–7], have commercial applications.

Uses

Ammonium molybdates are used to prepare high purity grade molybdenum metal powder, sheet, or wire; for colorimetric analysis of phosphates and arsenates; for decorating ceramics; and as catalysts.

Physical Properties

Colorless, monoclinic crystal; density 2.276 g/cm^3; decomposes on heating; soluble in water (decomposes); also soluble in acid; insoluble in alcohol and liquid ammonia.

Preparation

Ammonium molybdate is prepared by treating molybdenum oxide with excess ammonia in an aqueous solution. The crystals are obtained after evaporation of water.

$$MoO_3 + 2NH_3 + H_2O \rightarrow (NH_4)_2MoO_4$$

Reactions

Decomposes on heating or on treatment with alkalies; reacts with lead chloride and other metal salts to form their metal molybdates:

$$(NH_4)_2MoO_4 + PbCl_2 \rightarrow PbMoO_4 + 2NH_4Cl$$

Reacts with phosphates or arsenates to form ammonium phosphomolybdate $(NH_4)_3PO_4 \cdot 12MoO_3$, or ammonium arsenomolybdate, $(NH_4)_3AsO_4 \cdot 12MoO_3$.

Chemical Analysis

Elemental composition: H 4.11%, Mo 48.94%, N 14.29%; O 32.65.

$(NH_4)_2MoO_4$ is digested with nitric acid and the molybdenum metal is analyzed by atomic absorption or emission spectrophotometry. It is dissociated to ammonia, which may be measured by titration or by an ion-specific electrode technique (see Ammonia). Ammonium molybdate reacts under acid conditions with dilute orthophosphate solution to form molybdophosphoric acid which, in the presence of vanadium, forms yellow vanadomolybdophosphoric acid; the intensity of the yellow color may be measured by a spectrophotometer at 400 to 490 nm and is proportional to the trace amount of ammonium molybdate.

AMMONIUM NITRATE

[6484–52–2]
Formula: NH_4NO_3; MW 80.043

Uses

The ammonium salt produced or consumed in largest amounts is ammonium nitrate. It is used widely as a fertilizer, and is the leading nitrogen fertilizer in the world. An advantage of this compound over other ammonium fertilizers is that it provides both nitrate and ammonia to soil without changing the pH. Also, it is used as a mixed fertilizer with other compounds, such as calcium phosphate, or calcium carbonate. It also is used as an explosive for blasting, or as an ingredient of various mines, or in highway construction. The salt itself, or in combination with fuel oil, powdered aluminum, or carbonaceous matter, is a high explosive. Its blend with trinitrotoluene, known as Amatol, is a military explosive.

Other uses of ammonium nitrate are in the manufacture of nitrous oxide, an anesthetic, and as a component of freezing mixtures.

Physical Properties

White crystalline solid; occurs in five different crystallographic modifications as follows:

(i) tetragonal form below –18°C
(ii) rhombic form between –18 to 32.1°C
(iii) rhombic form between 32.1 to 84.2°C
(iv) tetragonal form between 84.2 to 125.2° C
(v) cubic form between 125.2 to 169.6°C;

density 1.725 g/m^3 at 20°C; highly hygroscopic; the finely divided powder cakes to a hard mass on storage; melts at 169.6°C; extremely soluble in water; its solubility in 100 g water is as follows:

0°C	118 g
20°C	150 g
40°C	297 g
60°C	410 g
80°C	576 g

Dissolution is endothermic, solution becomes cold (and hence its application in freezing bath); elevates the boiling point of water by 1°, 7.5°, 28.5° and 70°C at 10, 40, 80 and 95% (w/w) concentrations, respectively; vapor pressure of saturated solution, 11.2 torr at 20°C.

Thermochemical Properties

$\Delta H^\circ f$ (solid)	–87.37 kcal/mol
$\Delta H^\circ f$ (aq)	–81.23 kcal/mol
$\Delta G^\circ f$ (solid)	–43.98 kcal/mol
$\Delta G^\circ f$ (aq)	–45.58 kcal/mol
S° (solid)	36.11 cal/degree mol
S° (aq)	62.10 cal/degree mol
C_ρ (solid)	33.3 cal/degree mol

Manufacture

NH_4NO_3 is made by the neutralization reaction of ammonia with nitric acid:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 + \text{heat}$$

The reaction is carried out in aqueous phase using a slight excess of nitric acid. The heat of reaction is utilized to evaporate the water. Also, evaporation may be carried out under vacuum. Alternatively, solid ammonium nitrate is obtained by crystallization from a concentrated solution. The particle size of the dry product may be controlled by vacuum crystallization, granulation or other processes. (Young, R.D. 1978. Ammonium Compounds. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., Vol. 2, pp. 525–532. New York: Wiley Interscience.) The solid powder should be protected from moisture to minimize caking.

Ammonium nitrate alternatively may be prepared by double decomposition reactions of ammonium salt with a nitrate salt; e.g., ammonium sulfate and sodium nitrate:

$$(NH_4)_2SO_4 + 2NaNO_3 \rightarrow 2NH_4NO_3 + Na_2SO_4$$

Reactions

Ammonium nitrate volatilizes reversibly with dissociation at moderate temperatures:

$$NH_4NO_3(s) \leftrightarrow NH_3(g) + HNO_3(g) \qquad \Delta H = +41 \text{ kcal/mol}$$

Thermal decomposition occurs at 170°C producing nitrous oxide and water:

$$NH_4NO_3(l) \xrightarrow{200\text{–}260^\circ C} N_2O(g) + 2H_2O(g) \quad \Delta H = -5.5 \text{ kcal/mol}$$

N_2O evolves smoothly; however, above 250°C or if the solid is strongly shocked, violent decomposition occurs:

$$NH_4NO_3 \xrightarrow{>260^\circ C} N_2 + 2H_2O + \frac{1}{2}O_2$$

Aqueous solutions of ammonium nitrate undergo a double decomposition reaction with metal salts. NH_4NO_3 acts as an oxidizing agent in aqueous solutions and is reduced by various metals at ambient temperatures.

Spongy copper slowly reduces it to ammonium nitrite in the absence of air; however, no reaction occurs with copper wire or gauge. (Basset, H. and R. G. Durrant. 1922. *J. Chem. Soc.*, 121, 2631):

$$Cu + NH_4NO_3 \rightarrow NH_4NO_2 + CuO$$

Chemical Analysis

Ammonium nitrate dissociates in aqueous solution to NH_4^+ and NO_3^- ions. The former may be measured by ammonium ion-selective electrode and the latter by nitrate ion-selective electrode. The solid may be heated carefully at low temperature (around 90°C) and the evolved ammonia and nitric acid vapors are absorbed in water and measured by selective ion electrodes, respectively.

Hazard

Heating ammonium nitrate can present a severe explosion hazard. When heated above 210°C, its decomposition is exothermic, producing nitrous oxide and water vapor. In closed confinement, heating the molten mass can cause a pressure build-up. Above 300°C, there is rapid evolution of nitrogen, water vapor and oxygen—two mols solid producing seven mols of gaseous products. This can cause a dangerous explosion. In the presence of readily oxidizable substances, such as fuel oil soaked into the pores of the solid or finely divided metal, the ignition is self-sustained—occurring at lower temperatures, and the explosivity is enhanced. Also, it can explode dangerously in a fire. At ordinary temperatures, the compound is stable and safe to handle. Calcium carbonate, phosphate or other substances are mixed with fertilizer grade ammonium nitrate to reduce its explosivity. There are many cases of loss of human lives from ammonium nitrate fire or explosion.

AMMONIUM PHOSPHATE, DIBASIC

[7783–28–0]
Formula: $(NH_4)_2HPO_4$; MW 132.07;
Synonyms: diammonium hydrogen phosphate; secondary ammonium phosphate

Uses

Dibasic ammonium phosphate is used as a fertilizer; as a fire extinguisher; a flame retardant for plywood, papers, and fabrics; to prevent afterglow in matches; in purifying sugar; as a flux for soldering tin, copper, zinc and brass; and to control precipitation of alkali-soluble or acid-insoluble colloidal dyes on wool.

Physical Properties

Colorless monoclinic crystal; saline taste; refractive index 1.52; density 1.619 g/cm^3; melts at 155°C (decomposes); very soluble in water (57 g/100 g at 10°C and 106.7g/100g at 70°C, respectively); insoluble in alcohol, acetone, and liquid ammonia.

Preparation

$(NH_4)_2HPO_4$ is made by reacting ammonia with phosphoric acid:

$$2NH_3 + H_3PO_4 \rightarrow (NH_4)_2HPO_4$$

Reactions

Heating at 70°C results in decomposition to monoammonium phosphate and ammonia:

$$(NH_4)_2\ HPO_4 \rightarrow (NH_4)H_2PO_4 + NH_3$$

A boiling, dilute solution of diammonium phosphate evolves ammonia (the pH of the solution decreases), which also occurs slowly at ambient temperatures. The solid and its solution create an ammonia vapor pressure. Reactions with mineral acids produce the corresponding ammonium salts.

AMMONIUM PHOSPHATE, MONOBASIC

[7722–76–1]
Formula: $(NH_4)H_2PO_4$; MW 115.03;
Synonyms: ammonium dihydrogen phosphate; ammonium biphosphate; primary ammonium phosphate

Uses

Monobasic ammonium phosphate is used in fire extinguishers; as a flame retardant for papers, plywoods, and fabrics; in baking mixtures; and in fermentation process.

Physical Properties

White crystalline powder; odorless; density 1.80 g/cm^3; readily dissolves in water (40 g/ 100 g); pH of 0.2 molar solution 4.2; slightly soluble in alcohol; insoluble in acetone.

Preparation

Preparative method similar to its dibasic salt; obtained by reaction of equimolar amounts of ammonia and phosphoric acid:

$$NH_3 + H_3PO_4 \rightarrow (NH_4)H_2PO_4$$

Reactions

Thermal decomposition produces ammonia and phosphoric acid; reaction with sulfuric acid produces ammonium hydrogen sulfate:

$$(NH_4)H_2PO_4 + H_2SO_4 \rightarrow (NH_4)HSO_4 + H_3PO_4$$

$(NH_4)H_2PO_4$ decomposes under strong oxidizing conditions producing nitrogen, water, and phosphorus pentaoxide.

AMMONIUM SULFATE

[7783–20–2]
Formula: $(NH_4)_2SO_4$; MW 132.14;

Occurrence and Uses

Ammonium sulfate occurs in trace concentrations in the upper atmosphere. It is widely used as a fertilizer for rice and other crops. It is a source of sulfur for the soil. It is also used as an additive to supply nutrient nitrogen in fermentation processes (e.g., yeast production from molasses). It also is used for fireproofing timber and plastics, and in treatment of hides, and leather production.

Physical Properties

White crystalline solid; orthorhombic crystal; density 1.769 g/cm^3 at 20°C; melts between 511 to 515°C (in a closed system): however, in an open system, it melts with decomposition at 280°C; readily dissolves in water (solubility, 70.6 g and 104 g per 100 g water at 0°C and 100°C, respectively); insoluble in acetone, alcohol and ether.

Thermochemical Properties

$\Delta H°f$	–282.5 kcal/mol
$\Delta G°f$	–215.6 kcal/mol
S°	52.6 cal/degree mol
C_ρ	44.8 cal/degree mol

Manufacture

Ammonium sulfate is made by reacting synthetic ammonia (or by-product ammonia from coke-ovens) with sulfuric acid:

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

A mixture of ammonia gas and water vapor is introduced into a reactor (“saturator”) that contains a saturated solution of ammonium sulfate and about 2 to 4% free sulfuric acid at 60°C. Concentrated sulfuric acid is added continuously to keep the solution acidic, and to retain its level at 2 to 4% free acid. The heat of reaction keeps reactor temperature at 60°C. Ammonium sulfate formed crystallizes out of its saturated solution in the reactor.

Dry, powdered ammonium sulfate may be formed by spraying sulfuric acid into a reaction chamber filled with ammonia gas. The heat of reaction evaporates all water present in the system, forming a powdery salt.

Ammonium sulfate also is manufactured from gypsum salt, $CaSO_4 \cdot 2H_2O$. Finely divided gypsum is added to ammonium carbonate solution. Calcium carbonate precipitates out, leaving ammonium sulfate in solution.

$$(NH_4)_2CO_3 + CaSO_4 \rightarrow (NH_4)_2SO_4 + CaCO_3$$

Reactions

Ammonium sulfate decomposes upon heating at 100°C in an open system, forming ammonium bisulfate, NH_4HSO_4. As a salt of a strong acid and weak base, its solution is acidic; pH of 0.1*M* solution is 5.5.

In aqueous solution the reactions are those of NH_4^+ and SO_4^{2-} ions. For example, addition of barium chloride, $BaCl_2$ precipitates out barium sulfate, $BaSO_4$. The filtrate on evaporation yields ammonium chloride, NH_4Cl.

$(NH_4)_2SO_4$ forms many double salts (ammonium metal sulfates) when its solution is mixed with equimolar solutions of metal sulfates and the solution is slowly evaporated. Such double metal sulfates include ammonium cobaltous sulfate, $(NH_4)_2Co(SO_4)_2$; ferric ammonium sulfate, $(NH_4)_2Fe(SO_4)_2$, ammonium nickel sulfate, $(NH_4)_2Ni(SO_4)_2$; and ammonium cerous sulfate, NH_4CeSO_4.

Chemical Analysis

Elemental composition: H 6.10%, N 21.20%, O 48.43%, S 24.27%.

A small amount of solid may be dissolved in water and ammonium ion determined by the ion-selective electrode method, or miscellaneous colorimetric or titrimetric procedures (see Ammonia). Sulfate ion may be determined by ion chromatography.

AMMONIUM SULFIDE

[12135–76–1]
Formula: $(NH_4)_2S$; MW 68.143
Synonym: ammonium monosulfide

Uses

Ammonium monosulfide is used in photographic developer; to apply patina to bronze; and in textile manufacture.

Physical Properties

Unstable, decomposes at ambient temperature; forms yellow crystals below –18°C; hygroscopic; soluble in water and alcohol, very soluble in liquid ammonia.

Thermochemical Properties

$\Delta H°f$ (aq)	–55.4 kcal/mol
$\Delta G°f$	–17.4 kcal/mol
S°	50.7 cal/degree mol

Preparation

$(NH_4)_2S$ is obtained from reacting hydrogen sulfide with excess of ammonia:

$$H_2S + 2NH_3 \rightarrow (NH_4)_2S$$

Reactions

Ammonium sulfide decomposes to ammonia and ammonium hydrosulfide:

$(NH_4)_2S \rightarrow NH_3 + NH_4HS$

At elevated temperatures it forms polysulfides; also, it combines with sulfur, forming ammonium polysulfide:

$(NH_4)_2S + 2S \rightarrow (NH_4)_2S_3$

Ammonium sulfide forms ammonium chloride with HCl and ammonium nitrate with nitric acid, respectively.

Chemical Analysis

Elemental composition: H 11.83%, N 41.11%, S 47.05%. It may be analyzed by measuring its decomposition gaseous products, ammonia and hydrogen sulfide, either by gas chromatography using an FID or a TCD; or by selective ion electrode or colorimetric techniques.

AMMONIUM THIOCYANATE

[1762–95–4]

Formula: NH_4SCN; MW 76.122

Uses

Ammonium thiocyanate is used in the manufacture of herbicides, thiourea, and transparent artificial resins; in matches; as a stabilizing agent in photography; in various rustproofing compositions; as an adjuvant in textile dyeing and printing; as a tracer in oil fields; in the separation of hafnium from zirconium, and in titrimetric analyses.

Physical Properties

Crystalline solid forming monoclinic crystal; hygroscopic; melts at 149.6°C; decomposes at 170°C; density 1.305 g/cm^3; highly soluble in water (128 g/100 mL at 0°C); soluble in liquid ammonia, alcohol, and acetone.

Manufacture

Ammonium thiocyanate is made in the United States by the reaction of carbon disulfide with aqueous ammonia. Ammonium dithiocarbamate is formed as an intermediate in this reaction, which upon heating, decomposes to ammonium thiocyanate and hydrogen sulfide.

$CS_2 + 2NH_3(aq) \rightarrow NH_2C(=S)SNH_4 \rightarrow NH_4SCN + H_2S$

Ammonium cyanate also may be prepared by direct sulfurization of ammonium cyanide.

$$NH_4CN + S \xrightarrow{\text{heat}} NH_4SCN$$

Chemical Reactions

Ammonium thiocyanate is stable in air; however, upon heating it isomerizes to thiourea:

$$NH_4SCN \xrightarrow{heat} NH_2CSNH_2$$

The equilibrium mixtures at 150°C and 180°C contain 30.3% and 25.3% (by weight) thiourea, respectively. When heated at 200°C, the dry powder decomposes to ammonia, hydrogen sulfide, and carbon difsulfide, leaving a residue of guanidine thiocyanate [56960–89–5].

NH_4SCN is weakly acidic; reacts with caustic soda or caustic potash to form sodium thiocyanate (NaSCN) or potassium thiocyanate (KSCN). It reacts with ferric salts to form a deep-red ferric thiocyanate complex:

$$6\ SCN– + Fe^{3+} \rightarrow [Fe(SCN)_6]^{3-}$$

Ammonium thiocyanate reacts with several metal ions including copper, silver, zinc, lead, and mercury, forming their thiocyanate precipitates, which may be extracted into organic solvents.

Ammonium thiocyanate reacts with alkyl halides forming alkyl thiocyanates, RSCN, which may also rearrange to alkyl isothiocyanates, RNCS:

$$RCH_2Cl + NH_4SCN \rightarrow RCH_2SCN + NH_4Cl$$

$$RCH_2SCN \rightarrow RCH_2NCS$$

Forms thioureas with aliphatic or aromatic amine hydrochlorides:

$$RCH_2NH_2{\cdot}HCl + NH_4SCN \rightarrow RCH_2NHCSNH_2 + NH_4Cl$$

Ammonium thiocyanate reacts with nickel sulfate and ammoniacal solution of hydrzine sulfate forming a violet-blue crystalline precipitate:

$$2NH_4SCN + NiSO_4 + (N_2H_4)_2{\cdot}H_2SO_4 + 2NH_3 \rightarrow Ni(N_2H_4)_2(SCN)_2^+ + 2(NH_4)_2SO_4$$

AMMONIUM THIOSULFATE

[7783–18–8]
Formula: $(NH_4)_2S_2O_3$; MW 148.21

Uses

Two principal applications of ammonium thiosulfate are: (i) as a fertilizer blend, and (ii) in photography. It is blended with other nitrogenous fertilizers to provide sulfur to the soil. Also, the compound itself is a fertilizer: however, such applications are limited. In photography it dissolves undeveloped silver halides from negatives and prints. It is also used as a desiccant and defoliant in cotton, rice, soybean and other plants; in flue-gas desulfurization; and in metal cleaning. It is sold as an aqueous solution, a crystal slurry, or anhydrous crystal.

Physical Properties

Colorless, monoclinic crystal; hygroscopic; decomposes on heating above 100°C; density 1.679 g/cm^3; very soluble in water (64 g/100 g at 20°C), insoluble in alcohol, and slightly soluble in acetone.

Manufacture

Ammonium thiosulfate is made by the reaction of ammonium sulfite with sulfur at 85 to 110°C:

$$(NH_4)_2SO_3 + S \xrightarrow{\text{heat}} (NH_4)_2S_2O_3$$

or, by reacting ammonium sulfite with ammonium polysulfide:

$$(NH_4)_2SO_3 + (NH_4)_2S_8 \rightarrow (NH_4)_2S_2O_3 + (NH_4)_2S_7$$

or, using sulfur dioxide and ammonium sulfide instead of ammonium polysulfide:

$$(NH_4)_2SO_3 + 2(NH_4)_2S + 3SO_2 \rightarrow 3(NH_4)_2S_2O_3$$

Reactions

When heated over 100°C, it decomposes to ammonium sulfite and sulfur:

$$(NH_4)_2S_2O_3 + S \xrightarrow{\text{heat}} (NH_4)_2SO_3 + S$$

Also, its aqueous solution decomposes slowly below 50°C.

Chemical Analysis

Elemental composition: H 5.44%, N 18.90%, O 32.39%, S 43.27%. It is dissolved in water and the aqueous solution may be analyzed for thiosulfate by titrating against a standard solution of an oxidizing agent, such as potassium dichromate or potassium permanganate. Ammonium ion in the aqueous solution may be determined by colorimetry, titrimetry, or ion-specific electrode method (see Ammonia).

ANTIMONY

[7440-36-0]
Symbol Sb; atomic number 51; atomic weight 121.75; Group VA (group 15) element; atomic radius 1.41Å; ionic radius Sb^{3+} 0.76Å; covalent radius Sb^{3+} 1.21Å; electronic configuration [Kr] $4d^{10}5s^25p^3$; a metalloid element; electronegativity 1.82 (Allred-Rochow type); valence states +5, +3, 0 and -3; isotopes and natural abundance: Sb-121 (57.3%), Sb-123 (42.7%)
Synonym: Stibium

Occurrence and Uses

Antimony occurs in nature primarily in the mineral stibnite, and also in several other ores, such as valentinite, senarmontite, cervantite, kermasite, livingstonite, and jamisonite. It is also found in lead scraps from batteries.

Antimony alloys have many commercial applications. The metal makes its alloys hard and stiff and imparts resistance to corrosion. Such alloys are used in battery grids and parts, tank linings, pipes and pumps. The lead plates in the lead storage batteries constitute 94% lead and 6% antimony. Babbit metal, an alloy of antimony, tin, and copper is used to make antifriction machine bearings. Alloys made from very high purity grade antimony with indium, gallium and bismuth are used as infrared detectors, diodes, hall effect devices and thermoelectric coolers.

Physical Properties

Silvery-white, brittle metallic element; crystal system-hexagonal, rhombohedral; also, exists in two unstable allotropic forms—a yellow modification and a dark-grey lustrous amorphous powder—both of which revert to crystalline form; hardness 3.0 to 3.5 Mohs; density 6.697g/cm^3; melting point 630.5°C; boiling point 1635°C; electrical resistivity 39.1 microhm-cm at 0°C; magnetic susceptibility -0.87×10^{-6} emu/g.

Thermal Properties

Specific heat at 25°C	0.050 cal/g°C
Latent heat of fusion	38.5 cal/g
Latent heat of vaporization	161 cal/g
Coefficient of linear expansion at 25°C	9×10^{-6} /°C
Thermal conductivity at 25°C	0.185 watts/cm°C

Production

Antimony is obtained from its ores, stibnite, Sb_2S_3 or tetrahedrite, $3Cu_2S \cdot Sb_2S_3$. The metal is recovered from high-grade stibnite by reduction with iron:

$$Sb_2S_3 + 3\ Fe \rightarrow 2\ Sb + 3\ FeS$$

Alternatively, low-grade stibnite ore is converted to its oxide which is then reduced with carbon. Tetrahedrite may be treated with sodium sulfide solution. The solution containing thioantimonate formed is then electrolyzed in a diaphragm cell using a steel cathode and lead anode. The metal is further refined by oxidation or electrorefining process.

Sb may be made in the laboratory by reduction of antimony pentoxide with potassium cyanide.

Reactions

Antimony is stable in dry air and not readily attacked by moisture; slowly oxidized by moist air. Under controlled conditions oxidation may result forming tri-, tetra-, and pentaoxides; Sb_2O_3, Sb_2O_4 and Sb_2O_5, respectively.

Sb reacts with sulfur, combining in all proportions, forming tri-, and pentasulfides, Sb_2S_3 and Sb_2S_5, respectively.

Sb is oxidized by nitric acid, forming a gelatinous precipitate of hydrated antimony pentoxide. It does not react with cold dilute sulfuric acid. However, reaction occurs in hot concentrated acid: an oxysulfate of indefinite composition and low acid-solubility is formed. It reacts with hydrofluoric acid to form soluble antimony trifluoride and pentafluoride. Hydrochloric acid in the absence of air does not readily attack the metal; however, finely divided antimony reacts with hot concentrated acid forming chloride salt.

Sb reacts with chlorine or bromine forming antimony chloride or bromide; with iodine, the reaction occurs in boiling benzene or halogenated organic solvent to form antimony triiodide, SbI_3.

Analysis

The metal may most conveniently be analyzed in the aqueous phase by atomic absorption spectrophotometry using flame or a graphite furnace or by ICP emission spectrophotometry at wavelength 206.83 or 217.58 nm. Such measurements are accurate at trace concentration levels. The metal or its ore is digested with hot nitric acid and the acid extract is appropriately diluted and measured.

ANTIMONY PENTACHLORIDE

[7647–18–9]
Formula $SbCl_5$; MW 299.02; the solid is a dimer of two $SbCl_4$ units attached by two bridging Cl atoms.
Synonym: antimony perchloride

Uses

Antimony pentachloride is used as a catalyst in organic synthesis.

Physical Properties

Colorless or yellow oily liquid; fumes in air; freezes at 2.8°C; boils at 140°C with some decomposition; bp 85°C at 55 torr; density 2.336g/mL at 20°C; refractive index 1.601; decomposes in water; soluble in hydrochloric acid, chloroform and carbon tetrachloride.

Thermochemical Properties

$\Delta H°f$	–105.2 kcal/mol
$\Delta G°f$	–83.7 kcal/mol
S°	72 cal/deg mol

Preparation

Antimony pentachloride is prepared by passing chlorine gas into molten antimony trichloride:

$$SbCl_3 + Cl_2 \rightarrow SbCl_5$$

or by the reaction of the element with excess chlorine:

$$2\ \mathrm{Sb} + 5\ \mathrm{Cl_2} \rightarrow 2\ \mathrm{SbCl_5}$$

Reactions

Antimony pentachloride hydrolyzes to antimony pentaoxide in excess water, forming HCl:

$$2\ \mathrm{SbCl_5} + 5\ \mathrm{H_2O} \rightarrow \mathrm{Sb_2O_5} + 10\ \mathrm{HCl}$$

However, with calculated quantities of cold water or with moisture, monohydrate, $SbCl_5 \cdot H_2O$ and tetrahydrate, $SbCl_5 \cdot 4H_2O$ are formed. It reacts violently with many organics producing their chloro derivatives.

When added to a dilute solution of caustic soda or caustic potash, it forms $[Sb(OH)_6]^-$ ion in the solution, from which the sodium or potassium salt, $NaSb(OH)_6$ or $KSb(OH)_6$ crystallizes out. It forms two adducts with ammonia, a red triammine, $SbCl_5 \cdot 3NH_3$, and a colorless tetraammine, $SbCl_5 \cdot 4NH_3$. $SbCl_5$ dissociates on heating to trichloride and chlorine; dissociation comencing around 120°C and completing at 300°C.

$SbCl_5$ reacts with H_2S forming antimony (V) thiochloride:

$$\mathrm{SbCl_5} + \mathrm{H_2S} \rightarrow \mathrm{SbSCl_3} + 2\ \mathrm{HCl}$$

$SbCl_5$ undergoes vigorous reaction with carbon disulfide, producing carbon tetrachloride, antimony trichloride and sulfur:

$$2\ \mathrm{SbCl_5} + \mathrm{CS_2} \rightarrow \mathrm{CCl_4} + 2\ \mathrm{SbCl_3} + 2\ \mathrm{S}$$

Reaction with iodine forms iodine monochloride, ICl which combines with excess $SbCl_5$ to form adducts, $SbCl_5 \cdot 2ICl$ and $SbCl_5 \cdot 3ICl$; similarly reaction with chlorine trifluoride, ClF_3 gives antimony dichlorotrifluoride, $SbCl_2F_3$.

Analysis

Elemental composition: Sb 40.72%, Cl 59.28%.

The compound is digested with nitric acid and the solution is analyzed for antimony by AA or ICP spectrophotometry (see Antimony). To determine the chlorine content a measured amount of substance is heated at 300°C and the liberated Cl_2 is passed into an acidic solution of KI and analyzed by iodometric titration using a standard solution of sodium thiosulfate or phenyl arsine oxide and starch indicator.

Hazard

Antimony pentachloride reacts explosively with phosphonium iodide, PH_4I (Mellor, J. W. 1947. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Oxford, UK: Longmans and Green) and explodes mildly when treated with oxygen difluoride at 150°C (Bretherick, L. 1995. *Handbook of Reactive Chemical Hazards*, 5th edition, ed. P.G.Urben, p. 1420. Oxford, UK:

Butterworth-Heinemann). The liquid is corrosive to skin. Exposure to its dust can cause irritation of upper respiratory tract and slightly delayed abdominal pain; the effect attributed to HCl produced upon contact with moist tissues (Cordasco, E.M. 1974. *Angiology*, 25, p. 590).

ANTIMONY PENTAFLUORIDE

[7783–70–2]
Formula SbF_5; MW 216.74; linear polymeric chains in liquid state and cyclic tetramer structures in solid phase associated with F bridging atoms. Such F bridges exist even in the gas phase (Passmore, J. 1985. *J Chem. Soc.* Dalton Trans., p. 9)

Uses

Antimony pentafluoride is used as a fluorinating agent for fluorination of organic compounds.

Physical Properties

Colorless oily liquid; highly viscous; hygroscopic; freezes at 8.3°C; boils at 149.5°C; density 2.99 g/cm^3 at 23°C; soluble in excess water (with violent reaction) and glacial acetic acid; also soluble in potassium fluoride.

Preparation

Antimony pentafluoride is prepared by the reaction of antimony pentachloride with anhydrous hydrogen fluoride:

$$SbCl_5 + 5\ HF \rightarrow SbF_5 + 5\ HCl$$

It may also be prepared from antimony trifluoride and fluorine, or by treating antimony pentaoxide with aqueous hydrofluoric acid and evaporating water.

Reactions

Antimony pentafluoride reacts with calculated amount of water forming a solid dihydrate, $SbF_5 \cdot 2H_2O$. The reaction is violent in excess water when the dihydrate dissolves forming a clear solution. It hydrolyzes slowly in caustic alkalies forming a hexacoordinated complex anion, $Sb(OH)_6^-$. It reacts with organics forming their fluoro derivatives. It combines with iodine forming two dark-colored adducts, SbF_5I (m.p. 80°C) and $Sb_2F_{10}I$ (m.p. between 110°C to 115°C), both of which readily decompose in water. Similarly reaction with nitrosyl fluoride, NOF forms a stable adduct, $NOSbF_6$. It forms mixed pentahalides, such as $SbCl_4F$, $SbCl_3F_2$ and $SbCl_2F_3$. Sulfur dissolves in antimony pentafluoride forming a dark blue solution from which antimony thiopentafluoride, $SbSF_5$ crystallizes out.

Being a fluoride ion acceptor, $SbCl_5$ enhances the acidities of HF and HSO_3F solutions, forming SbF_6^- ion or more complex species. Thus, SbF_5 in liquid HF gives a conducting solution as per the following equation:

$$2\ HF + SbF_5 \rightarrow H_2F^+ + SbF_6^-$$

(Cotton, A. F. and G. Wilkinson, 1988. *Advanced Inorganic Chemistry*, 5th Ed., p. 394, New York: John Wiley)

Analysis

Elemental composition: Sb 56.17%, F 43.38%

The compound is cautiously dissolved in nitric acid and the solution is appropriately diluted for the analysis of antimony by AA spectrophotometry or ICP emission spectrophotometry; and fluoride ion is determined by ion–selective electrode or ion chromatography.

Hazard

The liquid is corrosive to skin; vapors can cause respiratory tract irritation.

ANTIMONY PENTASULFIDE

[1315–04–4]

Formula Sb_2S_5; MW 403.82 indefinite composition; antimony occurs in the trivalent state containing a variable amount of sulfur.

Synonyms: golden antimony sulfide; golden sulfide of antimony; antimonic sulfide

Uses

Antimony pentasulfide is used in vulcanization of rubber to produce red rubber; in fireworks; and as a pigment.

Physical Properties

Orange-yellow or reddish amorphous powder; density 4.12 g/cm^3; decomposes at 75°C; insoluble in water and alcohol; soluble in hydrochloric acid, caustic alkalies and ammonium hydrosulfide.

Preparation

The compound is made commercially by converting antimony trisulfide to tetrathioantimonate by boiling with sulfur in caustic soda solution:

$$4\ Sb_2S_3 + 8\ S + 18\ NaOH \rightarrow 5\ Na_3SbS_4 + 3\ NaSbO_3 + 9\ H_2O$$

The sparingly soluble sodium antimonate is filtered out of the solution. The yellow-orange antimony pentasulfide precipitates out on treatment with hydrochloric acid.

$$2\ Na_3SbS_4 + 6\ HCl \rightarrow Sb_2S_5 + 6\ NaCl + 3\ H_2S$$

It may also be prepared by the reaction of antimony pentachloride in HCl with hydrogen sulfide and removing any free sulfur by extraction with carbon disulfide:

$$2\ SbCl_5 + 5\ H_2S \rightarrow Sb_2S_5 + 10\ HCl$$

Reactions

Antimony pentasulfide reacts with caustic soda forming soluble sodium thioantimonate, Na_3SbS_4. It is sparingly soluble in sodium antimonate, $NaSbO_3$. It forms a yellow solution with ammonia, and leaves a residue of antimony trisulfide, Sb_2S_3 and sulfur.

Analysis

Elemental composition: Sb 60.30%, S 39.70%

Antimony is analysed using AA or ICP spectrophotometry.

ANTIMONY PENTOXIDE

[1314–60–9]

Formula Sb_2O_5; MW 323.50; always occurs in hydrated form, $Sb_2O_5 \cdot nH_2O$; commercial product is either hydrated Sb_2O_5 or $–Sb_2O_4$

Synonyms: antimony(V) oxide; antimonic acid (hydrated oxide)

Uses

Antimony pentoxide is used as an ion-exchange resin for a number of cations in acidic solution including Na^+ (especially for their selective retentions); and as a polymerization and oxidation catalyst.

Physical Properties

Yellow powdery solid; density 3.80 g/ cm^3; very slightly soluble in water; hydrated pentoxide is insoluble in nitric acid; dissolves in an aqueous solution of caustic potash.

Thermochemical Properties

$\Delta H°f$	–232.30 kcal/mol
$\Delta G°f$	–198.20 kcal/mol
S^o	29.9 cal/deg mol

Preparation

The hydrated oxide is prepared by hydrolysis of antimony pentachloride; or by acidification of potassium hexahydroxoantimonate(V), $KSb(OH)_6$ [12208–13–8]. The product, filtered and air dried at ambient temperature has approximate composition $Sb_2O_5 \cdot 3.5H_2O$. It may be also prepared by oxidation of antimony trioxide with nitric acid.

Reactions

When heated at 700°C the yellow hydrated pentoxide converts to an anhydrous white solid with a formula Sb_2O_{13} containing both Sb(III) and Sb(V). Heating at 900°C produces a white insoluble powder of SbO_2 of both α and β forms. The β form consists of Sb(V) in octahedral interstices and pyramidal $Sb(III)O_4$ units.

Hydrated pentoxide reacts with metal hydroxides to form hydrated antimonate(V) salts, with the general formula $M(SbO_3)_2 \cdot 12H_2O$. In these compounds Sb(V) atom is octahedrally coordinated to six –OH groups.

Treatment with NaOH solution produces sodium pyroantimonate, $Na(H_2O)_6\,[Sb(OH)_6]_2$ [10049–22–6] and sodium hexahydroxo antimonate(V), $Na[Sb(OH)_6]$ [12339–41–2]. Heating with metal oxides and carbonates produces various polyantimonate(V) derivatives.

ANTIMONY TRICHLORIDE

[10025–91–9]
Formula $SbCl_3$; MW 228.13; pyramidal molecular structure in the upper phase; Sb–Cl bond distance 2.38Å

Uses

Antimony trichloride is used as a catalyst for polymerization, hydrocracking and chlorination reactions; as a mordant; and in the production of other antimony salts. Its solution is used as an analytical reagent for chloral, aromatics and vitamin A.

Physical Properties

Colorless crystalline solid; orthorhombic crystal; hygroscopic; density 3.14 g/cm^3; melts at 73.4°C; boils at 220.3°C; readily dissolves in water undergoing hydrolysis; soluble in dilute hydrochloric acid, ethanol, acetone, benzene, dioxane and CS_2.

Thermochemical Properties

$\Delta H°f$	–91.4 kcal/mol
$\Delta G°f$	–77.4 kcal/mol
S°	44.0 cal/mol deg
C_ρ	25.8 cal/mol deg

Preparation

$SbCl_3$ is prepared by reaction of chlorine with antimony, antimony trioxide or antimony trisulfide. It also may be made by treating antimony trioxide with concentrated hydrochloric acid.

Reactions

Antimony trichloride hydrolyzes readily with water. With limited quantities of water and under carefully controlled conditions it becomes antimony chloride oxide, SbOCl, a butter-like mass, which is also formed when the trichloride picks up moisture from the air. A common hydrolysis product from partial hydrolysis is tetraantimony dichloride pentoxide, $Sb_4O_5Cl_2$, initially a thick white solid which changes to colorless crystal. Other partially hydrolyzed products include Sb_2OCl_4, $Sb_4O_3(OH)_3Cl_2$, $Sb_8O_{11}Cl_2$ and Sb_8OCl_{22}. With excess water hydrous antimony oxide, $Sb_2O_3 \cdot nH_2O$ is formed.

Heating with chlorine, or passing the gas into the molten trichloride yields antimony pentachloride, $SbCl_5$. Reaction with HF produces trifluoride, SbF_3.

$SbCl_3$ forms complexes with neutral donors. It also behaves as a Lewis acid forming chloroantimonate (III) ions, such as $SbCl_4^-$, $SbCl_5^{2-}$, $SbCl_6^{3-}$, $Sb_2Cl_7^{2-}$ etc., which are likely to form in the presence of metal ions and excess Cl^- ion. It forms a number of adducts with organic bases, such as, aniline and trimethylamine. Example of such adducts include $SbCl_3 \cdot H_2NC_6H_5$, $SbCl_3 \cdot (CH_3)_3N$, $2SbCl_3 \cdot (CH_3)_3N$, $SbCl_3 \cdot (C_2H_5)_2O$ and $SbCl_3 \cdot 2CH_3COCH_3$. It also forms 2:1 and 1:1 complexes with benzene, p–xylene, naphthalene and other aromatics, i.e., $2SbCl_3 \cdot C_6H_6$ and $SbCl_3 \cdot C_6H_6$.

Antimony trichloride also behaves as a Lewis base. However, such reactions are very limited. They include the formation of carbonyl complexes $Fe(CO)_3(SbCl_3)_2$ and $Ni(CO)_3SbCl_3$.

Analysis

Elemental composition: Sb 53.37%, Cl 46.63%. The compound may be identified from its melting and boiling points. Antimony may be analyzed by AA or ICP spectroscopy. The trichloride may be hydrolyzed with limited quantities of water, the thick white precipitate turns to colorless crystals of $Sb_4O_5Cl_2$ which is separated and analyzed for elemental composition.

Health Hazard

The compound is corrosive to skin. Inhalation of its vapors can produce upper respiratory tract irritation, slightly delayed abdominal pain, and loss of appetite (Taylor, P. J. 1966. *Brit. J. Ind. Med.*, 23, p. 318).

ANTIMONY TRIOXIDE

[1309–64–4]
Formula Sb_2O_3; MW 291.50
Synonyms: antimony(III) oxide; antimony sesquioxide

Occurrence and Uses

Antimony trioxide occurs in nature as minerals, valentinite [1317–98–2] and senarmontinite [12412–52–1]. It is used as a flame retardant in fabrics; as an opacifier in ceramics, glass and vitreous enamels; as a catalyst; as a white pigment in paints; as a mortar in the manufacture of tartar emetic; and in the production of metallic antimony.

Physical Properties

Occurs as colorless orthorhombic modifications, valentinite, or colorless cubic form, senarmontite; density 5.67 g/cm^3 (valentinite), 5.20g/cm^3 (senarmontite); cubic modification is dimeric consisting of Sb_2O_6 discrete molecules; refractive index 2.087; melts in the absence of oxygen at 656°C; boils at 1,550°C (sublimes); sublimes in vacuum at 400°C; very slightly soluble in water, insoluble in organic solvents; soluble in HCl, caustic alkalies and tartaric acid.

Thermochemical Properties

$\Delta H°f$	–164.90 kcal/mol
H_{fus}	46.3 cal/g

Preparation

Antimony trioxide is obtained by roasting stibnite:

$$2\ Sb_2S_3 + 9\ O_2 \rightarrow 2Sb_2O_3 + 6SO_2$$

Temperature and air feed is carefully controlled in the process to suppress any formation of antimony tetroxide (Sb_2O_4). Antimony trioxide is separated from any arsenic trioxide (As_2O_3) that may be present as an impurity by volatilization, as the latter is much more volatile than the former. It may be also prepared by alkaline hydrolysis of antimony trichloride and subsequent dehydration of hydrous oxide under controlled heating (rapid or vigorous heating may partially oxidize Sb(III) to Sb(V).

Antimony trioxide also may be made by heating the metallic element with oxygen or air. The volatilizing trioxide is condensed and collected.

Reactions

Antimony trioxide is an amphoteric oxide, exhibiting both acidic and basic behavior. It dissolves in strong acids forming antimony salts; e.g., reacts with aqueous hydrofluoric acid to form antimony trifluoride, SbF_3. It reacts with strong alkalies to form antimonites, such as sodium or potassium antimonites, Na_3SbO_3 or K_3SbO_3:

$$Sb_2O_3 + 6\ KOH \rightarrow 2\ K_3SbO_3 + 3\ H_2O$$

It is oxidized to antimony pentoxide, Sb_2O_5 on treatment with nitric acid; and forms potassium antimony tartrate (tartar emetic, $KSb(OH)_2 \cdot C_4H_2O_6$) when heated with acid potassium tartrate.

ANTIMONY TRISULFIDE

[1345–04–6]
Formula: Sb_2S_3; MW 339.72

Synonym: antimony sesquisulfide; antimony sulfide

Occurrence and Uses

Antimony trisulfide occurs in nature primarily as the mineral, stibnite, which consists of two parallel Sb_4S_6 chains linked together. It is used in fireworks; in certain types of safety matches; as a pigment in paints; and in the manufacture of ruby glass.

Physical Properties

Natural stibnite is black orthorhombic crystal; or grayish-black powder; the compound also exists as an amorphous substance in yellow-red modification; distorted octahedral arrangement; density 4.64 g/cm³ for the natural stibnite and 4.12 g/cm³ for the red modification; melts at 550°C; vaporizes around 1150°C; insoluble in water (1.75mg/L at 18°C) and acetic acid; soluble in hydrochloric acid and caustic soda solution; also, soluble in alcohol, ammonium hydrosulfide and potassium sulfide.

Thermochemical Properties

Black stibnite crystal	
$\Delta H°f$	–41.8 kcal/mol
$\Delta G°f$	–41.5 kcal/mol
S°	43.5 cal/deg mol
C_ρ	28.65 cal/deg mol
Red amorphous modification	
$\Delta H°f$	–35.2 kcal/mol

Preparation

The pure sulphide is obtained from its ore. Stibnite is separated from other ores by grinding and flotation. The ore is then heated to 550–600°C in a perforated vessel. The pure molten material is collected and cooled. It is also prepared by passing hydrogen sulfide into a solution of antimony trichloride:

$$2\ SbCl_3 + 3\ H_2S \rightarrow Sb_2S_3 + 6\ HCl$$

or treating antimony trichloride solution with sodium thiosulfate.

Alternatively, heating antimony metal or antimony trioxide with sulfur forms antimony trisulfide:

$$2\ Sb + 3\ S \rightarrow Sb_2S_3$$

$$2\ Sb_2O_3 + 9\ S \rightarrow 2\ Sb_2S_3 + 3\ SO_2$$

All these above preparative methods yield amorphous antimony trisulfide.

Reactions

Heating with sodium sulfide and sulfur or with sodium polysulfide produces sodium thioantimonate, Na_3SbS_4 (also, known as Schlippe’s salt),

$$Sb_2S_3 + 3Na_2S + 2\ S \rightarrow 2Na_3SbS_4$$

which on treatment with hydrochloric acid decomposes to antimony pentasulfide:

$$2Na_3SbS_4 + 6HCl \rightarrow Sb_2S_5 + 6\ NaCl + 3\ H_2S$$

Heating with sodium sulfide alone forms sodium thioantimonite:

$$Sb_2S_3 + 3\ Na_2S \rightarrow 2\ Na_3SbS_3$$

Sodium antimonate and thioantimonate are formed when a mixture of antimony trisulfide and sulfur are added to an excess boiling aqueous caustic soda solution:

$$4\ Sb_2S_3 + 8\ S + 18\ NaOH \rightarrow 5\ Na_3SbS_4 + 3\ NaSbO_3 + 9\ H_2O$$

It dissolves in and reacts with concentrated hydrochloric acid, liberating H_2S:

$$Sb_2S_3 + 6\ HCl \rightarrow 2SbCl_3 + 3\ H_2S$$

Analysis

Elemental composition: Sb 71.68%, S 28.32%

The compound is treated with concentrated HCl; H_2S is liberated and is identified from its odor; which also turns lead acetate paper black. The liberated H_2S is transported onto a GC port by helium carrier gas and determined by an FID, TCD or FPD. Antimony in the solution may be analyzed by flame or furnace AA or by ICP spectrophotometry. The solid powder may be characterized by X–ray diffraction technique.

ARGON

[7440–37–1]

Symbol Ar; atomic number 18; atomic weight 39.948; an inert gas element; electronic configuration $1s^22s^22p^63s^23p^6$; 1st ionization potential 15.76eV; stable isotopes and natural abundance: Ar–40 99.6%, Ar–36 0.337%, Ar–38 0.063%; unstable isotopes, half-life and disintegration mode:

Ar–35	1.83sec	α-decay
Ar–37	35 days	electron capture
Ar–39	265 yr	β^- decay
Ar–41	9.17 yr	β– decay
Ar–42	~3.5 yr	β– decay

Occurrence

The element was discovered by Lord Raleigh and Sir William Ramsay in 1894. Argon is the third most abundant element in the atmosphere. Its concentration in air is 0.934% by volume. Also, it occurs in earth's crust at a concentration of 3.4 mg/kg, and in the sea water at 4.3 µg/L. It was most likely formed in earth crust by radioactive decay of K–40 and seeped out into the atmosphere. Argon–40 has been detected in the atmosphere of Mars, estimated to be about 1.6% by volume.

Uses

Argon has numerous applications in metallurgy, cryogenic, electronic, laboratory and as light sources. It is used in low-pressure gas discharge tubes as a filler gas, emitting bluish light. It is also used mixed with other inert gases in mercury- and sodium-vapor lamps. In metallurgy it is used to shield and protect welding metal arcs; in surface cleaning of metals; as a working fluid in plasma arc devices; as an inert blanket in melting and casting of certain alloys; to atomize molten metals and produce their powder; and in high-temperature soldering and refining operations; and powder metal sintering. In the laboratory, argon is used as a carrier gas for gas chromatography; or for metal analysis by furnace atomic absorption or inductively coupled plasma emission spectrophotometry; and as a filler gas (often mixed with other gas) in Geiger–Muller, proportional cosmic ray and scintillation counters. It is also used as inert atmosphere in glove boxes to carry out reactions and handling of air-sensitive substances.

Argon is used as a low-temperature cryogenic fluid for isothermal baths. It is also used in air sampling by condensing the air in a trap and subsequently analyzing organic pollutants. In electronic industry argon and helium are used as protective atmosphere and heat-transfer medium to grow single crystals of ultrapure semiconductors; and as diluents and carriers of dopant gases such as phosphine or arsine.

Physical Properties

Colorless and odorless gas; heavier than air, density of the gas 1.7838 g/L at 0°C and 1.394 g/L for the liquid at the normal boiling point; liquefies at –185.9°C; solidifies at –189°C; critical temperature –122.3°C; critical pressure 48.34 atm; density at critical point 0.536 g/ml; viscosity of the gas 226.4 micropoise at 25°C and 1 atm and that for the liquid 2.75 millipoise at the boiling point; sonic velocity 307.8 m/sec at 25°C and 1 atm; practically insoluble in water (5.6 cc/100 cc at 0°C or 100 mg/L at 0°C).

Thermochemical Properties

Heat of vaporization (At the normal boiling point)	1550 cal/mol
Heat of fusion (At the triple point)	283 cal/mol
Heat capacity, Cp	4.99 cal/deg mol

Manufacture

Air is the primary source of argon. Argon is obtained by liquefaction of air followed by separation from liquid oxygen and nitrogen by distillation. High purity–grade gas is made from the crude gas by passage over heated copper or by selective adsorption. An alternative purification process involves addition of hydrogen followed by catalytic combustion of trace oxygen in argon and then reliquefication of argon to remove excess hydrogen.

Chemical Properties

No true chemical compound of argon is known. Its hydrate has been characterized; so have the ion molecules, such as $(ArH)^+$, $(ArXe)^+$ or $(ArKr)^+$ formed in electric discharge tubes. Unstable AgF [56617–31–3] is produced in excited state by electron-beam pumping or discharge pumping of argon and fluorine gas mixture. Also, it forms a clathrate with –hydroquinone (see under Argon Hydroquinone Clathrate). None of these above products shows atoms chemically bonded to argon.

Analysis

Argon is analyzed by mass spectrometry (characteristic ion m/z 40) or by gas-solid chromatography. Its concentration can be increased by several times by selective adsorption over a suitable adsorbent followed by thermal desorption of the gas onto the GC injection port.

ARGON HYDROQUINONE CLATHRATE

[14343–01–2]

Argon forms a cage-type clathrate with -hydroquinone where it fits into the small cage opening space or cavity of the hydroquinone structural unit. The diameter of the cage system is 0.42 nm. The molecular ratios of argon to hydroquinone in such nonstoichiometric inclusion substances are in the range 0.3 to 0.85 molecule of Ar for three molecules of hydroquine (in a three-dimensional network), which is equivalent to a mass of 3.6 to 10.3 g argon per 100 g hydroquinone. The heat of formation is in the range 5.86 kcal/mol. Argon is adsorbed to hydroquinone by weak Van der Waal force and there is no evidence of any type of chemical bonding. The clathrate is stable at room temperature and atmospheric pressure and can be stored for several weeks without much loss of argon. It may be noted that the presence of argon in the clathrate cages stabilizes modification of the hydroquinone molecule, which otherwise is unstable itself.

ARSENIC

[7440–38–2]

Symbol As; atomic number 33; atomic weight 74.922; covalent radius As^{3+} 1.21Å; electron configuration [Ar] $4s^23d^{10}4p^3$; a Group VA (Group 15) metalloid element; electronegativity 2.20 (Allred-Rochow type); principal valence states, +5, +3, 0, and –3; stable isotope As–75.

Occurrence

Arsenic is widely dispersed in nature: found in the minerals arsenopyrite, FeAsS; orpiment, As_2S_3; realgar, As_2S_2; lollengite, $FeAs_2$; enargite, CuS •

As_2S_5. Terrestrial abundance of this element is estimated to be 5 g/ton (Carapella (Jr), S. C. 1968. In *The Encyclopedia of the Chemical Elements,* ed. Clifford A. Hampel, pp. 29–33, New York: Reinhold Book Corp.).

Uses

The major uses are in metallurgy, primarily as an additive to lead, copper, brass and many lead-base bearing alloys to improve their mechanical and thermal properties. Small amounts are added to lead in the manufacture of lead shot to improve its sphericity; also added to lead-base cable sheathing and battery grid metal to improve hardness. Addition of very small quantities to copper enhances the corrosion resistance. It prevents cracking in brass.

Physical Properties

Steel-gray crystalline brittle metal; hexagonal crystal system; atomic volume 13.09 cc/g atom; three allotropes are known: namely, the α–metallic form, a black amorphous vitreous solid known as β–arsenic, and also a yellow allotrope. A few other allotropes may also exist but are not confirmed. Sublimes at 613°C when heated at normal atmospheric pressure; melts at 817°C at 28 atm; density 5.72 g/cc (β–metallic form) and 4.70 g/cm (β–amorphous form); hardness 3.5 Mohs; electrical resistivity (ohm–cm at 20°C) 33.3×10^{-6} (ß–metallic polycrystalline form) and 107 (β–amorphous form); insoluble in water.

Thermal Properties

Cp	0.082 cal/g/°C
ΔH_{fus}	88.5 cal/g
ΔH_{subli}	102 cal/g
Coeff. linear expansion, 20ºC	4.7×10^{-6}/°C

Manufacture

The metallic arsenic is obtained primarily from its mineral, arsenopyrite. The mineral is smelted at 650 to 700°C in the absence of air. However, the most common method of production of the metal involves reduction of arsenic trioxide, AsO_3 with charcoal. Arsenic trioxide is produced by oxidation of arsenic present in the lead and copper concentrates during smelting of such concentrates. The trioxide so formed, readily volatilizes and is collected in a dust flue system where further treatment and roasting can upgrade the trioxide content. The trioxide vapors are then condensed and further purified by pressure leaching and recrystallization techniques. It is then reduced with charcoal to give metallic arsenic.

Chemical Properties

Elemental arsenic is stable in dry air but exposure to moist air tarnishes its surface to a golden bronze color which converts to a black oxide on further exposure. Arsenic vapors react with oxygen to form arsenic trioxide (sesquioxide):

$$2\ As + 3\ O_2 \rightarrow As_2O_6$$

Ordinarily arsenic does not react with water, hydrogen, caustic soda or hydrochloric acid. However, in presence of an oxidant it reacts with concentrated HCl. In concentrated HCl solution it reacts with hydrogen sulfide to form a precipitate of yellow arsenic sulfide, As_2S_3. It forms orthoarsenic acid, H_3AsO_4 on reaction with concentrated nitric acid and chlorinated water.

When heated with chlorine, bromine or iodine vapors arsenic forms the corresponding trihalides; however, with fluorine, arsenic pentafluoride, AsF_5 is produced. With sulfur it forms mixtures of sulfides, As_2S_3, As_2S_2 and As_2S_5 in vitreous forms and varying proportions depending on the conditions of reactions.

Arsenic combines with electropositive metals to form their arsenides, i.e., Mg_3As_2 or AlAs.

Analysis

Microgram amounts may be measured by atomic absorption spectrophotometry either in flame or furnace mode. The metal is digested with nitric acid and converted to hydride vapors prior to flame AA determination. It may be determined over a much wider concentration range using inductively coupled plasma emission spectrometry. Also, it can be determined by neutron activation analysis, titration, gravimetry or by colorimetric techniques. Arsenic sample is treated with a strong HCl solution, distilled as trichloride, $AsCl_3$. The trichloride is precipitated as silver arsenate which is dissolved in HNO_3 and titrated by Volhard method. In trivalent state the metal may be titrated with iodine, $KMnO_4$ or $KBrO_3$. Trace quantities may be determined colorimetrically. The metal forms colored complex on treatment with diethyldithiocarbamate or molybdenum blue. Gravimetric methods may be applied to estimate arsenic in amounts greater than 1 mg. It may be precipitated as trisulfide by H_2S or as pentasulfide by treatment with thioacetamide and determined gravimetrically.

Toxicity

Elemental arsenic is much less toxic than its soluble compounds. Only its uncommon yellow allotrope is highly toxic. Inhalation of metal dusts can cause ulceration of nasal septum. Ingestion may produce systemic skin and gastrointestinal effects in humans. Arsenic and its compounds are human carcinogens producing liver tumors.

ARSENIC ACID

[7778–39–4]
Formula $H_3AsO_4 \cdot 0.5H_2O$; MW 150.95;
Synonyms: orthoarsenic acid, arsenic acid hemihydrate

Commercial arsenic acid is usually the orthoarsenic acid [7774–41–6] corresponding to the above hemihydrate formula. The aqueous solution of this acid behaves as a triprotic acid: the dissociation constants, K_1, K_2 and K_3 being $5.6x10^{-3}$, $1.7x10^{-7}$ and $3.0x10^{-12}$,respectively. The meta and pyro forms of the acid are also known, namely metaarsenic acid, $HAsO_3$ or $As(OH)O_2$ [10102–53–1] and the pyroarsenic acid, $H_4As_2O_7$ [13453–15–1]. All these forms are interconvertible. For example, orthoarsenic acid or its orthoarsenate salt is produced when the meta– or the pyro form is treated with cold water. Similarly heating at 100°C converts orthoarsenic acid to pyroarsenic acid. Further heating produces metaarsenic acid.

Physical Properties

Hygroscopic translucent crystals; density between 2 to 2.5 g/cm^3; melts at 35.5°C; loses water when heated to 160°C; highly soluble in cold water; soluble in alcohol, glycerol and alkalies.

Thermochemical Properties

$\Delta H°f$ (H_3AsO_4, solid)	–216.6 kcal/mol
$\Delta H°f$ (H_3AsO_4, aq)	–216.2 kcal/mol

Preparation

Arsenic acid is prepared by treating arsenic trioxide with concentrated nitric acid; or by combination of arsenic pentoxide with water. The latter reaction is very slow. It is also formed when meta- or pyroarsenic acid is treated with cold water.

Reactions

Arsenic acid reacts with metal salts forming their orthoarsenates, e.g., calcium orthoarsenate. Reaction with silver nitrate in neutral solution produces a chocolate-brown precipitate of silver orthoarsenate. It forms pyroarsenic acid (or pyroarsenate) on heating over 100°C. It is reduced to arsenous acid (or arsenites) when treated with reducing agents.

Toxicity

The solid or aqueous solution is highly toxic. Toxic symptoms are similar to other soluble arsenic compounds. See Arsenic.

ARSENIC PENTASULFIDE

[1303–34–0]
Formula: As_2S_5; MW 310.14;
Synonyms: diarsenic pentasulfide; arsenic (V) sulfide

Uses

Arsenic pentasulfide is used as pigment; and as a light filter in thin sheets.

Physical Properties

Yellow-brown glassy amorphous solid; sublimes on heating; decomposes around 500°C; insoluble in cold water (~1.4 mg/L at 0°C); dissolves in alkalies and solutions of alkali metal sulfides, and in nitric acid.

Preparation

Arsenic pentasulfide is prepared by precipitation from an acidic solution of orthoarsenic acid, H_3AsO_4, or arsenic pentachloride, $AsCl_5$ or any other soluble As(V) salt by passing hydrogen sulfide. It may be also prepared by heating a mixture of arsenic and sulfur, extracting the fused mass with ammonia solution and reprecipitating arsenic pentasulfide at low temperature by addition of HCl.

Reactions

Arsenic pentasulfide hydrolyzes in boiling water, giving arsenous acid, H_3AsO_3 and sulfur:

$$As_2S_5 + 6\,H_2O \rightarrow 2\,H_3AsO_3 + 2\,S + 3\,H_2S$$

It oxidizes in air at elevated temperatures producing arsenic oxides, the products and yields of which depend on the air supply. In alkali metal sulfide solutions arsenic pentasulfide forms thioarsenate anion, $[AsS_4]^{3-}$ and its alkali metal salts, e.g., Na_3AsS_4.

ARSENIC PENTOXIDE

[1303–28–2]
Formula: As_2O_5; MW 229.84;
Synonyms: arsenic(V) oxide; arsenic acid anhydride

Uses and Occurrence

Arsenic pentoxide is used to make colored glass; in fungicide formulations; in adhesive for metals; in wood preservatives; in dyeing and printing; and to prepare arsenates.

Physical Properties

White amorphous solid; deliquescent; density 4.32 g/cm³; melts at 315°C; dissolves slowly in water but is very soluble (230 g/100g at 20°C); also soluble in alcohol.

Thermochemical Properties

$\Delta H°f$	–221.2 kcal/mol
$\Delta G°f$	–187.1 kcal/mol
S°	25.20 cal/deg mol
C_ρ	27.86 cal/deg mol

Preparation

Arsenic pentoxide is prepared by dehydration of crystalline arsenic acid at 200°C or above. The former is made by treating arsenic metal or arsenious oxide with nitric acid. Also, the pentoxide can be prepared by the reaction of arsenic trioxide with oxygen under pressure.

Reactions

The aqueous solution of arsenic pentoxide is arsenic acid which probably corresponds to the hemihydrate formula $H_3AsO_4 \cdot 0.5H_2O$. See Orthoarsenic acid. It behaves as a triprotic acid forming various arsenate derivatives of metals.

Arsenic pentoxide loses oxygen on heating at 300°C, near its melting point, producing arsenic trioxide, As_2O_3. It is an oxidizing agent, liable to react vigorously with reducible substances, i.e., it liberates chlorine from HCl.

Toxicity

Highly toxic, LD_{50} oral (rat): 8 mg/kg; carcinogenic.

ARSENIC SESQUISULFIDE

[1303–33–9]
Formula As_2S_3; MW 246.04;
Synonyms: arsenic trisulfide; arsenic sulfide; arsenous sulfide; king's gold; king's yellow; orpiment; yellow arsenic sulfide

Occurrence and Uses

Arsenic sesquisulfide occurs in nature as the mineral orpiment. It is used as a pigment; in the manufacture of infrared-transmitting glass; in semiconductors and photoconductors; in pyrotechnics; in linoleum and oil cloth; for the removal of hairs from hides; and as a reducing agent.

Physical Properties

Yellow or orange monoclinic crystal or powder; a red allotrope modification also known; density 3.46 g/cm³; melts at 310°C; boils at 707°C; insoluble in water; soluble in liquid ammonia and alkalies.

Thermochemical Properties

$\Delta H°f$	–40.41 kcal/mol
$\Delta G°f$	–40.32 kcal/mol
S°	39.12 cal/deg mol
C_ρ	27.81 cal/deg mol

Preparation

Arsenic sesquioxide may be prepared by heating arsenic trioxide with hydrogen sulfide:

$$As_2O_3 + 3\ H_2S \rightarrow As_2S_3 + 3\ H_2O$$

Alternatively, it may be precipitated out from a solution of arsenous acid or arsenic trioxide in dilute hydrochloric acid by passing hydrogen sulfide into the solution:

$$2H_3AsO_3 + 3H_2S \rightarrow As_2S_3 + 6H_2O$$

Reactions

Arsenic sesquisulfide burns in air giving arsenic trioxide and sulfur dioxide:

$$2As_2S_3 + 9O_2 \rightarrow 2As_2O_3 + 6SO_2$$

Reaction with chlorine produces arsenic trichloride and sulfur chloride:

$$2As_2S_3 + 9Cl_2 \rightarrow 4AsCl_3 + 3S_2Cl_2$$

When mixed with sodium sulfide solution it forms sodium dithioarsenite:

$$As_2S_3 + Na_2S \rightarrow 2\ NaAsS_2$$

The reaction in polysulfide solution produces thioarsenate ion, AsS_4^{3-}. It is oxidized by common oxidants including nitric acid, hydrogen peroxide, ozone and permanganate undergoing vigorous to violent decomposition.

Analysis

Elemental composition: As 60.90%, S 39.10%. See Arsenic.

ARSENIC SULFIDE

[12279–90–2]
Formula As_4S_4; MW 427.95;
Synonyms: arsenic disulfide; arsenic monosulfide; red arsenic sulfide; ruby arsenic; realgar; red orpiment.

Occurrence and Uses

Arsenic sulfide occurs in nature as the mineral realgar. It is used as a pigment; in pyrotechnics to produce blue fire; in dyeing and calico printing; and as a depilatory for hides.

Physical Properties

Red monoclinic crystal; changes into a black allotropic modification at 267°C; density 3.50g/cm^3; melts at 320°C; boils at 565°C; insoluble in water; soluble in alkalies.

Thermochemical Property

$\Delta H°f$	–68.15 kcal/mol

Preparation

Arsenic sulfide is prepared commercially by heating a mixture of iron pyrites and arsenopyrite; or by heating arsenic trioxide with sulfur. The compound is then sublimed and collected. It may be also made from arsenic sesquisulfide – by either heating with sodium bicarbonate in a sealed tube or on prolong treatment with boiling solution of sodium carbonate.

Reactions

When heated in air at 800°C As_4S_4 vapors begin to dissociate to As_2S_2 which then ignites to form arsenic oxides. Ignition in chlorine produces arsenic chloride. Reaction with fluorine forms arsenic trifluoride. It is stable in water; and also in the air at ambient temperatures. It does not react with hot concentrated HCl but is decomposed by nitric acid. It forms thioarsenite ion, AsS_3^{3-} and elemental arsenic when warmed with caustic soda solution. Similar reaction occurs with sodium sulfide.

Analysis

Elemental composition: As 70.03%, S 29.97%. See Arsenic.

ARSENIC TRICHLORIDE

[7784–34–1]
Formula $AsCl_3$; MW 181.28; pyramidal structure; dipole moment in molecule in the gas phase1.59 μ/D; Synonym: arsenic (III) chloride; arsenic chloride

Uses

Arsenic trichloride is used in the preparation of many chloroderivatives of arsenic that have pharmaceutical and insecticide applications.

Physical Properties

Colorless oily liquid; fumes in air; density 2.163 g/ml at 20°C; refractive index 1.621 at 14°C; melts at 0.16°C; boils at 130.2°C; vapor pressure 9.75 torr at 25°C; decomposes in water; soluble in alcohol, ether, HCl and HBr.

Thermochemical Properties

$\Delta H°f$ (liq)	–72.9 kcal/mol
$\Delta H°f$ (gas)	–62.5 kcal/mol
$\Delta G°f$ (liq)	–59.5 kcal/mol
S° (liq)	51.7 cal/deg mol
S° (gas)	78.17 cal/deg mol
C_ρ (liq)	18.10 cal/deg mol
ΔH_{vap}	8.9 kcal/mol

Preparation

The compound is generally made from arsenic trioxide by (i) passing chlorine over it or (ii) treating the trioxide with sulfur monochloride, S_2Cl_2. Alternatively it is prepared from arsenic trioxide by distillation with either concentrated hydrochloric acid or a mixture of sulfuric acid and a metal chloride. Arsenic trichloride may also be prepared by combination of arsenic and chlorine.

Reactions

Hydrolysis with water gives arsenous acid and HCl:

$$AsCl_3 + 3H_2O \rightarrow As(OH)_3 + 3HCl$$

Reaction with potassium bromide or iodide forms arsenic tribromide or arsenic triiodide.

Analysis

Elemental composition: As 41.32%, Cl 58.68%. See Arsenic.

Toxicity

Highly toxic by all routes of exposure, LC_{LO} inhalation (cat): 100 mg/m^3/1 hour; human carcinogen.

ARSENIC TRIFLUORIDE

[7784–35–2]
Formula AsF_3; MW 131.91

Physical Properties

Colorless oily liquid; fumes in air; etches glass; density 2.666 g/ml at 0°C; boils at 60.4°C; vapor pressure 100 torr at 13.2°C; solidifies at –8.5°C; decomposes in water; soluble in alcohol, ether, benzene and ammonia solution.

Thermochemical Properties

ΔH°ƒ(liq)	–196.3 kcal/mol
ΔH°ƒ(gas)	–187.8 kcal/mol
ΔG°ƒ(liq)	–184.0 kcal/mol
S°(liq)	43.31 cal/deg mol
S°(gas)	69.07 cal/deg mol
C_ρ (liq)	30.25 cal/deg mol
C_ρ (gas)	15.68 cal/deg mol

Preparation

The compound is prepared by reaction of arsenic trioxide with fluorosulfonic acid. Also it may be prepared by treating arsenic trioxide with a mixture of sulfuric acid and calcium fluoride.

Reactions

Arsenic trifluoride is hydrolyzed by water. It reacts with chlorine gas at ice-cold temperature to form arsenic dichloride trifluoride, $AsCl_2F_3$, a solid hygroscopic product that consists of the ions $AsCl_4^+$ and AsF_6^-.

It forms nitrosonium hexafluoroarsenate(V), $[NO][AsF_6]$ with nitrosyl fluoride; and a stable adduct with sulfur trioxide having the formula $2AsF_3 \cdot 3SO_3$.

Analysis

Elemental composition As 56.79%, F 43.21%. See Arsenic.

Toxicity

Highly toxic by all routes of exposure; LC_{LO} inhalation (mouse): 2000 mg/m^3/10 min; a human carcinogen.

ARSENIC TRIIODIDE

[7784–45–4]
Formula AsI_3; MW 455.635; pyramidal molecule with covalent bonding;
Synonym: arsenic (III) iodide; triiodoarsine; arsenous triiodide

Uses

Formerly the compound was used in dermatitides.

Physical Properties

Red solid; density 4.39 g/cm^3 at 15°C; melts at 146°C; boils at 403°C; sparingly soluble in cold water (6 g/100 ml at 25°C), decomposes in hot water; readily dissolves in chloroform, benzene and toluene and moderately soluble in alcohol, ether and carbon disulfide (5.8%).

Thermochemical Properties

$\Delta H°f$	–13.9 kcal/mol
$\Delta G°f$	–14.2 kcal/mol
S°(s)	50.92 cal/deg mol
S°(g)	92.79 cal/deg mol
C_ρ (s)	25.28 cal/deg mol
C_ρ (g)	19.27 cal/deg mol

Preparation

Arsenic triiodide is prepared by treating elemental arsenic with a solution of iodine in carbon disulfide. Alternatively, it can be precipitated out from a hot solution of arsenic trioxide or arsenic trisulfide in hydrochloric acid on treatment with potassium or sodium iodide. Also, it is made by the reaction of arsenic trichloride with potassium iodide.

Reactions

Hydrolysis occurs slowly in water forming arsenic trioxide and hydriodic acid. The reaction proceeds via formation of arsenous acid which exists in equilibrium with HI:

$$AsI_3 + 3\,H_2O = H_3AsO_3 + 3\,HI$$

The aqueous solution is highly acidic, pH of 0.1N solution is 1.1. It readily decomposes to arsenic trioxide, elemental arsenic and iodine when heated in air at 200°C. The decomposition, however, commences at 100°C:

$$6\ AsI_3 + 3\ O_2 \rightarrow 2As_2O_3 + 2\ As + 9\ I_2.$$

Analysis

Elemental composition: As 16.44%, I 83.56%. See Arsenic.

Toxicity

Toxic and carcinogen.

ARSENIC TRIOXIDE

[1327–53–3]
Formula: As_2O_3; MW 197.82
Synonyms: arsenic oxide; arsenic sesquioxide; white arsenic; arsenic (III) oxide; arsenious acid anhydride

Uses

Arsenic trioxide is used as a starting material to prepare metallic arsenic and a number of arsenic compounds. It is also used as a decolorizer for bottle glass; in pigments and ceramic enamels; for preserving hides; as a wood preservative; as an analytical standard in oxidimetry titrations; and in many rodenticide and herbicide formulations.

Physical Properties

White crystalline solid; occurs in two modifications, namely, an octahedral or cubic form known as arsenolite and a monoclinic form, claudetite; arsenolite consist of dimeric, As_2O_6 arranged in a diamond-type lattice, subliming above 135°C and dissociating above 800°C to As_2O_3; density 3.86 and 3.74 mg/cm^3 for arsenolite and claudetite, respectively; melts at 274°C (arsenolite) and 313°C (claudetite); boils at 460°C; vapor pressure 5 torr at 234°C; sparingly soluble in cold water (1.7% at 25°C, dissolves very slowly), moderately soluble in boiling water (6.7%); soluble in dilute acids and alkalies; practically insoluble in organic solvents.

Thermochemical Properties

$\Delta H°f$(arsenolite)	–314 kcal/mol
$\Delta H°f$(claudetite)	–313 kcal/mol
S° (arsenolite)	51 cal/deg mol
S° (claudetite)	55 cal/deg mol

Preparation

Arsenic trioxide is obtained by roasting the mineral arsenopyrite, FeAsS, in air at 650 to 700°C. It is also obtained as a by-product during the smelting of copper and lead concentrates during the extraction of these metals from their ores that contain arsenic. The latter readily oxidizes to arsenic trioxide which is volatilized. The vapors are then condensed and collected. High purity–grade oxide can be obtained by resublimation of the crude trioxide or by pressure leaching and recrystallization. Arsenic trioxide may also be prepared by hydrolysis of arsenic trichloride, –tribromide or –trifluoride.

Reactions

Arsenic trioxide dissolves in water to a slight extent, undergoing a slow hydrolysis reaction, forming weakly acidic orthoarsenous acid, $As(OH)_3$.

Its solution exhibits amphoteric behavior. It dissolves in aqueous bases to give arsenite ions that have formulas, $[AsO(OH)_2]^-$, $[AsO_2(OH)]^{2-}$ and $[AsO_3]^{3-}$.

Arsenic trioxide reacts with oxygen under pressure to form arsenic pentoxide, As_2O_5, a thermally unstable compound which dissociates around 300°C. It is oxidized by most common oxidizing agents including nitric acid, dichromate, permanganate, hypochlorite and iron(III) ion. Treatment with concentrated nitric acid produces arsenic acid, $H_3AsO_4 \cdot nH_2O$.

Arsenic trioxide is reduced by stannous chloride, $SnCl_2$ in HCl to arsenic monohydride, As_2H_2, a brown amorphous powder.

Reactions with fluorine and chlorine give arsenic trifluoride AsF_3 and arsenic trichloride $AsCl_3$, respectively.

Similarly, arsenic tribromide $AsBr_3$ forms when the trioxide reacts with bromine vapors. Reaction with concentrated HCl under heating produces arsenic trichloride.

Arsenic trioxide dissolves in concentrated H_2SO_4 forming arsenyl sulfate, $(AsO_2)_2SO_4$, a hygroscopic crystalline solid. Reaction with sulfur trioxide, SO_3 at 100°C produces arsenic trisulfate, $As_2(SO_4)_3$. It forms arsenic monosulfide, As_4S_4 when heated with sulfur.

Analysis

Elemental composition: As 75.74%, O 24.26%. See Arsenic.

Toxicity

Toxic by all routes of exposure and a carcinogen. Systemic effects from oral intake include muscle weakness, hypermotility, sleep change, diarrhea and cardiac arrhythmias. LD_{50} oral (rat): 14.6 mg/kg.

ARSENOUS ACID

[13464–58–9]
Formula H_3AsO_3 or $As(OH)_3$; MW 125.94.

Arsenous acid is a weak acid, known to exist only in solution. Its molecule has three –OH groups attached to the arsenic atom. The dissociation constant of this acid is 8.0×10^{-16} at 25°C. It is produced by hydrolysis of arsenic trioxide in water. The trioxide is sparingly soluble in water and the rate of hydrolysis is generally slow, taking several hours before equilibrium is reached. It forms arsenite ions in aqueous bases, and all its reactions in the aqueous phases are those of arsenic trioxide (see Arsenic Trioxide).

ARSINE

[7784–42–1]
Formula AsH_3; MW 77.95;
Synonyms: arsenic trihydride; hydrogen arsenide

Uses and Occurrence

Arsine is used as a reducing agent; and to synthesize many organoarsine derivatives. It is also used as a doping agent for solid state electronic components. Earlier, it was used as a military poison gas. It does not occur freely in nature but is susceptible to form upon contact of arsenic compounds with acid in presence of a metal. Thus commercial acids stored in metal tanks and contaminated with arsenic impurities may produce arsine.

Physical Properties

Colorless gas; garlic-like unpleasant odor; liquefies at –55°C; solidifies at –116.3°C; heavier than air; gas density 2.695 (air =1); sparingly soluble in cold water (~ 20 mg/100 g water or about 640 mg/L at the NTP); soluble in chloroform and benzene.

Thermochemical Properties

$\Delta H°f$	15.88 kcal/mol
$\Delta G°f$	16.47 kcal/mol
S°	53.22 cal/deg mol
C_ρ	9.10 cal/deg mol

Preparation

Arsine is produced by the reaction of arsenic trichloride, arsenic trioxide or any inorganic arsenic compound with zinc and sulfuric acid. It is also made by treating a solution of sodium arsenide or potassium arsenide in liquid ammonia with ammonium bromide:

$$Na_3As + 3\ NH_4Br \xrightarrow{\text{liq } NH_3} AsH_3 + 3\ NaBr + 3\ NH_3$$

It may be also prepared by decomposition of alkali metal arsenides by water; or arsenides of other metals with acids:

$$Ca_3As_2 + 6\ HCl \rightarrow 2\ AsH_3 + 3\ CaCl_2$$

A poor yield may be obtained if water is substituted for acids. Thus calcium arsenide reacts with water to produce about 15% arsine.

Reactions

Oxidation in air at elevated temperatures form arsenic along with arsenic trioxide or arsenic pentoxide, the nature of the product depending on the arsine to oxygen ratio:

$$4\ AsH_3 + 3\ O_2 \rightarrow 4\ As + 6\ H_2O$$

$$2\ AsH_3 + 3\ O_2 \rightarrow As_2O_3 + 3\ H_2O$$

$$2\ AsH_3 + 4\ O_2 \rightarrow As_2O_5 + 3\ H_2O$$

Such oxidation in air, however, does not occur at ordinary temperatures. Moist arsine decomposes readily in the presence of light forming deposits of shiny black arsenic. When heated in the absence of air it decomposes to its elements.

Arsine is a strong reducing agent, reducing many oxidizing agents, i.e, reduces chlorine to hydrogen chloride:

$$2\ AsH_3 + 3\ Cl_2 \rightarrow 2\ As + 6\ HCl$$

At low temperatures partial reduction of chlorine occurs, forming yellow unstable chloro derivatives, arsenic dihydrogen chloride and arsenic hydrogen dichloride:

$$AsH_3 + Cl_2 \rightarrow AsH_2Cl + HCl$$

$$2\ AsH_3 + 3\ Cl_2 \rightarrow 2\ AsHCl_2 + 4\ HCl$$

Reaction with mercuric chloride gives mercuric arsenide, Hg_3As_2:

$$2\ AsH_3 + 3\ HgCl_2 \rightarrow Hg_3As_2 + 6\ HCl$$

Arsine reacts with cupric chloride solution to give cupric arsenide. Oxidation with stannic chloride, $SnCl_4$, forms hydrogen diarsenide, As_4H_2. It reacts with dilute silver nitrate solution forming metallic silver.

Arsine forms a hexahydrate, $AsH_3 \cdot 6H_2O$ at temperatures below –10°C or under pressure.

Analysis

Elemental composition: As 96.12%, H 3.88%. Arsine may be absorbed in potassium permanganate solution or in bromine water and the solution may be analyzed for arsenic by atomic absorption or emission spectrophotometry (see Arsenic). Alternatively arsine may be oxidized by moist air in presence of light to arsenic which may then be digested with nitric acid and determined as above.

Toxicity

Arsine is a dangerously acute toxicant and a carcinogen. Exposure to 250 ppm for 30 minutes can be fatal to human.

At lower concentrations toxic effects may manifest few hours after exposure. The symptoms include headache, weakness, dizziness, dyspnea, abdominal pain, nausea, vomiting and bronze skin. Chronic exposure can produce jaundice, hemolytic anemia and hemoglobinuria. PEL–TWA and TLV–TWA 0.05 ppm or 0.2 mg/m^3 (OSHA and ACGIH).

ASTATINE

[7440–68–8]

Symbol At; atomic number 85; a radioactive halogen group element; electronic configuration [Xe]$4f^{14}5d^{10}6s^26p^5$; most stable isotope At–210. The half-lives and decay modes of astatine isotopes are given below (Hyde, E. K., Perlman, I., and Seaborg, G. T. 1964. In *The Nuclear Properties of Heavy Elements*, Vol. II, pp. 1081–1082. Englewood Cliffs, NJ: Prentice-Hall);

At–200	0.8 min	α–decay
At–201	1.5 min	α–decay
At–202	3 min	electron capture (88%) α–decay (12%)
At–203	7.4 min	electron capture (86%) α–decay (14%)
At–204	9.3 min	electron capture (95.5%) α–decay (4.5%)
At–205	26 min	electron capture (82%) α–decay (18%)
At–206	29 min	electron capture (99.1%) α–decay (0.9%)
At–207	1.8 hr	electron capture (90%) α–decay (10%)
At–208	1.7 hr	electron capture (99.5%) α–decay (0.5%)
At–209	5.5 hr	electron capture (95%) α–decay (5%)
At–210	8.3 hr	electron capture (99.8%) α–decay (0.17%)
At–211	7.2 hr	electron capture (59%) α–decay (41%)
At–212	0.2 sec	α–decay
At–213	<1 sec	α–decay
At–214	0.002 sec	α–decay
At–215	10^{-4} sec	α–decay
At–216	3×10^{-4} sec	α–decay

At–217	0.018 sec	α–decay
At–218	2 sec	α–decay
At–219	0.9 min	α–decay (97%) ß–decay (3%)

Occurrence

Astatine is one of the rarest elements in nature. Extremely small amounts of short–lived isotopes At–215, At–217, At–218 and At–219 are naturally found occurring in equilibrium with uranium, neptunium and thorium isotopes. The element was named by Corson, MacKenzie and Segre who produced the first of its isotope At–211 in 1940 by bombarding bismuth with alpha particles. Since then many isotopes in the mass range 200 to 219 have been synthesized. All isotopes, however, are unstable, their half–lives ranging between a few microseconds to less than ten hours. The most stable ones are At–210, At–211 and At–209. No use of this element is known so far.

Physical Properties

Physical properties of this element have not been well investigated due to short half–lives of isotopes. The element is volatile; may be distilled in vacuum at room temperature in a glass apparatus; and condensed in a dry ice trap. It is soluble in chloroform, ether, hexane and many other organic solvents. Solubility in water should be of low order.

Synthesis

The more stable astatine isotopes may be synthesized in a nuclear reactor by bombarding bismuth with energenic alpha particles:

$$^{209}_{83}Bi + ^{4}_{2}He \longrightarrow ^{210}_{85}At + 3n$$

$$^{209}_{83}Bi + ^{4}_{2}He \longrightarrow ^{211}_{85}At + 2n$$

$$^{209}_{83}Bi + ^{4}_{2}He \longrightarrow ^{209}_{85}At + 4n$$

The isotopes formed are distilled out from target by heating in air. Isotopes of low masses may be synthesized from other nuclei, i.e., fusion of gold and carbon atoms.

Reactions

Reactions of astatine should be similar to that of iodine. However, there is no evidence of existence of diatomic molecule, At_2. In aqueous solution it is known to exist in oxidation states –1, 0, +5 and +7 and several compounds or polyanions are known. Such species include HAt; interhalogen compounds AtCl, AtBr and AtI; polyhalide complex ions $AtCl^{2-}$, AtI^{2-} $AtIBr^{-}$, $AtICl^{-}$ and $AtBr^{2+}$; astatine anion AtO^{3-} and several organic compounds such as C_6H_5At, $C_6H_5AtCl_2$, $At(C_3H_5N)_2ClO_4$, *p*–AtC_6H_4COOH and HOC_6H_4At.

Analysis

The element may be determined from its radioactivity using tracer techniques. Isotopes of the element may be identified by mass spectrometry.

Health Hazard

Exposure to radiation may cause cancer. Studies on experimental animals show it induces tumors.

BARIUM

[7440–39–3]
Symbol Ba; atomic number 56; atomic weight 137.327; a Group IIA (Group 2) alkaline earth element; electronic configuration [Xe]s^2; valence state +2; ionic radius of Ba^{2+} in crystal (corresponding to coordination number 8) 1.42 Å; first ionization potential 10.00eV; stable isotopes and their percent abundances: Ba–138 (71.70), Ba–137 (11.23), Ba–136 (7.85), Ba–135 (6.59), Ba–134 (2.42); minor isotopes: Ba–130 (0.106) and Ba–132 (0.101); also twenty-two radioisotopes are known.

Occurrence

Barium was discovered in 1808 by Sir Humphrey Davy. Its abundance in the earth's crust is about 0.0425% (425 mg/kg). The element also is found in sea water at trace concentration, 13 µg/L. It occurs in the minerals barite or heavy spar (as sulfate) and witherite (as carbonate).

Uses

The most important use of barium is as a scavenger in electronic tubes. The metal, often in powder form or as an alloy with aluminum, is employed to remove the last traces of gases from vacuum and television picture tubes. Alloys of barium have numerous applications. It is incorporated to lead alloy grids of acid batteries for better performance; and added to molten steel and metals in deoxidizing alloys to lower the oxygen content. Thin films of barium are used as lubricant suitable at high temperatures on the rotors of anodes in vacuum X-ray tubes and on alloys used for spark plugs. A few radioactive isotopes of this element find applications in nuclear reactions and spectrometry.

Physical Properties

Silvery-white metal; soft and ductile; density 3.51 g/cm^3; melts at 727° C; vaporizes at 1897°C; vapor pressure 0.1 torr at 730°C; electrical resistivity 34.0 microohm-cm at 25°C; reacts with water.

Thermochemical Properties

$\Delta H°f$ (cry)	0.0	kcal/mol
$\Delta H°f$ (gas)	43.04	kcal/mol
$G° f$ (gas)	34.93	kcal/mol
$S°$ (gas)	40.70	cal/degree mol
C_ρ (gas)	4.97	cal/degree mol

Manufacture

The metal is obtained by the reduction of barium oxide with finely divided aluminum at temperatures between 1,100 to 1,200°C:

$$4\ \mathrm{BaO} + 2\ \mathrm{Al} \rightarrow \mathrm{BaO{\cdot}Al_2O_3} + 3\mathrm{Ba}\ \text{(gas)}$$

Barium vapor is cooled by means of a water jacket and condensed into the solid metal. The solid block may be cast into rods or extruded into wires. Being a flammable solid, it is packaged under argon in steel containers or plastic bags.

Reactions

Barium metal reacts exothermically with oxygen at ambient temperatures forming barium oxide. The reaction is violent when the metal is present in powder form. It also reacts violently with water forming barium hydroxide and liberating hydrogen:

$$\mathrm{Ba} + 2\mathrm{H_2O} \rightarrow \mathrm{Ba(OH)_2} + \mathrm{H_2}$$

Barium reacts violently with dilute acids, evolving hydrogen. Reactions with halogens give barium halides:

$$\mathrm{Ba} + \mathrm{Cl_2} \rightarrow \mathrm{BaCl_2}$$

Barium is a strong reducing agent. The E° for the reaction:

$$\mathrm{Ba^{2+}}\,(aq) + 2e^{-} \longleftrightarrow \mathrm{Ba}(s) \quad \text{is} - 2.90\ \mathrm{V}$$

It reduces oxidizing agents reacting violently. The metal combines with nitrogen and hydrogen at elevated temperatures producing barium nitride, $\mathrm{Ba_3N_2}$, and barium hydride, $\mathrm{BaH_2}$, respectively.

Barium reduces oxides, chlorides and sulfides of less reactive metals producing the corresponding metals; e.g.,

$$\mathrm{Ba} + \mathrm{CdO} \rightarrow \mathrm{BaO} + \mathrm{Cd}$$

$$\mathrm{Ba} + \mathrm{ZnCl_2} \rightarrow \mathrm{BaCl_2} + \mathrm{Zn}$$

$$3\mathrm{Ba} + \mathrm{Al_2S_3} \rightarrow 3\mathrm{BaS} + 2\mathrm{Al}$$

When heated with nitrogen in the presence of carbon, it forms barium cyanide:

$$\mathrm{Ba} + \mathrm{N_2} + 2\mathrm{C} \rightarrow \mathrm{Ba(CN)_2}$$

Barium combines with several metals including aluminum, zinc, lead, and tin, forming a wide range of intermetallic compounds and alloys.

Hazard

The finely divided powder is pyrophoric. It can explode in contact with air or oxidizing gases. It is likely to explode when mixed and stirred with halogenated hydrocarbon solvents. It reacts violently with water.

All barium salts, especially the water and acid-soluble compounds, are highly toxic. Barium ion can cause death through ventricular fibrillation of the heart. It is a stimulant to the heart muscle. Intake of a few grams of barium salt can be lethal to humans. The insoluble salts such as barium sulfate, however, have little toxic action.

Analysis

The metal may be analyzed in the solid matrices by x-ray fluorescence or x-ray diffraction, and neutron activation techniques. Trace quantities in solution may be measured by flame or furnace atomic absorption spectrophotometry or by ICP emission technique. Measurements at further lower concentrations may be made by an ICP, coupled with a mass spectrometer (ICP/MS). Also, barium ion in solution may be measured by various wet methods, including gravimetry and volumetric analysis. In gravimetry, the metal is precipitated in slightly acidic solution as insoluble sulfate or chromate. Complexometric titration using the complexing agent, diethylenetriamine-pentaacetic acid, and Eriochrome Black T as indicator, measures calcium and strontium along with barium and, therefore, is not suitable to analyze barium in a mixed solution.

BARIUM ACETATE

[543–80–6]
Formula: $Ba(C_2H_3O_2)_2$; MW 255.42

Uses

Barium acetate is used as a mordant for printing textile fabrics; for drying paints and varnishes; in lubricating oil; in the preparation of other acetates; and as a catalyst in organic synthesis.

Physical Properties

White powdery solid; density 2.47g/cm^3; decomposes on heating; highly soluble in water (55.8g /100g at 0°C), sparingly soluble in methanol (~1.43 g per liter).

Preparation

Barium acetate is made by the reaction of barium carbonate with acetic acid:

$$BaCO_3 + 2CH_3COOH \rightarrow (CH_3COO)_2Ba + CO_2 + H_2O$$

The solution is concentrated and the anhydrous barium acetate crystallizes at a temperature above 41°C. At temperatures between 25 to 40°C, barium acetate monohydrate, $Ba(C_2H_3O_2)_2 \cdot H_2O$ [5908–64–5] (density 2.19 g/cm^3) crystallizes out of solution.

Barium acetate also may be prepared by treating barium sulfide with acetic acid, followed by slow evaporation and subsequent crystallization of the salt from the solution:

$$BaS + 2CH_3COOH \rightarrow (CH_3COO)_2Ba + H_2S$$

Reactions

Barium acetate converts to barium carbonate when heated in air at elevated temperatures. Reaction with sulfuric acid gives barium sulfate; with hydrochloric acid and nitric acid, the chloride and nitrate salts are obtained after evaporation of the solutions. It undergoes double decomposition reactions with salts of several metals. For example, it forms ferrous acetate when treated with ferrous sulfate solution and mercurous acetate when mixed with mercurous nitrate solution acidified with nitric acid. It reacts with oxalic acid forming barium oxalate.

Analysis

Elemental composition: Ba 53.77%, C 18.81%, H 2.37%, O 25.05%. The salt may be digested with nitric acid, diluted appropriately, and analyzed for barium. (See Barium.)

Toxicity

The salt or its aqueous solution is highly toxic. LD_{10} (oral) rabbit: 236 mg/kg; LD_{10} (subcutaneous) rabbit: 96 mg/kg. See Barium.

BARIUM AZIDE

[18810–58–7]
Formula: $Ba(N_3)_2$; MW 221.37

Uses

Barium azide is used in explosives. A saturated solution is generally used.

Physical Properties

Colorless monoclinic crystal; density 2.936 g/cm^3; decomposes at 120°C; soluble in water, slightly soluble in ethanol.

Preparation

Barium azide may be prepared by reacting sodium azide with a soluble barium salt. The solution is concentrated to allow crystals grow. Crystals will explode if fully dried, or subject to friction. Product should be stored damp with ethanol.

Hazard

The dry solid is sensitive to shock, impact and friction. It decomposes explosively when heated to 275°C. Contact with acid can produce the explosive compound hydrazoic acid. Contact with lead, silver, and many other metals can form the explosive azides of those metals. Presence of sodium, potassium, barium and iron ions as impurities can enhance the shock sensitivity of barium azide. Barium azide also is a toxic compound. The toxic effects are similar to those of other soluble salts of barium.

BARIUM BROMIDE

[10553–31–8]
Formula: $BaBr_2$; MW 297.14

Uses

Barium bromide is used to make photographic compounds, phosphors, and other bromides.

Physical Properties

White orthorhombic crystal; density of anhydrous $BaCl_2$ 4.78 g/cm^3, and dihydrate $BaCl_2 \cdot 2H_2O$ 3.58 g/cm^3; melts at 857°C; vaporizes at 1,835°C; readily dissolves in water (92.2 g/100 g water at 0°C)

Thermochemical Properties

$\Delta H°f$ (gas)	–181.1 kcal/mol
G° (gas)	–176.2 kcal/mol
S° (gas)	34.9 cal/degree mol
ΔH_{fus}	7.64 kcal/mol

Preparation

Barium bromide is prepared by the reaction of barium carbonate or barium sulfide with hydrobromic acid:

$$BaCO_3 + 2HBr \rightarrow BaBr_2 + CO_2 + H_2O$$

$$BaS + 2HBr \rightarrow BaBr_2 + H_2S$$

The white crystal of the dihydrate, $BaBr_2 \cdot 2H_2O$ is crystallized from aqueous solution. The anhydrous salt is obtained by heating the dihydrate at 120°C.

Reactions

Reactions in aqueous phase are similar to those of barium chloride. When treated with sulfuric acid, hydrofluoric acid, phosphoric acid or oxalic acid, the insoluble barium salts of these anions are formed. Similarly, many insoluble barium salts may form by double decomposition reactions when treated with soluble salts of other metals.

Analysis

Elemental composition: Ba 46.22%, Br 53.78%. Barium may be determined by various instrumental or wet methods (see Barium). Bromide may be analyzed by ion chromatography or titrimetry. Presence of other halide ions can interfere in titrimetry tests.

Toxicity

Ingestion of the salt or its aqueous solution can produce severe poisoning.

BARIUM CARBONATE

[513–77–9]
Formula: $BaCO_3$; MW 197.37

Occurrence and Uses

Barium carbonate is found in nature as mineral witherite. The compound has many major commercial applications in brick, glass, ceramics, oil-drilling, photographic and chemical industries. It is mixed with wet clay to immobilize many water-soluble salts in making uniform red bricks. In the glass industry, barium is added to glass as barium carbonate or barium oxide to improve the refractive index of optical glass; also to promote sintering and lower the viscosity of melted glass to make glass bead formation easy. It is used in the manufacture of television picture tubes and photographic paper. Another important application involves its use as a fluxing ingredient in ceramic industry for enamels, glazes and ceramic bodies. Barium carbonate is used in oil-well drilling to insolubilize gypsum and inhibit coagulation; in ferrous metallurgy for steel carburizing; in chlor-alkali cells for treating salt brines to remove sulfates; and to make ferrite, and barium titanate. Many barium salts are prepared from barium carbonate.

Physical Properties

White powder; orthorhombic crystal system; density 4.286 g/cm^3; refractive index 1.60; hardness 3.50 Mohs; melts at 811°C; insoluble in water (c. 25 mg/L at 25°C); K_{sp} 2.0×10^{-9}

Manufacture

Barium carbonate is made commercially from barium sulfide either by treatment with sodium carbonate at 60 to 70°C (soda ash method) or by passing carbon dioxide at 40 to 90°C:

$$BaS + Na_2CO_3 \rightarrow BaCO_3 + Na_2S$$

$$BaS + CO_2 + H_2O \rightarrow BaCO_3 + H_2S$$

In the soda ash process, solid or dissolved sodium carbonate is added to barium sulfide solution, and the barium carbonate precipitate is filtered, washed, and dried.

Reactions

Barium carbonate decomposes to barium oxide and carbon dioxide when heated at 1,300°C. In the presence of carbon, decomposition occurs at lower temperatures. Barium carbonate dissolves in dilute HCl and HNO_3 liberating CO_2. Similar reaction occurs in acetic acid. The solid salts, chloride, nitrate and acetate that are water soluble may be obtained by evaporation of the solution. Dissolution in HF, followed by evaporation to dryness, and then heating to red heat, yields barium fluoride.

Barium carbonate forms barium iodide on treatment with ferrous iodide solution:

$$BaCO_3 + FeI_2 \rightarrow BaI_2 + FeCO_3$$

Barium carbonate produces barium potassium chromate, a pale yellow pigment, known as Pigment E, when heated with potassium dichromate.

Calcination at 1,300°C with titanium dioxide yields barium metatitanate, $BaTiO_3$:

$$BaCO_3 + TiO_2 \xrightarrow{1300^\circ C} BaTiO_3 + CO_2$$

Analysis

Elemental composition: Ba 69.58%, C 6.09%, O 24.32%. The compound is digested with nitric acid under heating and the solution is analyzed for barium by atomic absorption or emission spectrometry (see Barium). Carbon dioxide may be determined by treating a small amount of the solid with dilute HCl and analyzing the evolved gas by GC using a thermal conductivity detector or a mass spectrometer. The characteristic mass of CO_2 is 44.

BARIUM CHLORIDE

[10361–37–2]

Formula $BaCl_2$; MW 208.23; also forms a dihydrate, $BaCl_2 \cdot 2H_2O$ [10326–27–9]

Uses

Barium chloride is used to make red pigments and color lakes. Two such common pigments are Lithol Red [50867–36–2] and Red Lake C [5160–02–1]. It is used for weighting and dyeing textile fabrics and as a mordant for acid dyes. Other commercial uses of this compound include its application as an ingredient in eutectic mixtures for heat-treating baths; for tanning leather; as a flux in the production of magnesium metal; for softening of water in boilers; in additives for lubricating oils; and as a reagent for sulfate analysis by wet methods. It may be used to prepare other barium salts.

Physical Properties

White crystal or powder; (crystal systems: anhydrous $BaCl_2$ is orthogonal, transition to cubic form occurs at 925°C, and the dihydrate, $BaCl_2 \cdot 2H_2O$ is monoclinic); hygroscopic; bitter, salty taste; density 3.856 g/cm^3 (dihydrate 3.0979/cm^3); melts at 962°C; vaporizes at 1,560°C; readily dissolves in water; also dissolves in methanol, but is insoluble in other polar organic solvents.

Thermochemical Properties

$\Delta H°f$	–205.3 kcal/mol
$\Delta G°f$	–193.8 kcal/mol
S°	29.6 cal/degree mol
C_ρ	17.9 cal/degree mol

Manufacture

Barium chloride usually is prepared by treatment of barium sulfide with hydrochloric acid:

$$BaS + 2HCl \rightarrow BaCl_2 + H_2S$$

Impurities such as heavy metal sulfides are filtered out. Water-soluble sulfur compounds are oxidized to insoluble barium sulfate and removed. The solution is then evaporated to crystallize barium chloride.

Barium chloride may also be made by treating barium carbonate with HCl; or by heating a mixture of barium sulfate, calcium chloride and carbon:

$$BaSO_4 + CaCl_2 + 2C \xrightarrow{heat} BaCl_2 + CaS + 2CO_2$$

Reactions

Anhydrous barium chloride adsorbs moisture forming dihydrate, $BaCl_2 \cdot 2H_2O$. The latter forms a monohydrate, $BaCl_2 \cdot H_2O$ when shaken with methanol. In an aqueous solution with sulfuric acid it forms a precipitate of barium sulfate. Similar precipitation reactions occur with hydrofluoric acid, arsenic acid, phosphoric acid and oxalic acid forming sparingly soluble barium fluoride, BaF_2, and insoluble barium arsenate, $Ba_3(AsO_4)_2$, barium phosphate, $Ba_3(PO_4)_2$, and barium oxalate, BaC_2O_4, respectively. Reactions with alkali metal carbonate, molybdate, niobate, selenate, ferrocyanide and hexafluorosilicate produce insoluble barium salts of these anions. Anhydrous barium chloride forms lower melting eutectics with alkali metal chlorides.

Analysis

Elemental composition: Ba 65.95%, Cl 34.05%. The metal may be analyzed by various instrumental and wet methods (see Barium). Chloride ion may be determined in an aqueous solution of the salt by ion chromatography or by titrimetry using either silver nitrate titrant and an indicator such as potassium chromate; or by mercuric nitrate titration using diphenyl carbazone indicator to detect the end point.

Toxicity

The acute toxicity is high by all routes of exposure. The effects are similar to other soluble compounds of barium (see Barium). The oral and subcutaneous lethal doses in dogs are as follows: (R. N. Lewis (Sr.). 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed., New York: Van Nostrand Reinhold.)

LD_{LO} oral (dog):	90mg/kg
LD_{LO} subcutaneous (dog):	10 mg/kg

BARIUM CHROMATE(VI)

[10294–40–3]

Formula: $BaCrO_4$; MW 253.32; Cr occurs in +6 oxidation state.

Synonyms: lemon yellow; permanent yellow; C.I. Pigment yellow 31; Baryta yellow; ultramarine yellow; C. I. 77103; Steinbuhl yellow.

Uses

Barium chromate is used as a pigment in paints, ceramics, coloring glasses, fuses, and porcelains; as a corrosion inhibitor to prevent elecrochemical corrosion at the joints of dissimilar metals; in safety matches; in metal primers; in ignition control devices; in pyrotechnic compositions; and as an initiator for explosives.

Physical Properties

Yellow orthorhombic crystal; density 4.50 g/cm^3; darkens on heating; insoluble in water and organic solvents; dissolves in mineral acid with decomposition.

Analysis

Elemental composition: Barium: 54.21%, chromium 20.53%, oxygen 25.26%. The compound is digested in nitric acid, diluted, and analyzed for barium and chromium by flame- or furnace-AA or ICP-AES (see Barium and Chromium). Also, it may be characterized by x-ray diffraction, and the metal content determined by other x-ray techniques.

Toxicity

Barium chromate is a toxic substance and an EPA-confirmed human carcinogen.

BARIUM CYANIDE

[542–62–1]
Formula: $Ba(CN)_2$; MW 189.36

Uses

Barium cyanide is used in electroplating and other metallurgical processes.

Physical Properties

White crystalline powder; slowly decomposes in air; highly soluble in water, soluble in alcohol.

Preparation

Barium cyanide is prepared by reacting barium hydroxide with hydrocyanic acid:

$$Ba(OH)_2 + 2HCN \rightarrow Ba(CN)_2 + 2H_2O$$

The product is crystallized from the solution.

Reactions

Barium cyanide reacts with acids producing hydrogen cyanide:

$$Ba(CN)_2 + H_2SO_4 \rightarrow 2HCN + BaSO_4$$

$Ba(CN)_2$ can form many insoluble cyanides from double decomposition reactions.

Analysis

Elemental composition: Ba 72.52%, C 12.68%, N 14.79%. Barium metal can be analyzed by various instrumental and wet methods (see Barium). Cyanide ion in the aqueous solution of the compound may be determined by using a cyanide ion–specific electrode or by colorimetry using pyridine-barbituric acid reagent (APHA, AWWA, and WEF. 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed., Washington, DC: American Public Health Association).

Toxicity

Barium cyanide is a deadly poison. Ingestion of a small amount can cause death.

BARIUM HYDROXIDE

[17194–00–2]
Synonyms: caustic baryta; barium hydrate

Formula $Ba(OH)_2$

Uses

Barium hydroxide is used to produce barium soaps which are additives for high temperature lubricants. Other chemical applications include refining of vegetable oils; vulcanization of synthetic rubber; in drilling fluids; in corrosion inhibitors; as an ingredient in sealing compositions; in plastics stabilizers; for softening water; and to prepare other alkalies.

Physical Properties

Monohydrate, $Ba(OH)_2 \cdot H_2O$ is a white powder; density 3.743 g/cm^3; slightly soluble in water; soluble in dilute mineral acids. Octahydrate, $Ba(OH)_2 \cdot 8H_2O$ is a colorless monoclinic crystal; density 2.18 g/cm^3 at 16°C; refractive index 1.50; melts at 78°C; vapor pressure 227 torr; loses seven molecules of water of crystallization when its solution is boiled in the absence of atmospheric CO_2 forming solid monohydrate; further heating produces anhydrous $Ba(OH)_2$ melting at 407°C; readily dissolves in water (3.76 g/100 g at 20°C and 11.7 g/100 g at 50°C); aqueous solution highly alkaline; also soluble in methanol; slightly soluble in ethanol; insoluble in acetone.

Thermochemical Properties

$\Delta H°f$	–225.9 kcal/mol
ΔH_{fus}	3.99 kcal/mol

Preparation

Barium hydroxide is made by dissolving barium oxide in hot water. The octahydrate, $Ba(OH)_2 \cdot 8H_2O$, crystallizes upon cooling. It also is prepared by precipitation with caustic soda from an aqueous solution of barium sulfide:

$$BaS + 2NaOH \rightarrow Ba(OH)_2 + Na_2S$$

Reactions

Barium hydroxide decomposes to barium oxide when heated to 800°C. Reaction with carbon dioxide gives barium carbonate. Its aqueous solution, being highly alkaline, undergoes neutralization reactions with acids. Thus, it forms barium sulfate and barium phosphate with sulfuric and phosphoric acids, respectively. Reaction with hydrogen sulfide produces barium sulfide. Precipitation of many insoluble, or less soluble barium salts, may result from double decomposition reaction when $Ba(OH)_2$ aqueous solution is mixed with many solutions of other metal salts.

Analysis

Elemental composition: Ba 80.15%, H 1.18%, O 18.67%. (See Barium.)

Toxicity

An acute poison; toxic symptoms are similar to other soluble salts of barium (see Barium).

BARIUM NITRATE

[10022–31–8]
Formula: $Ba(NO_3)_2$; MW 261.37;
Synonym: nitrobarite

Uses

Barium nitrate is used to produce green color in flares, pyrotechnic devices; in green signal lights; and in tracer bullets.

Physical Properties

White cubic crystal; density 3.24 g/cm^3; melts at 590°C; soluble in water (5 g and 10.5 g/100 g at 0°C and 25°C, respectively), insoluble in alcohol.

Thermochemical Properties

$\Delta H°f$	–237.11 kcal/mol
$G° f$	–190.42 kcal/mol
$S°$	51.1 cal/degree mol
C_ρ	36.2 cal/degree mol

Preparation

Barium nitrate is prepared by the reaction of barium carbonate or barium sulfide with nitric acid:

$$BaCO_3 + 2HNO_3 \rightarrow Ba(NO_3)_2 + CO_2 + H_2O$$

Barium carbonate is suspended in nitric acid. The solution is filtered and the product crystallizes out. Alternatively, barium carbonate and nitric acid are added to a saturated solution of barium nitrate. The product is obtained by crystallization. It also may be prepared by adding sodium nitrate to a saturated solution of barium chloride. Barium nitrate precipitates out from the solution. The precipitate is filtered, washed and dried.

Reactions

At elevated temperatures, barium nitrate decomposes to barium oxide, nitrogen dioxide, and oxygen:

$$2Ba(NO_3)_2 \xrightarrow{heat} 2BaO + 4NO_2 + O_2$$

In an atmosphere of nitric oxide, thermal decomposition produces barium nitrite, $Ba(NO_2)_2$. Reactions with soluble metal sulfates or sulfuric acid yield barium sulfate. Many insoluble barium salts, such as the carbonate, oxalate and phosphate of the metal, are precipitated by similar double decomposition reactions. $Ba(NO_3)_2$ is an oxidizer and reacts vigorously with common reducing agents. The solid powder, when mixed with many other metals such as aluminum or zinc in their finely divided form, or combined with alloys such as aluminum-magnesium, ignites and explodes on impact.

Analysis

Elemental composition: Ba 52.55%, N 10.72%, O 36.73%. Barium may be determined by various instrumental techniques (see Barium). The nitrate ion can be determined by preparing an aqueous solution of the compound and analyzing by ion-chromatography, or nitrate ion-selective electrode.

Toxicity

Barium nitrate exhibits high-to-moderate toxicity by oral, subcutaneous and other routes. The oral lethal dose in rabbit is 150 mg/kg and the oral LD_{50} in rat is 355 mg/kg (Lewis Sr., R. J. 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed., New York: Van Nostrand Reinhold).

BARIUM OXIDE

[1304–28–5]
Formula: BaO; MW 153.33
Synonyms: calcined baryta; barium monoxide; barium protoxide.

Uses

Barium oxide is used to remove water from alcohols, aldehydes, ketones, petroleum ether, and other organic solvents; and for drying gases. It also is used in the manufacture of detergent for lubricating oil.

Physical Properties

Colorless cubic crystal or white yellowish powder; density 5.72 g/cm^3; melts at 2,013°C; moderately soluble in water at ambient temperatures (3.48 g/ 100 g at 20°C), highly soluble in boiling water (90.8 g/100 g at 100°C); aqueous solution highly alkaline; also, soluble in ethanol, dilute mineral acids and alkalies; insoluble in acetone and liquid ammonia.

Thermochemical Properties

$\Delta H°f$	–132.35 kcal/mol
$\Delta G°f$	–125.56 kcal/mol
S°	16.8 cal/degree mol
C_ρ	11.4 cal/degree mol
ΔH_{fus}	14.1 kcal/mol

Preparation

Barium oxide is made by heating barium carbonate with coke, carbon black or tar:

$$BaCO_3 + C \xrightarrow{heat} BaO + 2CO$$

It may be also prepared by thermal decomposition of barium nitrate.

Reactions

Barium oxide reacts with water forming hydroxide, and with carbon dioxide it forms barium carbonate. Both reactions are rapid and exothermic:

$$BaO + H_2O \rightarrow Ba(OH)_2 \qquad (\Delta H_{rxn} = -24.4 \text{ kcal/mol})$$
$$BaO + CO_2 \rightarrow BaCO_3 \qquad (\Delta H_{rxn} = -63.1 \text{ kcal/mol})$$

It readily forms barium peroxide BaO_2 when heated in air or oxygen at 450°C to 500°C:

$$2BaO + O_2 \xrightarrow{500^\circ C} 2BaO_2$$

When heated with silica to incandescence, it forms monobarium silicate, $BaO \cdot SiO_2$ or Ba_3SiO_5.

Aqueous solution of barium oxide undergoes neutralization reactions with acids forming precipitates of insoluble barium salts, such as $BaSO_4$ and $Ba_3(PO_4)_2$.

BaO reacts slowly with alcohols forming barium alcoholates.

Analysis

Elemental composition: Ba 89.57%, O 10.43%. The oxide is identified by x-ray diffraction and barium content determined by AA or ICP.

Hazard

Barium oxide is toxic by subcutaneous route. Because of its affinity for moisture, the compound is corrosive to skin. Contact with water or CO_2 evolves much heat. Therefore, any use of CO_2 to extinguish a BaO fire may cause further incandescence. Accumulation of barium oxide or peroxide dust can create a fire hazard.

BARIUM PEROXIDE

[1304–29–6]
Formula: BaO_2; MW 169.33
Synonyms: barium dioxide; barium superoxide.

Uses

Barium peroxide is used as a bleaching agent for fibers and straw. It also is used to decolorize glass; in dyeing textiles; to produce pure oxygen; to prepare hydrogen peroxide; and as an oxidizing agent.

Physical Properties

Grayish-white, heavy powder; tetragonal crystal system; density 4.96 g/cm^3; melts at 450°C; insoluble in water.

Preparation

Barium peroxide is prepared by heating barium oxide with air or oxygen at

500°C:

$$2BaO + O_2 \rightarrow 2BaO_2$$

Reactions

Barium peroxide decomposes to barium oxide and oxygen when heated to 700°C. At lower temperatures, decomposition occurs slowly. It also decomposes slowly in contact with water, forming barium hydroxide. It reacts with dilute acids to form hydrogen peroxide:

$$BaO_2 + 2HCl \rightarrow BaCl_2 + H_2O_2$$

Analysis

Elemental composition: Ba 81.11%, O 18.89%. The compound is decomposed by dilute HCl and the barium content by AA or ICP-AES.

Hazard

Barium peroxide may ignite or explode in contact with reducible substances. Also, it is toxic by the subcutaneous route.

LD_{50} subcutaneous (mouse): 50 mg/kg

BARIUM SULFATE

[7727–43–7]
Formula: $BaSO_4$; MW 233.39
Synonyms: barite; baryte; heavy spar; blanc fixe

Occurrence and Uses

Barium sulfate is widely distributed in nature and occurs as the mineral barite (also known as barytes or heavy spar). It often is associated with other metallic ores, such as fluorspar. Barites containing over 94% $BaSO_4$ can be processed economically.

Barium sulfate has many commercial applications. It is used as natural barite, or precipitated $BaSO_4$. The precipitated salt in combination with equimolar amount of co-precipitated zinc sulfide formerly was used as a white protective coating pigment, known as lithophone. Similarly, in combination with sodium sulfide, it is used to produce fine pigment particles of uniform size, known as blanc fixe. Natural barite, however, has greater commercial application than the precipitated salt. It is used as drilling mud in oil drilling to lubricate and cool the drilling bit, and to plaster the walls of the drill hole to prevent caving. It is used as a filler in automotive paints, plastics and rubber products. It also is used in polyurethane foam floor mats; white sidewall rubber tires; and as a flux and additive to glass to increase the refractive index.

Other chemical applications of barium sulfate are as the opaque ingredient in a barium meal for x-ray diagnosis; as a pigment for photographic paper; and to prepare many barium salts.

Physical Properties

Soft crystalline solid; rhombic crystal; pure salt is white but color may vary; the color of the mineral barite may vary among red, yellow, gray or green depending on impurities; density 4.50 g/cm^3; refractive index 1.64; melts around 1,580°C; decomposes above 1,600°C; hardness 4.3 to 4.6 Mohs; insoluble in water (285 mg/L at 30°C) and alcohol; K_{sp} 1.1 x 10^{-10}; soluble in concentrated sulfuric acid.

Thermochemical Properties

$\Delta H°f$	–352.3 kcal/mol
$\Delta G°f$	–325.7 kcal/mol
S°	31.6 cal/degree mol
C_ρ	24.3 cal/degree mol
ΔH_{fus}	9.71 kcal/mol

Production

Natural barium sulfate or barite is widely distributed in nature. It also contains silica, ferric oxide and fluoride impurities. Silica is the prime impurity which may be removed as sodium fluorosilicate by treatment with hydrofluoric acid followed by caustic soda.

Very pure barium sulfate may be precipitated by treating an aqueous solution of a barium salt with sodium sulfate:

$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2NaCl$$

Precipitated $BaSO_4$ is often used in many industrial applications. Blanc fixe and Lithopone are made by the reactions of barium sulfide with sodium sulfate and zinc sulfate, respectively.

Reactions

Barium sulfate is one of the most insoluble salts of barium. It does not undergo double decomposition reactions in aqueous phase. It dissolves in concentrated H_2SO_4 to form an acid sulfate which breaks down to $BaSO_4$ upon dilution.

Reduction with coke under heating produces barium sulfide:

$$BaSO_4 + 4C \xrightarrow{heat} BaS + 4CO$$

$BaSO_4$ reacts violently when heated with aluminum or explosively when mixed with potassium.

Analysis

Elemental composition: Ba 58.84%, O 27.42%, S 13.74%. Barite may be identified by x-ray diffraction. The metal may be analyzed by various instrumental techniques (see Barium).

BARIUM SULFIDE

[21109–95–5]
Formula: BaS; MW 169.39

Barium also forms several other sulfides. Among them are: Barium hydrosulfide, $Ba(SH)_2$ [25417–81–6]; Barium disulfide, BaS_2 [12230–99–8]; Dibarium trifulfide, Ba_2S_3 [53111–28–7]; Barium trisulfide, BaS_3 [12231–01–5]; Barium tetrasulfide monohydrate, $BaS_4 \cdot H_2O$ [12248–67–8]; Barium pentasulfide, BaS_5 [12448–68–9].

Occurrence and Uses

Barium sulfide occurs in the form of black ash, which is a gray to black impure product obtained from high temperature carbonaceous reduction of barite. It is the starting material in the manufacture of most barium compounds including barium chloride and barium carbonate. It is used in luminous paints; for dehairing hides; as a flame retardant; and for generating H_2S.

Physical Properties

Colorless crystalline solid; density 4.25 g/cm^3; refractive index 2.155; melts at 1,200°C; soluble in water (decomposes); insoluble in alcohol.

Thermochemical Properties

$\Delta H°f$	–110 kcal/mol
$\Delta G°f$	–109 kcal/mol
S°	18.7 cal/degree mol
C_ρ	11.8 cal/degree mol

Preparation

Barium sulfide is prepared by heating barite with coal or petroleum coke in a rotary kiln at 1,000°C to 1,250°C in an oxygen-free atmosphere:

$$BaSO_4 + 4C \xrightarrow{1000\text{-}1250^\circ C} BaS + 4CO$$

The product, black ash, is a gray or black powder containing carbonaceous impurities and unreacted barite. Barium sulfide is separated from impurities by extraction with hot water and filtration. It is obtained as an aqueous solution of 15 to 30% strength. The commercial product is 80% to 90% BaS.

Barium sulfide may also be made by high temperature reduction of barium sulfate with methane.

Reactions

Barium sulfide dissolves in water, dissociating to 10%, forming barium hydrosulfide and barium hydroxide:

$$2BaS + 2H_2O \rightarrow Ba(SH)_2 + Ba(OH)_2$$

The solution is highly alkaline. When the aqueous solution is cooled, crystals of barium hydroxide appear first.

The aqueous solution of barium sulfide oxidizes slowly in the air forming elemental sulfur and various anions of sulfur including sulfite, thiosulfate, polysulfides and sulfate. The yellow color of barium sulfide solution is attributed to the presence of dissolved elemental sulfur that results from its slow oxidation in the air. In the presence of an oxidizing agent, barium sulfate is formed. Violent to explosive oxidation may occur when heated with strong oxidants such as phosphorus pentoxide or potassium chlorate.

Barium sulfide undergoes double decomposition reactions with hydrochloric acid and nitric acid, giving barium chloride and barium nitrate, respectively, when the solution is evaporated.

Reaction with carbon dioxide produces barium carbonate and hydrogen sulfide:

$$BaS + CO_2 + H_2O \rightarrow BaCO_3 + H_2S$$

Analysis

Elemental composition: Ba 81.08%, S 18.92%. The metal may be analyzed by various instrumental techniques (see Barium). In the powder form, the compound may be identified by x-ray methods. In solution, it undergoes hydrolysis forming barium hydroxide and hydrosulfide. The former is neutralized by acid titration to a pH of 8.4 while the hydrosulfide is titrated with acid to pH 4.2 for neutralization.

Toxicity

Highly toxic by ingestion (see Barium).

BARIUM TITANATE

[12047–27–7]
Formula: $BaTiO_3$; MW 233.19
Synonyms: barium metatitanate; barium titanate (IV)

Uses

Barium titanate has many important commercial applications. It has both ferroelectric and piezoelectric properties. Also, it has a very high dielectric constant (about 1,000 times that of water). The compound has five crystalline modifications, each of which is stable over a particular temperature range. Ceramic bodies of barium titanate find wide applications in dielectric amplifiers, magnetic amplifiers, and capacitors. These storage devices are used in digital calculators, radio and television sets, ultrasonic apparatus, crystal microphone and telephone, sonar equipment, and many other electronic devices.

Physical Properties

White crystalline solid; exists in five crystal modifications; the common tetragonal form has a Curie point of 120°C; exhibits ferroelectric and piezoelectric properties; density 6.02 g/cm^3; melts at 1,625°C; insoluble in water and alkalies; slightly soluble in dilute mineral acids; dissolves in concentrated sulfuric acid and hydrofluoric acid.

Preparation

Barium titanate is made by sintering a finely powdered mixture of barium carbonate and titanium dioxide in a furnace at 1,350°C. The calcined mass is finely ground and mixed with a binder (plastic). The mixture is subjected to extrusion, pressing or film casting to obtain ceramic bodies of desired shapes. Plastic is burnt off by heating and the shaped body is sintered by firing and then polished.

The compound also may be prepared by other methods. These include ignition of barium and titanium alcoholates in an organic solvent; treatment of tetraethyl titanate or other alkyl ester of titanium with an aqueous solution of barium hydroxide; and ignition of barium titanyloxalate.

Analysis

Elemental composition: Ba 58.89%, Ti 20.53%, O 20.58%. The solid is digested with a mixture of concentrated H_2SO_4 and HNO_3, diluted and the aqueous solution is analyzed for the metals Ba and Ti by flame or furnace atomic absorption or ICP emission spectrophotometry. The compound in the crystalline powdered form may be identified by various x-ray techniques.

BERKELIUM

[7440–71–3]

Symbol Bk; atomic number 97; atomic weight of most stable isotope 247.07; a transuranium radioactive element; synthesized in the laboratory; electronic configuration [Rn]$5f^9 7s^2$.; oxidation states +3 and +4. Isotopes, half-life and decay modes are given below:

Isotopes	**Half-Life**	**Decay Mode**
Bk-241	2.4 min.	electron capture
Bk–242	7 min.	electron capture
Bk–243	4.5 hr.	electron capture
Bk–244	4.4 hr.	electron capture
Bk–245	4.95 days	electron capture
Bk–246	1.8 days	electron capture
Bk–247	1,400 years	alpha particle emission
Bk–248	23.7 hr.	beta decay, electron capture
Bk–249	320 days	beta decay
Bk–250	3.2 hr.	beta decay
Bk–251	56 min.	beta decay

Occurrence and Uses

Berkelium does not occur in nature. The element was synthesized in 1949 at the Lawrence Berkeley Laboratory in Berkeley, California by Thompson, Ghiorso and Seaborg (Thompson, S.G., Ghiorso, A. and G. T. Seaborg. 1950. *Phys. Rev.*, 77, 838). It has 12 isotopes. It is the fifth man-made transuranium element. Presently, the element has no commercial application.

Physical Properties

Physical properties of the element are anticipated or calculated. Silvery metal having two allotropic forms: (i) alpha form that should have a double hexagonal closed-packed structure and (ii) a face-centered cubic type beta form; density 14.78 g/cm^3 (alpha form), and 13.25 g/cm^3 (beta form); melting point 985°C; soluble in dilute mineral acids.

Synthesis

All isotopes of the element are synthesized in the nuclear reactor. The first isotope synthesized had the mass 241, produced by irradiation of milligram quantities of americium–241 with alpha particles of 35 MeV in a cyclotron:

$$^{241}_{95}\mathrm{Am} + ^{4}_{2}\mathrm{He} \rightarrow ^{243}_{97}\mathrm{Bk} + 2\,^{1}_{0}n$$

The product was separated by ion exchange.

While the lighter isotopes are prepared by alpha particle bombardment, the heavier ones by neutron irradiation of large quantities of americium, curium or plutonium:

$$^{243}_{95}\mathrm{Am} + ^{1}_{0}n \rightarrow ^{244}_{95}\mathrm{Am}$$

$$^{244}_{95}\mathrm{Am} \rightarrow ^{244}_{96}\mathrm{Cm} + \mathrm{e}^{-}$$

$$^{249}_{96}\mathrm{Cm} \rightarrow ^{249}_{97}\mathrm{Bk} + \mathrm{e}^{-}$$

Only a small fraction of Bk–249 is obtained by the above reaction because neutrons also induce fission. Alternatively, uranium–238 may be converted to Bk–249 by very short but intense neutron bombardment followed by five successive beta decays.

Chemical Properties

The chemical properties of berkelium are rare earth-like character because of its half-filled 5*f* subshell and should be similar to cerium. The element readily oxidizes to berkelium dioxide, BkO_2 when heated to elevated temperatures (500°C). In aqueous solutions, the most common oxidation state is +3 which may undergo further oxidation to +4 state. A few compounds have been synthesized, the structures of which have been determined by x-ray diffraction methods. These include the dioxide, BkO_2; sesquioxide, Bk_2O_3; fluoride,

BkF_3; chloride, $BkCl_3$; oxychloride, BkOCl; and the hydroxides, $Bk(OH)_3$ and $Bk(OH)_4$.

Toxicity

Berkelium accumulates in the skeletal system. The radiation can cause damage to red blood cells. The maximum permissible body burden reported for the isotope Bk–249 in the human skeleton is 0.4 ng (Cunningham, B.B., 1968, Berkelium. In *The Encyclopedia of the Chemical Elements*. C.A. Hampel, ed., p. 48. New York: Reinhold Book Corporation).

BERYLLIUM

[7440–41–7]
Symbol Be; atomic number 4; atomic weight 9.012; a Group IIA (Group 2) metal; the lightest alkaline-earth metallic element; atomic radius 1.06Å; ionic radius (Be^{2+}) 0.30Å; electronic configuration $1s^22s^2$; ionization potential, Be^+ 9.32eV, Be^{2+} 18.21 eV; oxidation state +2

Occurrence and Uses

Beryllium is widely distributed in the earth's crust at trace concentration, 2.8 mg/kg. The element was first discovered by Vauquelin in 1797. Wohler and Bussy in 1828 independently isolated beryllium in the metallic form from its oxide. In nature, beryllium occurs in several minerals, mostly combined with silica and alumina. The most common minerals are beryl, $3BeO \cdot Al_2O_3 \cdot 6SiO_2$; chrysoberyl, $BeO \cdot Al_2O_3$; phenacite, $2BeO \cdot SiO_2$; and bertrandite, $4BeO \cdot 2SiO_2 \cdot H_2O$. Also, it is found in trace amounts in the ore feldspar, and in volcanic ash. It's abundance in the sea water is estimated in the range 5.6 ppt.

Beryllium oxide is a component of precious stones, emerald, aquamarine and topaz. Beryllium is utilized in nuclear reactors to moderate the velocity of slow neutrons. It is hot-pressed to appropriate shapes and sizes that yield high strength and ductility for its applications.

Production

Metallic beryllium is produced by reduction of beryllium halide with sodium, potassium or magnesium. Commercially, it is obtained primarily from its ore, beryl. Beryllium oxide is separated from silica and alumina in ore by melting the ore, quenching the solid solution, and solubilizing in sulfuric acid at high temperatures and pressure. Silica and alumina are removed by pH adjustment. Beryllium is converted to its hydroxide. Alternatively, beryl is roasted with complex fluoride. The products are dissolved in water and then pH is adjusted to produce beryllium hydroxide.

The impure hydroxide obtained above is purified by converting to a double salt, ammonium beryllium fluoride, which subsequently, on thermal decomposition, gives beryllium fluoride. The latter is heated with magnesium metal to form pure beryllium metal:

$$BeF_2 + Mg \xrightarrow{heat} Be + MgF_2$$

It finally is purified by either vacuum melting or chelation with an organophosphate reagent followed by liquid-liquid extraction.

Beryllium halide alternatively may be reduced to the metal or converted to alloy by electrolysis.

Physical Properties

Grayish metal; hexagonal close-packed crystal system, lattice constant, a=2.286 Å and c=3.584 Å; density 1.85 g/cm^3; permeable to x-rays; highly ductile; modulus to weight ratio very high, elastic modulus 44.5 x 10^6 at 25°C (for hot-pressed block and sheet); melting point 1,287°C; vaporizes at 2,471°C; sound transmission velocity 12,600 m/sec; reflectivity (white light) 55%; thermal neutron absorption cross-section 0.0090 barns/atom; electrode potential, Be/Be^{2+}(aq) 1.85 V; electrical resistivity 3.36 x 10^{-10} ohm.m (at 20°C).

Thermochemical Properties

Specific heat (at 25°C)	0.436 cal/g°C
ΔH_{fus}	210 cal/g
ΔH_{vap}	5917 cal/g
Coefficient of linear expansion, (at 25°C)	11.3 x 10^{-6} /°C
Thermal conductivity, (at 27°C)	2.00 W/cm K

Reactions

Most chemical reactions of beryllium are similar to those of aluminum and, to a lesser extent, magnesium. In general, all the common mineral acids attack beryllium forming their corresponding salts with evolution of hydrogen:

$$Be + 2HCl \rightarrow BeCl_2 + H_2$$

Cold, concentrated nitric acid, however, has no effect when mixed with the metal.

Reactions with alkalies first produce insoluble beryllium hydroxide with evolution of hydrogen. Excess alkali converts the hydroxide to water-soluble beryllate:

$$Be(OH)_2 + 2NaOH \rightarrow Na_2BeO_2 + H_2O$$

Beryllium does not react with oxygen at ordinary temperatures and normal atmosphere. When heated above 700°C, the metal combines with nitrogen, (in an oxygen-free atmosphere) forming beryllium nitride, Be_3N_2.

Beryllium combines with carbon when heated above 900°C in the absence of air to form beryllium carbide.

$$2Be + C \xrightarrow{>900^\circ C} Be_2C$$

Beryllium reacts incandescently with fluorine or chlorine, producing beryllium fluoride or chloride.

Analysis

Elemental Be may be analyzed in acidified aqueous solutions at trace concentrations by flame or furnace atomic absorption spectrophotometer. Also, the analysis may be performed by ICP emission spectrophotometry. In both the furnace-AA and the ICP spectrometry, concentrations at the low ppb levels in aqueous matrices may be analyzed accurately. Be may be measured at an even lower detection level (low ppt) by ICP-mass spectrometry. In the absence of these instruments, the element in aqueous matrices may be analyzed at low ppb levels by colorimetry. An aluminum (aurintricarboxylic acid triammonium salt) buffer reagent is added to aqueous sample to form a beryllium lake and the color developed is measured at 515 nm by spectrophotometer or filter photometer. A small amount of ethylenediamine tetraacetic acid is added as a complexing agent to prevent interference from other metals in the analysis. (APHA, AWWA and WEF. 1998. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington, DC: American Public Health Association.) The element in solid matrix is brought into solution by heating and digesting with nitric acid.

The metal also may be analyzed in solid matrices by nondestructive methods such as x-ray diffraction or x-ray fluorescence techniques.

Toxicity

Elemental Be and its compounds are very poisonous by inhalation or intravenous route. Chronic inhalation of beryllium dusts or fumes can cause a serious lung disease, berylliosis, after a latent period ranging from several months to many years. Inhalation of airborne dusts can also cause an acute disease manifested as dyspnea, pneumonitis and tracheobronchitis with a short latency period of a few days. Skin contact with soluble salts of the metal can cause dermatitis. Beryllium also is a carcinogen. There is sufficient evidence of its inducing cancer in animals and humans.

It is one of the US EPA's listed priority pollutant metals in the environment.

BERYLLIUM CARBIDE

[506–66–1]
Formula: Be_2C; MW 30.035

Uses

Beryllium carbide is used in a nuclear reactor as core material.

Physical Properties

Red cubic crystal; hard and refractory; density 1.90 g/cm^3; decomposes when heated above 2,100°C; reacts with water.

Preparation

Beryllium carbide is prepared by heating the elements beryllium and carbon at elevated temperatures (above 900°C). It also may be prepared by reduction of beryllium oxide with carbon at a temperature above 1,500°C:

$$2BeO + 3C \xrightarrow{1500^\circ C} Be_2C + 2CO$$

Beryllium carbide decomposes very slowly in water:

$$Be_2C + 2H_2O \rightarrow 2BeO + CH_4$$

The rate of decomposition is faster in mineral acids with evolution of methane. However, in hot concentrated alkalies the reaction is very rapid, forming alkali metal beryllate and methane:

$$Be_2C + 4NaOH \rightarrow 2Na_2BeO_2 + CH_4$$

Analysis

Elemental composition: Be 60.02%, C 39.98%. Beryllium may be analyzed by various instrumental techniques (see Beryllium). Additionally, the compound may be treated with a dilute mineral acid. The product methane gas slowly evolved is then analyzed by GC equipped with a TCD, or by GC/MS.

BERYLLIUM CHLORIDE

[7787–47–5]
Formula: $BeCl_2$; MW 79.92

Uses

Beryllium chloride, an electron-deficient compound similar to aluminum chloride, is a Lewis acid. The anhydrous salt is used as a catalyst in organic reactions. Its applications, however, are limited.

Physical Properties

White or yellowish orthorhombic crystal; hygroscopic; density 1.90 g/cm^3; melts at 399°C; vaporizes at 482°C; sublimes in vacuum (at ~2 torr) at 300°C; highly soluble in water; moderately soluble in alcohol, ether and pyridine; insoluble in benzene, choroform, acetone and ammonia.

Thermochemical Properties

$\Delta H^\circ f$	–117.3 kcal/mol
$\Delta G^\circ f$	–106.6 kcal/mol
S°	19.6 cal/degree mol

C_ρ	15.5 cal/degree mol
ΔH_{fus}	2.07 kcal/mol
ΔH_{vap}	25.1 kcal/mol

Preparation

Beryllium chloride is prepared by passing chlorine over beryllium oxide and carbon:

$$BeO + C + Cl_2 \rightarrow BeCl_2 + CO$$

It also is made by combination of beryllium with chlorine.

Reactions

Beryllium chloride is stable in dry air, but absorbs moisture forming tetrahydrate, $BeCl_2 \cdot 4H_2O$. It readily dissolves in water undergoing hydrolysis and evolving hydrogen chloride:

$$BeCl_2 + 2H_2O \rightarrow Be(OH)_2 + 2HCl$$

Cold aqueous solution of $BeCl_2$ reacts with H_2S forming beryllium sulfide, BeS, which decomposes on heating.

Toxicity

Highly toxic by ingestion (see Beryllium); LD_{50} oral (rat): 86 mg/kg. It is a confirmed carcinogen and can cause an adverse reproductive effect.

Analysis

Elemental composition: Be 11.28%, Cl 88.72%. Beryllium may be analyzed in aqueous solution or in solid form by different instrumental techniques (see Beryllium). Chloride may be measured in aqueous solution (after appropriate dilution) by titration with a standard solution of silver nitrate or mercuric nitrate; or by ion chromatography or a selective chloride ion electrode.

BERYLLIUM FLUORIDE

[7787–49–7]
Formula: BeF_2; MW 47.01

Uses

Beryllium fluoride is the intermediate compound in the magnesium-reduction process to produce beryllium metal. The compound also is used in the manufacture of glass, and in nuclear reactors.

Physical Properties

Glassy solid; tetragonal crystal system; hygroscopic; density 2.1 g/cm^3; melts at 552°C; vaporizes at 1,169°C; very soluble in water; sparingly soluble in alcohol.

Thermochemical Properties

$\Delta H°f$	–245.5 kcal/mol
$\Delta G°f$	–234.2 kcal/mol
S°	12.77 cal/degree mol
C_ρ	12.39 cal/degree mol
ΔH_{fus}	1.14 kcal/mol

Preparation

Beryllium fluoride is made by thermal decomposition of ammonium beryllium fluoride at 900 to 950°C:

$$(NH_4)_2BeF_4 \xrightarrow{900-950^\circ C} BeF_2 + 2NH_3 + 2HF$$

Analysis

Elemental composition: Be 19.17%, F 80.83%. The metal is analyzed by instrumental techniques (see Beryllium), and fluoride may be determined in the aqueous solution by a selective fluroide ion electrode.

Toxicity

Highly toxic by all routes of exposure and also a carcinogen:
LD_{50} oral (mouse): 100 mg/kg; LD_{50} subcutaneous (mouse): 20 mg/kg.

BERYLLIUM HYDRIDE

[7787–52–2]
Formula: BeH_2; MW 11.03

Uses

Beryllium hydride has few commercial applications. It is used in rocket fuels.

Physical Properties

White amorphous solid; density 0.65 g/cm^3; decomposes at 250°C; reacts with water.

Preparation

Beryllium hydride is made by treating an ethereal solution of beryllium borohydride with triphenylphosphine, or by pyrolysis of di-*tert*-butylberyllium.

Reactions

Beryllium hydride reacts with water, dilute acids, and methanol, liberating hydrogen. The reactions with acids are violent, presenting a fire risk. Also, it reacts violently with oxidizing agents and organic matter. It decomposes, rapidly liberating hydrogen when heated at 220°C.

BERYLLIUM HYDROXIDE

[13327–32–7]
Formula $Be(OH)_2$; MW 43.03 Synonym: beryllium hydrate

Uses

Beryllium hydroxide is used to produce beryllium oxide and other beryllium compounds.

Physical Properties

Crystalline solid or amorphos powder; exists in two forms, alpha and beta forms; the alpha form is a granular powder; the beta form is a gelatinous mass of indefinite composition; density 1.92 g/cm^3; decomposes to beryllium oxide when heated at elevated temperatures (decomposition commences at 190°C and completes at red heat); practically insoluble in water and dilute alkalies; soluble in acids and hot concentrated caustic soda solution.

Thermochemical Properties

$\Delta H°f$	–215.8 kcal/mol
$\Delta G°f$	–194.9 kcal/mol
S°	12.4 cal/degree mol

Preparation

Beryllium hydroxide is prepared by treating basic beryllium acetate, $Be_4O(C_2H_3O_2)_6$ with caustic soda solution; or by precipitation from a strongly alkaline solution of sodium beryllate. The precipitate is dried at 100°C.

Toxicity

The compound is poisonous by intravenous route and a carcinogen; intravenous lethal dose in rat is about 4 mg/kg.

BERYLLIUM NITRATE TRIHYDRATE

[13597–99–4]
Formula: $Be(NO_3)_2 \cdot 3H_2O$; MW 187.07

Uses

$Be(NO_3)_2 \cdot 3H_2O$ is used to produce beryllium oxide; and as a mantle hardener in incandescent acetylene or other gas lamps.

Physical Properties

White or yellowish crystalline solid; deliquescent; melts at 60°C; decomposes on further heating; very soluble in water, moderately soluble in alcohol.

Preparation

Beryllium nitrate is made by dissolving beryllium oxide or hydroxide in concentrated nitric acid, followed by crystallization. Also, it may be prepared by mixing beryllium sulfate and barium nitrate solutions followed by evaporation and crystallization.

Analysis

Elemental composition: Be 4.82%, N 14.97%, H 3.23%, O 76.98%

Toxicity

$Be(NO_3)_2 \cdot 3H_2O$ is toxic by subcutaneous, intravenous and intraperitoneal routes; and also is a carcinogen. LD_{50} intraperitoneal (mouse): 5 mg/kg

BERYLLIUM NITRIDE

[1304–54–7]
Formula: Be_3N_2; MW 55.05

Uses

Beryllium nitride is used in nuclear reactors; and to produce radioactive carbon–14 isotope for tracer applications.

Physical Properties

Gray cubic crystal; hard and refractory; density 2.71 g/cm^3; melts at 2,200°C; decomposes in acid or alkali; slowly reacts with water.

Preparation

Beryllium nitride may be prepared by heating beryllium metal powder with dry nitrogen in an oxygen-free atmosphere above 700°C:

$$3Be + N_2 \xrightarrow{700^\circ - 1400^\circ C} Be_3N_2$$

Reactions

Beryllium nitride reacts with mineral acids producing ammonia and the corresponding salts of the acids:

$$Be_3N_2 + 6HCl \quad 3BeCl_2 + 2NH_3$$

In strong alkali solutions, a beryllate forms, with evolution of ammonia:

$$Be_3N_2 + 6NaOH \rightarrow 3Na_2BeO_2 + 2NH_3$$

Both the acid and alkali reactions are brisk and vigorous. Reaction with water, however, is very slow:

$$Be_3N_2 + 6H_2O \rightarrow 3Be(OH)_2 + 2NH_3$$

When heated above its melting point, it vaporizes first, and then on further heating dissociates to its elements:

$$Be_3N_2 \xrightarrow{>2250^\circ C} 3Be + N_2$$

Reactions with oxidizing agents are likely to be violent. It is oxidized when heated at 600°C in air.

Analysis

Elemental composition: Be 49.11%, N 50.89%. Analysis may be performed by treatment with HCl. The soluble $BeCl_2$ solution is then measured for Be by AA or ICP techniques. The ammonia liberated is determined by titrimetry, colorimetry or by ammonia-selective electrode (see Ammonia).

BERYLLIUM OXIDE

[1304–56–9]
Formula: BeO; MW 25.01
Synonym: beryllia

Uses

Beryllium oxide shows excellent thermal conductivity, resistance to thermal shock, and high electrical resistance. Also, it is unreactive to most chemicals. Because of these properties the compound has several applications. It is used to make refractory crucible materials and precision resistor cores; as a reflector in nuclear power reactors; in microwave energy windows; and as an additive to glass, ceramics and plastics.

Physical Properties

White amorphous powder; density 3.02 g/cm^3; hardness 9 Mohs; melts at 2,507°C; vaporizes at 3,900°C; insoluble in water; dissolves slowly and sparingly in concentrated acids and concentrated aqueous solutions of alkalies.

Thermochemical Properties

$\Delta H°f$	–145.72 kcal/mol
$\Delta G°f$	–138.7 kcal/mol
S°	3.30 cal/degree mol
C_ρ (at 100° C)	7.48 cal/degree mol
ΔH_{fus}	20.36 kcal/mol

Preparation

Beryllium oxide is obtained by thermal dissociation of beryllium nitrate or hydroxide:

$$Be(NO_3)_2 \xrightarrow{heat} BeO + N_2O_5$$

$$Be(OH)_2 \xrightarrow{heat} BeO + H_2O$$

Also, it may be prepared by heating beryllium sulfate at elevated temperatures. Dissociation begins at 550°C and completes at 1,000°C.

Analysis

Elemental composition: Be 36.03%, O 63.97%. The solid powder may be characterized by x-ray techniques. The metal can be analyzed by microwave-assisted, strong acid digestion followed by flame or furnace AA or ICP spectrophotometric determination.

Toxicity

Chronic inhalation of the powder can cause cancer and adverse reproductive effects.

BERYLLIUM SULFATE

[13510–49–1]
Formula: $Be(SO_4)_2$; MW 105.08; also forms a tetrahydrate $Be(SO_4)_2 \cdot 4H_2O$ [7787–56–6] (MW 177.14)

Uses

No major commercial application of beryllium sulfate is known.

Physical Properties

Colorless crystalline solid; tetragonal crystal system; hygroscopic; density 2.50 g/cm^3 (tetrahydrate 1.71 g/cm^3); tetrahydrated salt loses water of crystallization on heating; further heating to 550°C causes decomposition; soluble in water, tetrahydrate more soluble in water (30.5g/100g at 30°) than the anhydrous salt; insoluble in alcohol.

Thermochemical Properties

$\Delta H°f$	–288.2 kcal/mol
$\Delta G°f$	–261.5 kcal/mol
S°	18.63 cal/degree mol
C_ρ	20.49 cal/degree mol

Preparation

Beryllium sulfate may be prepared by treating an aqueous solution of any beryllium salt with sulfuric acid, followed by evaporation of the solution and crystallization. The hydrated product may be converted to anhydrous salt by heating at 400°C.

Analysis

Elemental composition: Be 8.58%, S 30.51%, O 60.91%. The metal may be analyzed by various instrumental techniques (see Beryllium). Sulfate may be measured in the aqueous solution of the salt by gravimetric method (adding $BaCl_2$ solution and precipitating $BaSO_4$) or by ion chromatography.

Toxicity

The compound is acutely toxic by all routes of exposure, and a carcinogen. LD_{50} oral (mouse): 50 mg/kg.

BISMUTH

[7440–69–9]
Symbol Bi; atomic number 83; atomic weight 208.98; a heavy metallic element of the nitrogen group in the periodic table; atomic radius 1.88Å (coordination number 12); ionic radii in crystals corresponding to coordination number 6: Bi^{3+} 1.03Å, Bi^{5+} 0.76 Å; atomic volume 21.3 cc/g-atom; electronic configuration [Xe] $4f^{14}5d^{10}6s^26p^3$; ionization potentials, Bi(+3) 25.56eV and Bi(+5) 56.0 eV; electron affinity 0.946 eV; electronegativity (Allred-Rochow type) 1.67; valence states +3, +5.

Occurrence and Uses

Bismuth occurs in nature in ores, bismite (Bi_2O_3), bismuth glance or bismuthinite (Bi_2S_3), tetradymite (a mixed sulfide and telluride), and also as carbonates in bismutite and bismutophaerite. It also is found in elemental form or native bismuth in small quantities associated with the ores of zinc, silver, tin and lead. The concentration of bismuth in the earth's crust is estimated to be in the range 8.5×10^{-3} mg/kg and in sea 20 ng/L (ppt). The major commercial applications of bismuth are in pharmaceuticals and as fusible alloys. Some bismuth compounds also find catalytic applications in the manufacture of acrylic fibers. It is used in electric fuses, fusible boiler plugs, low-melting solders, thermoelectric materials, and semiconductors, and as an additive to steel and other metals. Many bismuth compounds are used in medicine as antacids, antisyphilitics and anti-infectives; and in cosmetics such as lipsticks, powder and eye shadow.

Physical Properties

Grayish-white metal with pinkish tinge; high metallic luster; soft and brittle; rhombohedral crystal system (a= 4.7457Å, axial angle 57° 14.2'); density 9.79 g/cm^3; hardness (Brinnel) 7; melting point 271°C (contracts on melting, volume expansion on solidification 3.32%); vaporizes at 1,564°C; vapor pressure 10, 100 and 400 torr at 1,100, 1,200, and 1,400°C, respectively; poor conductor of electricity, electrical resistivity 106.8 and 160.2 microhm-cm at 0 and 100°C, respectively (higher in solid than in liquid state); greatest Hall effect (increase in resistance when placed in a magnetic field) among all metals; mass susceptibility –1.35 x 10^6 (highly diamagnetic).

Thermochemical Properties

$\Delta H°f$ (g)	49.52 kcal/mol
$G° f$ (g)	40.22 kcal/mol
$S°$ (g)	44.7 cal/degree mol
C_ρ (g)	6.10 cal/degree mol
Specific heat (20°C)	0.0294 cal/g°C
Coeff. Lin. expansion	13.3 x 10^{-6}/°C
Thermal conductivity	
at 20°C	0.020 cal/sec/cm^3
at 250°C	0.018 cal/sec/cm^3
at 400°C	0.037 cal/sec/cm^3
ΔH_{fus}	2.70 kcal/mol
ΔH_{vap}	42.7 kcal/mol

Production

Bismuth is obtained as a by-product in smelting and refining of lead, copper or tungsten ores. The metal is partially volatilized when the ore is smelted at the high temperature. Separation from copper is achieved by electrolytic refining, bismuth accumulating in the anode slimes with lead, arsenic, antimony, tellurium, and other metal impurities. All throughout the smelting and refining operations bismuth accompanies lead. It finally is removed from lead by Betterton-Kroll or Betts processes. The Betterton-Kroll process involves the addition of calcium-lead alloy or magnesium metal to lead slime, thus converting bismuth to high-melting bismuthides of calcium or magnesium, Ca_3Bi_2 or Mg_3Bi_2, respectively. These bismuthides liquate from the bath and are separated as dross. Bismuth dross is then melted in kettles forming $Bi_7Mg_6K_9$ which liquates to the top of the bath and is removed from the molten lead. Treatments with caustic soda finally produce the high quality bismuth.

In a modified process, potassium substitutes for calcium to form $Bi_7Mg_6Ca_9$ which liquates to the top of the bath and is removed from the molten lead. The Betts process is based on electrolytic refining using a solution of lead fluorosilicate and fluorosilicic acid. While lead is deposited on the cathode, bismuth goes to the anode where it is collected with other impurity metals. It is then filtered, dried, smelted, and further refined, depending on the purity desired. Impurities are removed by adding molten caustic and zinc, and finally by chlorination.

Bismuth may be obtained from other ores, too. The recovery process however, depends primarily on the chemical nature of the ores. For example, the sulfide ore requires smelting, carbon reduction, and the addition of iron (to decompose any bismuth sulfide present). Oxide ores, on the other hand, are treated with hydrochloric acid to leach bismuth from the mineral. The bismuth chloride solution is then diluted with water to precipitate bismuth oxychloride. The precipitate is roasted with lime and charcoal. Satisfactory recovery of the metal from its carbonate ore may be achieved by both the above techniques.

Bismuth is sold in the form of rod, lump, powder, and wire.

Reactions

Bismuth forms trivalent and pentavalent compounds. The trivalent compounds are more common. Many of its chemical properties are similar to other elements in its group; namely, arsenic and antimony.

Bismuth is stable to both dry and moist air at ordinary temperatures. At elevated temperatures, the vapors of the metal combine rapidly with oxygen, forming bismuth trioxide, Bi_2O_3. The element dissolves in concentrated nitric acid forming bismuth nitrate pentahydrate, $Bi(NO_3)_3 \cdot 5H_2O$. Addition of water to this salt solution precipitates an oxysalt, $Bi_2O_3N_2O_5 \cdot 2H_2O$. Reaction with hydrochloric acid followed by evaporation of the solution produces bismuth trichloride, $BiCl_3$.

Bismuth reacts with chlorine, bromine and iodine vapors forming chloride, bromide and iodide of the metal, respectively. Molten bismuth and sulfur combine to form bismuth sulfide, Bi_2S_3.

Analysis

The metal in trace quantities may be analyzed by furnace or flame AA or by ICP emission or ICP/MS techniques. The solid or liquid sample is digested with nitric acid and the solution is diluted appropriately and analyzed. The element may also be determined in solid salts or mixtures by various x-ray methods.

Hazard

In powder form, the metal is pyrophoric. The toxicity of bismuth and its compounds is very low.

BISMUTH CHLORIDE

[7787–60–2]
Formula: $BiCl_3$; MW 315.34
Synonyms: bismuth trichloride

Uses

Bismuth chloride is used to prepare several other bismuth salts; as a catalyst in organic synthesis; and as a constituent in pigments and cosmetics.

Physical Properies

Yellowish-white crystalline solid; cubic crystals; hygroscopic; density 4.75

g/cm^3; melts at 230°C; vaporizes at 447°C; vapor pressure 5 torr at 242°C; reacts with water; soluble in acids, alcohol and acetone.

Thermochemical Properties

$\Delta H°f$	–117.3 kcal/mol
$\Delta G°f$	–106.6 kcal/mol
S°	19.8 cal/degree mol
C_ρ	15.5 cal/degree mol
ΔH_{fus}	2.61 kcal/mol
ΔH_{vap}	17.36 kcal/mol

Preparation

Bismuth chloride may be synthesized directly by passing chlorine over bismuth. Alternatively, the chloride salt may be prepared by adding hydrochloric acid to basic bismuth chloride and evaporating the solution:

$$Bi(OH)_2Cl + 2HCl \rightarrow BiCl_3 + 2H_2O$$

Also, the compound can be prepared by dissolving bismuth in concentrated nitric acid and then adding solid sodium chloride into this solution. Another method of preparation is treating the metal with concentrated hydrochloric acid:

$$2Bi + 6HCl \rightarrow 2BiCl_3 + 3H_2$$

Analysis

Elemental composition: Bi 66.27%, Cl 22.73%. The metal may be analyzed by various instrumental techniques (see Bismuth). The solid salt may be identified nondestructively by x-ray methods.

BISMUTH HYDROXIDE

[10361–43–0]
Formula: $Bi(OH)_3$; MW 260.00;
Synonyms: bismuth hydrate; hydrated bismuth oxide.

Uses

Bismuth hydroxide is used as an absorbent and in the hydrolysis of ribonucleic acid. It also is used in the isolation of plutonium from irradiated uranium.

Physical Properties

Yellowish-white amorphous powder; density 4.96 g/cm^3; insoluble in water, soluble in acids; K_{sp} 3.2 x 10^{-40}

Thermochemical Properties

$\Delta H°f$	–170.1 kcal/mol

Preparation

Bismuth hydroxide is precipitated by adding sodium hydroxide to a solution of bismuth nitrate.

Analysis

Elemental composition: Bi 80.38%, H 1.16%, O 18.46%. See Bismuth.

BISMUTH NITRATE PENTAHYDRATE

[10035–06–0]
Formula: $Bi(NO_3)_3 \cdot 5H_2O$; MW 485.07

Uses

The primary use of this compound is to produce a number of other bismuth compounds. It also is used in luminous paints and enamels; applied on tin to produce bismuth luster; and for precipitation of alkaloids.

Physical Properties

Lustrous triclinic crystals; acid taste; hygroscopic; density 2.83 g/cm^3; decomposes at 75°C; reacts slowly with water; soluble in acids and acetone; insoluble in alcohol .

Preparation

Bismuth nitrate is prepared by dissolving bismuth in concentrated nitric acid, followed by evaporation and crystallization .

Reactions

Addition of water precipitates out an oxysalt, $Bi_2O_3N_2O_5 \cdot H_2O$. The degree of hydrolysis and the product composition can vary with the amount of water and the reaction temperature .

Thermal dissociation gives bismuth trioxide and dinitrogen pentoxide:

$$2Bi(NO_3)_3 \xrightarrow{heat} Bi_2O_3 + 3N_2O_5$$

Bismuth nitrate reacts with gallic acid in glacial acetic acid to form bismuth subgallate, $C_6H_2(OH)_3COOBi(OH)_2$.

$Bi(NO_3)_3$ forms bismuth oxychloride, BiOCl in dilute nitric acid solution, upon addition of sodium chloride.

$Bi(NO_3)_3$ reacts with sodium hydroxide to form bismuth hydroxide, $Bi(OH)_3$:

$$Bi(NO_3)_3 + 3NaOH \rightarrow Bi(OH)_3 + 3NaNO_3$$

Reaction with potassium chromate produces bismuth chromate:

$$2Bi(NO_3)_3 + 3NaOH \rightarrow Bi(OH)_3 + 3NaNO_3$$

$Bi(NO_3)_3$ forms bismuth sulfide, Bi_2S_3 when hydrogen sulfide is passed through its solution in nitric acid.

BISMUTH OXYCHLORIDE

[7787–59–9]
Formula: BiOCl; MW 260.43
Synonyms: bismuth chloride oxide; basic bismuth chloride; bismuth subchloride; bismuthyl chloride

Uses

Bismuth oxychloride is used in face powder and other cosmetics. It also is used in pigments; dry-cell cathodes; to make artificial pearls; and in medicines.

Physical Properties

White powder or tetragonal crystals; density 7.72 g/cm^3; practically insoluble in water, alcohol and acetone; soluble in hydrochloric and nitric acids (with decomposition); K_{sp} 7.0 x 10^{-9}.

Thermochemical Properties

$\Delta H°f$	–87.7 kcal/mol
$\Delta G°f$	–77.0 kcal/mol
S°	28.8 cal/degree mol

Preparation

Bismuth oxychloride is made by treating bismuth chloride with water and then drying the white precipitate so formed to expel a molecule of water:

$$BiCl_3 + 2H_2O \rightarrow Bi(OH)_2Cl + 2HCl$$

$$Bi(OH)_2Cl \xrightarrow{heat} BiOCl + H_2O$$

Also, the compound is prepared by treating a dilute nitric acid solution of bismuth nitrate with sodium chloride.

Analysis

Elemental composition: Bi 80.24%, Cl 13.61%, O 6.14%. The metal may be analyzed by various instrumental techniques. (See Bismuth.)

BISMUTH OXYCARBONATE

[5892–10–4]
Formula: $(BiO)_2CO_3$; MW 509.97
Synonyms: bismuth subcarbonate; bismuth carbonate, basic; bismuth basic

carbonate

Uses

Bismuth oxycarbonate is used in cosmetics, enamel fluxes, ceramic glazes, plastic and artificial horn products. It also is used as an opacifier in x–ray diagnosis; and in medicine for treatment of gastric ulcers, diarrhea and enteritis.

Physical Properties

White powder; density 6.86 g/cm^3; insoluble in water and alcohol; soluble in mineral acids.

Preparation

Bismuth oxycarbonate is prepared by adding sodium carbonate to a suspension of bismuth subnitrate in water.

$$BiONO_3 + Na_2CO_3 \rightarrow (BiO)_2CO_3 + 2NaNO_3$$

$(BiO)_2CO_3$ also may be prepared by adding ammonium carbonate to a solution of bismuth salt. The nature of the product in the preparative processes depends on the nature of the subnitrate or the bismuth salt used, the amount of water and the temperature.

BISMUTH OXYNITRATE

[10361–46–3]
Formula: $BiONO_3$; MW 286.98
Synonyms: bismuth subnitrate; basic bismuth nitrate; bismuthyl nitrate; bismuth white

Uses

Bismuth oxynitrate is used in cosmetics, enamel fluxes and ceramic glazes. Medical applications include treatment of diarrhea, and gastric ulcers; and opacifier in x–ray diagnosis of alimentary canal .

Physical Properties

White powder; density 4.93 g/cm^3; decomposes at 260°C; insoluble in water and ethanol; dissolves in acids.

Preparation

Bismuth oxynitrate is prepared by hydrolysis of bismuth nitrate using either water or sodium bicarbonate solution under mild heating (between 30 to 70°C) and stirring. The composition of the product formed can vary depending on the strength of nitric acid and the quantity of water used.

Reactions

At 260°C or above, bismuth oxynitrate decomposes to bismuth oxide and oxides of nitrogen. The compound is practically insoluble in water. However, as a suspension in water, it reacts with many compounds, such as, sodium and other alkali metal bicarbonates, several soluble metal iodides and phosphates, and sulfur, forming precipitates of insoluble bismuth compounds.

BISMUTH SULFIDE

[1345–07–9]
Formula: Bi_2S_3; MW 514.16
Synonym: bismuth trisulfide

Occurrence and Uses

Bismuth sulfide occurs in nature as the mineral bismuthinite (bismuth glance). It is used as a starting material to produce many other bismuth compounds.

Physical Properties

Brownish black orthogonal crystal; density 6.78 g/cm^3; hardness 2 Mohs; melts at 850°C; insoluble in water; soluble in acids.

Thermochemical Properties

$\Delta H°f$	–34.22 kcal/mol
$\Delta G°f$	–33.62 kcal/mol
S°	47.9 cal/degree mol
C_ρ	29.2 cal/degree mol

Preparation

The compound occurs in nature as mineral bismuthinite. It can be prepared in the laboratory by passing hydrogen sulfide into a solution of bismuth chloride or any soluble bismuth salt:

$$2BiCl_3 + 3H_2S \rightarrow Bi_2S_3 + 6HCl$$

Alternatively, bismuth sulfide may be obtained by melting a mixture of bismuth and sulfur:

$$2Bi + 3S \xrightarrow{heat} Bi_2S_3$$

Analysis

Elemental composition: Bi 81.29%, S 18.71%. The metal may be determined by digesting the compound in nitric acid followed by instrumental analysis (see Bismuth). Sulfur may be measured in the acid extract by ICP/AES technique.

BISMUTH TRIOXIDE

[1304–76–3]
Formula: Bi_2O_3; MW 465.96
Synonyms: bismuth oxide; bismite; bismuth yellow; bismuthous oxide

Occurrence and Uses

Bismuth trioxide occurs in nature as mineral bismite. The oxide is used in fireproofing of papers and polymers; in enameling cast iron ceramic; and in disinfectants.

Physical Properties

Yellow monoclinic crystal or powder; density 8.90 g/cm^3; melts at 817°C; vaporizes at 1,890°C; insoluble in water; soluble in acids.

Thermochemical Properties

$\Delta H°f$	–137.2 kcal/mol
$\Delta G°f$	–118.1 kcal/mol
S°	36.2 cal/degree mol
C_ρ	27.1 cal/degree mol

Preparations

Bismuth trioxide is commercially made from bismuth subnitrate. The latter is produced by dissolving bismuth in hot nitric acid. Addition of excess sodium hydroxide followed by continuous heating of the mixture precipitates bismuth trioxide as a heavy yellow powder. Also, the trioxide can be prepared by ignition of bismuth hydroxide.

Reactions

Oxidation with ammonium persulfate and dilute caustic soda gives bismuth tetroxide, Bi_2O_4. The same product can be obtained by using other oxidizing agents such as potassium ferricyanide and concentrated caustic potash solution.

Electrolysis of bismuth trioxide in hot concentrated alkali solution gives a scarlet red precipitate of bismuth pentoxide, Bi_2O_5.

Bismuth trioxide reacts with hydrofluoric acid forming bismuth trifluoride, BiF_3.

Reaction with acetic anhydride and oleic acid gives bismuth trioleate, $Bi(C1_8H_{33}O_2)_3$.

Analysis

Elemental composition: Bi 89.70%, O 10.30%. The compound may be analyzed by x-ray diffraction technique. Alternatively, it may be digested with nitric acid and the solution analyzed for Bi by AA or ICP spectrophotometry.

BORAX, ANHYDROUS

[1330–43–3]
Formula $Na_2B_4O_7$; MW 201.22
Synonyms: sodium tetraborate; disodium tetraborate; anhydrous borax

Uses

Anhydrous borax is used in the manufacture of glasses, glass wool, and metallurgical fluxes. Other uses are in enamels, frits, and glazes. It also is applied in fertilizers.

Physical Properties

Colorless glassy solid; also exists in several crystalline forms; hygroscopic; density 2.37 g/cm^3 (glassy form), 2.27 g/cm^3 (crystalline form); melts at 743°C; vaporizes at 1,575°C; the α–form stable above 600°C; dissolves slowly in cold water; soluble in methanol (16.7% as fine crystal), and ethylene glycol (30% as fine crystal).

Thermochemical Properties

$\Delta H°f$	–786.6 kcal/mol
$\Delta G°f$	–740.0 kcal/mol
S°	45.29 cal/degree mol
C_ρ	44.65 cal/degree mol
ΔH_{fus}	19.4 kcal/mol
ΔH_{soln}	–10.28 kcal/mol
$\Delta H_{hydration}$ (to decahydrate)	38.5 kcal/mol

Preparation

Anhydrous borax is made from its hydrated forms by calcination and fusion. In the United States, it is produced by US Borax and Kerr-McGee Corporations. The starting material is borax decahydrate. The amorphos form is obtained by rapid cooling of molten borax. The molten material on long standing produces the crystalline form.

Analysis

The B_2O_3 content of borax may be determined by extraction into HCl solution followed by complexation with mannitol and titration with dilute NaOH. The Na_2O content of borax may be measured by titration of an aqueous solution with dilute HCl. Boron and sodium metals in the acid extract of borax may be analyzed by atomic absorption or emission spectroscopy after appropriate dilution of the extract. In the solid phase B_2O_3 and Na_2O may be measured nondestructively by x-ray techniques.

Hazard

None

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BORAX DECAHYDRATE

[1303–96–4]
Formula: $Na_2B_4O_7 \cdot 10H_2O$; MW 381.37
Synonym: disodium tetraborate decahydrate

Occurrence and Uses

Borax decahydrate occurs in nature as mineral, borax (tincal). It is one of the most common sodium borate ores. The compound has several industrial applications. The refined material is mostly used in household cleaning products. It is used to make pyrex and other borosilicate glasses. Borax is added to fertilizers in small quantities as a source of boron, as a trace nutrient for plants. High purity grade borax is used in cosmetics, toilet products and electrolytic capacitors. It also is used in fire retardants, adhesives and herbicides.

Physical Properties

White monoclinic crystal; density 1.73 g/cm^3; decomposes at 75°C; soluble in water; the vapor pressure of the pure compound 1.6 torr at 20°C and that of a saturated solution 130 torr at 58°C; the pH of a 1% aqueous solution 9.24 (the pH is nearly independent of concentration); readily dissolves in alcohols

Production

Borax decahydrate is produced from borate ores, primarily colemanite and also from dry lake brines. When produced from its ore, the ore is crushed and then blended with B_2O_3. The blend is mixed with hot recycle liquor in a dissolving plant. Rock and clay particles from the liquor are removed over vibrating screens. The liquor is then fed to thickeners for settling of insolubles after which the underflow mud is washed with water. The strong liquor of borax hydrates is then pumped into continuous vacuum crystallizers for the separation of the pentahydrate first and then the decahydrate. The products are dried in rotary or fluid bed driers.

In most commercial processes, borax is obtained from lake brines, tincal and colemanite. The primary salt constituents of brine are sodium chloride, sodium sulfate, sodium carbonate and potassium chloride. The percent composition of borax as $Na_2B_4O_7$ in brine is generally in the range 1.5 to 1.6%. Borax is separated from these salts by various physical and chemical processes. The brine solution (mixed with mother liquor) is subject to evaporation and crystalization for the continuous removal of NaCl, Na_2CO_3 and Na_2SO_4, respectively. The hot liquor consists of concentrated solution of potassium salts and borate components of the brine. The insoluble solid particles are filtered out and the liquor is cooled rapidly in continuous vacuum crystallizers under controlled conditions of temperatures and concentrations to crystallize KCl. Cystallization of borax along with KCl from the concentrated liquor must not occur at this stage. KCl is separated from the liquor by filtration. Bicarbonate then is added to the liquor to prevent any formation of sodium metaborate. The liquor then is evaporated and refrigerated to crystallize borax.

Reactions

Reactions with acids and bases produce borates with varying Na_2O/B_2O_3 mole ratios. While acids produce borates with Na_2O/B_2O_3 mole ratios less than 0.5, their ratio is greater than 0.5 with bases. Treatment with sulfuric acid produces boric acid and sodium sulfate:

$$Na_2B_4O_7 \cdot 10H_2O + H_2SO_4 \rightarrow 4H_3BO_3 + Na_2SO_4 + 5H_2O$$

Reaction with hydrofluoric acid produces boron trifluoride, BF_3.

Dehydration gives pentahydrate, $Na_2B_4O_7 \cdot 5H_2O$ and other lower hydrates. Calcination at elevated temperatures gives anhydrous borax.

Analysis

Water of crystalization can be analyzed by TGA or DTA methods. The theoretical water content of borax decahydrate is 47.2%. The salt is digested with acid and the boron and sodium content may be measured by AA or ICP spectrophotometry. The compound may be identified by x-ray methods.

BORAX PENTAHYDRATE

[12045–88–4]
Formula: $Na_2B_4O_7 \cdot 5H_2O$; MW 291.30
Synonyms: disodium tetraborate pentahydrate; sodium tetraborate pentahydrate; tincalconite (mineral)

Occurrence and Uses

Borax pentahydrate occurs in nature as mineral tincalconite, formed by dehydration of borax. It has several industrial applications, mostly the same as its decahydrate. The pentahydrate is used in the manufacture of borosilicate glass. It also is used in cleaning agents; ceramic glaze; adhesives; cosmetics; antifreeze; and herbicide formulations. It is added to fertilizers to provide boron as a nutrient to the plants.

Physical Properties

Hexagonal crystal; density 1.88 g/cm^3; decomposes on heating; reversibly converts to an amorphous dihydrate when heated at 88°C at 2 torr; soluble in water (13% at 45°C), soluble in alcohols (17% in methanol and 31% in ethylene glycol by weight).

Thermochemical Properties

$\Delta H°f$	–273.3 kcal/mol
Specific heat	316 cal/g°C

Production

Borax pentahydrate is produced from various sodium borate and magnesium borate ores. In the United States, it is produced from dry lake brines, colemanite and tincal. It is commercially produced along with the decahydrate. The production processes are similar to decahydrate (see Borax decahydrate).

BORIC ACID

[10043–35–3]
Formula: $B(OH)_3$; MW 61.833;
Synonyms: orthoboric acid; boracic acid

Uses

Boric acid is used to prepare a variety of glasses including fiber glass, heat resistant borosilicate glass, and sealing glasses. It also is used to make porcelain. A major application of boric acid is to prepare a number of boron compounds including inorganic borate salts, boron halides, borate esters, fluoborates, and many boron alloys. The compound is used as a component of welding and brazing fluxes.

Boric acid is used as an antiseptic in mouthwashes, eye washes, and ointments; a preservative in natural products; to protect wood against insect damage; in washing citrus fruits; as a catalyst in hydrocarbon oxidation; as a flame retardant in cellulose insulation; in nickel electroplating baths; and as a buffer in ammonia analysis of wastewaters by acid titration.

Physical Properties

Colorless, transparent triclinic crystal or white granule or powder; density 1.435 g/cm^3; melts at 171°C under normal heating; however, slow heating causes loss of water; sparingly soluble in cold water (4.7% at 20°C); pH of 0.1M solution 5.1; readily dissolves in hot water (19.1% at 80°C and 27.5% at 100°C); also soluble in lower alcohols and moderately soluble in pyridine.

Thermochemical Properties

$\Delta H_f°$ (cry)	–261.5 kcal/mol
$\Delta H_f°$ (gas)	–231.5 kcal/mol
$\Delta G_f°$ (cry)	–237.6 kcal/mol
S°	21.22 cal/degree mol
C_ρ	19.46 cal/degree mol

Preparation

Boric acid is produced from borax, colemanite, or other inorganic borates by reaction with sulfuric acid or hydrochloric acid, and cooling the solution to proper temperature:

$$Na_2B_4O_7 \cdot 10H_2O + H_2SO_4 \rightarrow 4H_3BO_3 + Na_2SO_4 + 5H_2O$$

It also may be prepared by extraction of weak borax brine with a kerosene solution of an aromatic diol, such as 2–ethyl–1,3–hexanediol or 3–chloro–2–hydroxy–5–(1,1,3,3–tetramethylbutyl)benzyl alcohol. The diol–borate chelate formed separates into a kerosene phase. Treatment with sulfuric acid yields boric acid which partitions into aqueous phase and is purified by recrystallization.

Reactions

In dilute aqueous solutions, the boric acid molecule remains undissociated $B(OH)_3$; but in concentrated solutions, $B(OH)_4^-$ and complex polyborate anions, such as $B_3O_3(OH)_4^-$ are formed. Reactions with fluoride ion produce fluoroborates, $BF(OH)_3^-$, $BF_2(OH)_2^-$, $BF_3(OH)^-$, BF_4^-, and $B_3O_3F_6^{3-}$ in stepwise sequence. It forms similar polyions with amides and borates.

Boric acid on slow heating loses water around 130°C, forming metaboric acid HBO_2 which converts into different crystal modifications that depend on the temperature. Further heating dehydrates metaboric acid to pyroboric acid, $H_2B_4O_7$ and boric oxide, B_2O_3.

Boric acid forms complexes with a number of inorganic ions and organic molecules. Ammonia, hydrazine, hydroxides and oxyhalides from complexes with boric acid. The organics include diols, thiols, dioxane, pyridine and many other solvents in which boric acid dissolves.

Heating with metal oxides at elevated temperatures produces anhydrous borates. Reactions with halogens in the presence of carbon at temperatures above 500°C give boron trihalides. Heating a mixture of boric acid, ammonia and calcium phosphate in an electric furnace produces boron nitride.

Analysis

Elemental composition: B 17.50%, H 4.88%, O 77.62%. Boric acid may be analysed by adding calcium chloride (in excess) and sorbitol or mannitol to its solution, followed by acid-base titration using a strong base to phenolphthalein endpoint. Elemental boron may be analyzed by AA or ICP spectrophotometry.

BORIC OXIDE

[1303–86–2]
Formula: B_2O_3; MW 69.620
Synonyms: boric anhydride; boron oxide; diboron trioxide

Uses

Boric oxide is used to produce many types of glass including low-sodium, continuous filaments for glass-belted tires, and fiberglass plastics. It also is used to make ceramic coatings, porcelain enamels and glazes. Also, the compound is used as an acid catalyst in organic synthesis; and to prepare several other boron compounds.

Physical Properties

Colorless glassy solid or vitreous crystal; hexagonal crystal system; slightly bitter taste; hygroscopic; density 2.55 g/cm^3; melts at 450°C; vaporizes at 1,500°C; slightly soluble in cold water (3.3%), soluble in alcohol and boiling water (20%).

Thermochemical Properties

$\Delta H_f°$ (cry)	–304.4 kcal/mol
$\Delta H_f°$ (gas)	–201.7 kcal/mol
$\Delta Gf°$ (cry)	–285.4 kcal/mol
$\Delta Gf°$ (gas)	–198.9 kcal/mol
S° (cry)	12.9 cal/degree mol
S° (gas)	66.9 cal/degree mol
C_ρ (gas)	16.0 cal/degree mol

Preparation

Boric oxide is produced by treating borax with sulfuric acid in a fusion furnace. At temperatures above 750°C, the molten boric acid layer separates out from sodium sulfate. It then is decanted, cooled, and obtained in 96–97% purity. Boric acid above 99% purity may be obtained by fusing granular material.

Boric oxide may be prepared by heating boric acid:

$$2B(OH)_3 \xrightarrow{\text{heat}} B_2O_3 + 3H_2O$$

Reactions

Boric oxide reacts with water forming boric acid:

$$B_2O_3 + 2\ H_2O \rightarrow 2\ B(OH)_3$$

The reaction is exothermic ($\Delta H°f$ hydration is –18.15 kcal/mol B_2O_3). In the molten state, it reacts with water vapor to form gaseous metaboric acid, HBO_2.

$$B_2O_3\ (\text{glass}) + H_2O\ (g) \rightarrow 2HBO_2\ (g)$$

Reaction with hydrochloric acid or chlorine in the presence of carbon at elevated temperatures produces boron trichloride:

$$B_2O_3 + 6HCl + 3C \xrightarrow{900\text{-}1400°C} 2BCl_3 + +3CO + 3H_2$$

Similar reactions occur with many other chlorine-containing compounds, BCl_3 being produced (see Boron Trichloride reactions). Anhydrous borax and BCl_3 are obtained when it is heated with sodium chloride at 800°C:

$$7B_2O_3 + 6NaCl \xrightarrow{800°C} 2BCl_3 + 3Na_2O \bullet 2B_2O_3$$

Reaction with hydrofluoric acid produces boron trifluoride:

$$B_2O_3 + 6HF \rightarrow 2BF_3 + 3H_2O$$

When heated in an electric furnace, B_2O_3 is reduced by carbon to form boron carbide, B_4C, and reacts with calcium phosphate and ammonia to form boron nitride, BN. It reacts with sulfuric acid to produce a borate derivative, $H[B(HSO_4)_4]$. It combines with several metal oxides to form mixed oxides when heated above 1,000°C.

BORON

[7440–42–8]
Symbol: B; atomic number 5; atomic weight 10.811; a Group III A (Group 13) metalloid element; atomic volume 4.70 cc/g-atom; electron affinity 0.277 eV; electronic configuration $1s^22s^22p^1$; valence state +3; naturally occurring stable isotopes are B–10 and B–11 and their abundance 19.57% and 80.43%, respectively.

Occurrence and Uses

The element was discovered in 1808 independently by Sir Humphrey Davy and also by GayLussac and Thenard. Boron does not occur in nature in free elemental form but is found in many borate ores. The principal borate minerals are as follows:

sassolite	[10043–35–3],	$B(OH)_3$
borax (tincal)	[1303–96–4],	$Na_2O \cdot 2B_2O_3 \cdot 10H_2O$
kernite	[12045–87–3],	$Na_2O \cdot 2B_2O_3 \cdot 4H_2O$
tincalconite	[12045–88–4],	$Na_2O \cdot 2B_2O_3 \cdot 5H_2O$
colemanite	[12291–65–5],	$2CaO \cdot 3B_2O_3 \cdot 5H_2O$
ulexite	[1319–33–1],	$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$
probertite	[12229–14–0],	$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 10H_2O$
hydroboracite	[12046–12–7],	$CaO \cdot MgO \cdot 3B_2O_3 \cdot 6H_2O$
szaibelyite	[12447–04–0],	$2MgO \cdot B_2O_3 \cdot H_2O$

The major borate minerals found in the United States are tincal, kernite, brine, colemanite, ulexite and probertite. Boron also is found in many volcanic spring waters. Its abundance in the earth's crust is estimated to be 0.001%, and in seawater 4.4 mg/L

The most important application of boron is to make fibers or whiskers of single crystal or ceramic crystal. The addition of boron to metals, alloys, or other solids, imparts resistance to plastic flow, and thereby produces unusual strength in the material. Amorphous boron is used in rockets as an igniter, and in pyrotechnic flares to give green color. Many boron compounds, such as borax, boron hydrides, and boron halides, have important commercial applications (see individual compounds).

Physical Properties

Black hard solid or brownish black amorphous powder; also occurs as tetragonal, α-rhombohedral and β-rhombohedral crystal forms; density 2.34 g/cm³ (crystal), 2.45 g/cm³ (amorphos powder); hardness 9.3 Mohs; melts at 2,075°C; vaporizes at 4,000°C; electrical resistivity 3,000,000 ohm-cm at

100°C.

Thermochemical Properties

$\Delta H_f°$(gas)	135.1 kcal/mol
$G_f°$ (gas)	124.6 kcal/mol
S° (gas)	36.68 cal/degree mol
C_ρ (gas)	4.97 cal/degree mol
ΔH_{fus}	12.0 kcal/mol
ΔH_{vap}	114.8 kcal/mol

Preparation

Boron may be prepared by several methods, such as chemical reduction of boron compounds, electrolytic reduction in nonaqueous phase, or by thermal decomposition. Many boron compounds including boron oxides, borates, boron halides, borohydrides, and fluoroborates can be reduced to boron by a reactive metal or hydrogen at high temperatures:

$$B_2O_3 + 3Ca \xrightarrow{heat} 2B + 3CaO$$

The metal is obtained as a black amorphous product.

$$2BCl_3 + 3H_2 \xrightarrow{heat} 2B + 6HCl$$

High purity grade boron may be prepared by such hydrogen reduction at high temperatures using a hot filament.

Electrolytic reduction and thermal decomposition have not yet been applied in large scale commercial methods. Electrolysis of alkali or alkaline earth borates produces boron in low purity. Electrolytic reduction of fused melts of boron trioxide or potassium tetrafluroborate in potassium chloride yield boron in high purity. Also, boron tribromide or boron hydrides may be thermally dissociated by heating at elevated temperatures.

Impurities from boron may be removed by successive recrystallization or volatilization at high temperatures. Removal of certain impurities such as oxygen, nitrogen, hydrogen or carbon from boron are more difficult and involve more complex steps.

Reactions

Reactivity of boron is relatively much lower than practically all other metals in the periodic table. Also, reactivity varies with physical state and particle size of the element: the micron amorphous form is more reactive than the crystalline modifications. The element exhibits +3 oxidation state in most of its compounds.

Boron does not react with water at ambient temperatures. The powdered amorphous form, however, reacts slowly at 100°C producing boric acid. The amorphous metal reacts slowly with dilute mineral acids at ambient temperatures; the crystalline form is inert. The former, however, reacts vigorously with concentrated nitric acid. The amorphous powder ignites in oxygen at

700°C.

Boron reacts with halogens to form boron halides. The reaction is instantaneous with fluorine but occurs at elevated temperatures with other halogens. With chlorine, bromine and iodine, the formation of halides completes around 400°C, 600°C and 900°C, respectively. Again, the amorphous powder of the metal is more reactive than the crystalline form.

Boron combines with nonmetals at elevated temperatures. It readily combines with oxygen at 1,000°C forming boron oxide, B_2O_3; with hydrogen around 850°C, producing diborane and other boron hydrides; and with nitrogen at red heat forming boron nitride, BN. It also combines with carbon at high temperatures to give boron carbide B_4C. It reacts with B_2O_3 at above 1,000°C to form boron monoxide and suboxides of various compositions.

Boron combines with refractive metals forming their borides; e.g., AlB_{12}, SiB_6, CrB_2, ZrB_2, and TiB_2 . Many of these borides have important industrial applications. Most reactions occur at temperatures in the range 1,100°C to 2,000°C. The reactions are exothermic and can be rapid.

Analysis

Boron may be analyzed by various instrumental methods, such as atomic absorption (AA) and atomic emission spectrophotometry (ICP/AES). Individual isotopes at an exceedingly trace concentration in solution phase may be measured by ICP/MS. The later method should be preferred over the AA techniques.

Also, boron can be analyzed by colorimetry techniques (APHA, AWWA, and WEF. 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington DC: American Public Health Association). Boron in acidified aqueous phase reacts with curcumin to form a red-colored product, rosocyanine. Presence of calcium and magnesium at high concentrations can interfere in the test. Another colorimetric measurement involves the reaction of boron with carmine or carminic acid in concentrated sulfuric acid. The color of the solution changes from bright red to bluish red or blue, depending on boron concentration.

Toxicty

Boron in the elemental form is nontoxic. Rubbing the amorphous powder on the skin can produce irritation. Some compounds of boron, however, are poisonous (see under individual compounds).

BORON CARBIDE

[12069–32–8]
Formula: B_4C; MW 55.255

Uses

Boron carbide is used in sandblast nozzles, ceramic armor plates and abrasive powder grinding wheels. Because of its high neutron absorptivity and chemical inertness, it also is used as a shielding material in nuclear reactors.

Physical Properties

Black hard crystal; density 2.50 g/cm^3; hardness 9.3 Mohs; melts at 2,350°C; vaporizes above 3,500°C; insoluble in water and acid; inert to most chemicals at ordinary temperatures; rapidly attacked by hot alkalies.

Preparation

Boron carbide is prepared by reduction of boric oxide either with carbon or with magnesium in presence of carbon in an electric furnace at a temperature above 1,400°C. When magnesium is used, the reaction may be carried out in a graphite furnace and the magnesium byproducts are removed by treatment with acid.

BORON HYDRIDES

Boron forms a class of binary compounds known as boron hydrides or boranes with hydrogen (Numbers in parentheses are the number of hydrogen atoms in each compound.) The names, CAS Numbers, and formulas of some of these compounds are:

diborane(6)	[19287–45–7]	B_2H_6
tetraborane(10)	[18283–93–7]	B_4H_{10}
pentaborane(9)	[19624–22–7]	B_5H_9
pentaborane(11)	[19433–84–6]	B_5H_{11}
hexaborane(10)	[23777–80–2]	B_6H_{10}
nonaborane(15)	[19465–30–6]	B_9H_{15}
decaborane(14)	[17702–41–9]	$B_{10}H_{14}$

Uses

Boron hydrides are used in rocket propellants. They are ideal water-reactive fuels, liberating high energy when exposed to moist air or traces of water. Two other major applications of these compounds are in preparative chemistry, to produce borohydrides and many organoboranes, and as reducing agents. These substances find limited applications in catalysis. Diborane is a polymerization catalyst for olefins. Some minor applications of these compounds include vulcanization of rubber, corrosion inhibition, dye stripping, mothproofing, and as fluxing agents. Diborane also is used as a doping agent for ρ–type semiconductors.

Physical Properties

Diborane(6) and tetraborane(10) are colorless gases at ambient temperature and pressure. Diborane has a repulsive odor. Higher boranes up to nine boron atoms are colorless liquids. Decaborane(14) is a colorless crystalline solid. Pentaborane(11) and hexaborane(12) are unstable compounds. The densities and melting and boiling points of selected boron hydrides are shown in the following table:

boranes	densities g/mL	mp °C	bp °C
diborane(6)	1.214 g/L	–165.5	–92.4
tetraborane(10)	2.34 g/L	–121	18
pentaborane(9)	0.60	–46.6	60
pentaborane(11)	—	–123	63
hexaborane(10)	0.67	–62.3	108 (decomposes)
hexaborane(12)	—	–82	80
nonaborane(15)	2.6	—	—
decaborane(14)	0.94	99.6	213

Boron hydrides are soluble in carbon disulfide, diglyme and ethyl acetate. They react with water.

Thermochemical Properties

borane(BH_3)	$\Delta H_f°$	23.9 kcal/mol
diborane(6)	$\Delta H_f°$	8.509 kcal/mol
	$\Delta G_f°$	20.72 kcal/mol
	S°	55.47 cal/degree mol
	C_ρ	13.6 cal/degree mol
	$\Delta H_{\text{vap at bp}}$	3.41 kcal/mol
tetraborane(10)	$\Delta H_f°$	15.798 kcal/mol
	$\Delta H_{\text{vap at bp}}$	6.477 kcal/mol
pentaborane(9)	$\Delta H_f°$(l)	10.206 kcal/mol
	$\Delta H_f°$(g)	17.495 kcal/mol
	$\Delta G_f°$ (l)	41.06 kcal/mol
	$\Delta G_f°$ (g)	41.826 kcal/mol
	S° (g)	44.02 cal/degree mol
	C_ρ (g)	36.11 cal/degree mol
pentaborane(11)	$\Delta H_f°$(l)	17.495 kcal/mol
	$\Delta H_f°$(g)	24.69 kcal/mol
	$\Delta H_{\text{vap at bp}}$	7.60 kcal/mol
hexaborane(10)	$\Delta H_f°$(l)	13.456 kcal/mol
	$\Delta H_f°$(g)	22.61 kcal/mol
decaborane(14)	$\Delta H_f°$(s)	7.529 kcal/mol
	$\Delta G_f°$ (s)	51.649 kcal/mol
	S° (s)	84.37 cal/degree mol

Preparation

Diborane is prepared by the reaction of sodium borohydride with iodine or boron trifluoride or trichloride in diglyme:

$$2NaBH_4 + I_2 \xrightarrow{diglyme} B_2H_6 + 2NaI + H_2$$

$$3NaBH_4 + I_2 \xrightarrow{diglyme} 2B_2H_6 + 3NaBF_4$$

It also may be prepared by the reaction of sodium borohydride with sulfuric acid:

$$2NaBH_4 + H_2SO_4 \rightarrow B_2H_6 + 2H_2 + Na_2SO_4$$

Diborane also can be made by reduction of boron trichloride with either sodium hydride at room temperature in diglyme or with hydrogen over aluminum at 350 to 500°C :

$$2BCl_3 + 6H_2 \xrightarrow[350-500°C]{Al} B_2H_6 + 6HCl$$

Tetraborane too can be prepared from sodium borohydride. The reaction, however, is carried out at a high temperature. The product sodium octahydroborate is treated with hydrochloric acid to yield tetraborane:

$$2NaBH_4 + I_2 \xrightarrow[100^\circ C]{diglyme} NaB_2H_8 + 2H_2 + 2NaI$$

$$4NaB_2H_8 + 4HCl \rightarrow 2B_4H_{10} + 4NaCl + 8H_2$$

Higher boranes can be produced from diborane by pyrolysis.

Reactions

Boranes oxidize in air to form boron oxides. Diborane spontaneously ignites in air around 50°C. The presence of impurities can lower the ignition temperature. Tetraborane decomposes slowly at ordinary temperatures but rapidly on heating. Decaborane is very stable at ordinary temperatures. When heated at 300°C, it slowly decomposes to boron and hydrogen. All boranes decompose to their elements at elevated temperatures.

Boron hydrides react with water, hydrolyzing to boric acid and hydrogen:

$$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$$

Decaborane is soluble in cold water but hydrolyzed in hot water.

Reactions with halogens give boron halides. While reaction with chlorine can be explosive with diborane, it is slow with bromine. Diborane reacts with alkanes forming alkylboranes. Reactions with aromatics give arylboranes.

Boranes undergo a variety of reactions, such as proton abstraction, electrophilic substitution, fragmentation and adduct formation. Some of these reactions are highlighted below with selective examples.

Lewis bases such as ammonia cleave boron hydrides unsymmetrically into BH_2^- and $B_{(n-1)}H^-_{(m-1)}$ fragments:

$$B_4H_{10} + 2NH_3 \rightarrow [H_2B(NH_3)_2]^+ [B_3H_8]^-$$

$$B_2H_6 + 2(CH_3)_2O \rightarrow 2(CH_3)_2O \cdot BH_3$$

Alkali metal hydrides react with diborane to form metal borohydrides:

$$B_2H_6 + 2NaH \rightarrow 2NaBH_4$$

Decaborane reacts with pyridine, triphenyl phosphine, triethylamine, acetonitrile and other weak bases forming an adduct with liberation of hydrogen:

$$C_{10}H_{14} + 2C_5H_5N \rightarrow C_{10}H_{12} \cdot 2C_5H_5N + H_2$$

Deuterium exchange studies on decaborane and other boranes indicate acidic character of bridge hydrogens. They react with bases undergoing proton abstraction reactions:

$$B_{10}H_{14} + KOH \rightarrow K[B_{10}H_{13}] + H_2O$$

$$B_4H_{10} + NaOH \rightarrow Na[B_4H_9] + H_2$$

Alkali metal hydrides too abstract protons from boranes. While water is produced with basic hydroxides, hydrogen is liberated with hydrides. Except diborane, all other boron hydrides undergo similar reactions, liberating hydrogen:

$$B_4H_{10} + NaH \rightarrow Na[B_4H_9] + H_2$$

Many boron hydrides, especially the higher boranes, undergo halogenation, alkylation and other substitution reactions when treated with electrophiles. Such reactions are catalyzed by acids, yielding a variety of stable products.

Diborane and other lower boranes pyrolyze when treated with borohydrides and other metallo borane derivatives at elevated temperatures undergoing polyhedral expansion:

$$2NaBH_4 + 5B_2H_6 \xrightarrow[diglyme]{heat} Na_2B_{12}H_{12} + 13H_2$$

Similarly, $[B_3H_8]^-$ pyrolyze at 230°C forming $[B_9H_9]_2^-$, $[B_{10}H_{10}]_2^-$, and

$[B_{12}H_{12}]_2^-$ borane anions.

Diborane forms stable adducts with many electron donors:

$$B_2H_6 + 2N(C_2H_5)_3 \rightarrow 2(C_2H_5)_3N \cdot BH_3$$

$$B_2H_6 + (CH_3)_2S \rightarrow 2(CH_3)_2S \cdot BH_3$$

Boranes react with carbon monoxide forming more than one adduct:

$$B_5H_{11} + 2CO \rightarrow BH_3(CO) + B_4H_8(CO)$$

Analysis

Diborane in air may be analyzed by passing air through a PTFE filter and oxidizer-impregnated charcoal. It is oxidized to boron and desorbed with 3% H_2O_2. Boron is measured by plasma emission spectrometry or ICP emission spectrometry (NIOSH. 1984. *Manual of Analytical Methods*, 3rd ed. Cincinnati, OH: National Institute for Occupational Safety and Health). Boron hydrides can be analyzed by FTIR techniques.

Hazard

Diborane ignites spontaneously in moist air. Its flash point is in the range 38 to 52°C, and it forms explosive mixtures with air over a wide range: the lower and upper flammable limits are 0.8 to 88% by volume in air, respectively. Diborane explodes in contact with chlorine and ignites with fuming nitric acid. All boron hydrides react violently with halogenated extinguishing agents.

Exposure to boron hydride gases or vapors can cause irritation of respiratory passages, acute poisoning of lungs, and pulmonary edema. Ingestion of decaborane can cause spasm, tremor, and convulsion. For decaborane, LD_{50} oral (mouse) is 41 mg/kg; LD_{50} skin (mouse) is 740 mg/kg; and LC_{50} inhalation (40 hr.) (mouse) is 12 ppm.

BORON NITRIDE

[10043–11–5]
Formula: BN; MW 24.818

Uses

Boron nitride is extremely hard and very resistant to both chemical attack and thermal shock. Because of these properties, BN has many industrial applications. Cubic crystals of boron nitride under the name Borazon are incorporated into abrasive wheels for grinding nickel and ferrous alloys. They also are used to make cutting tools for other hard alloys. The hexagonal crystal form is applied to construct refractory materials, such as vessels, crucibles, rectifying tubes, transistor mounting wafers, specialized equipment, and heatshields for plasma that need high temperature electrical and thermal insulation. Boron nitride is used to make heat resistant, high strength fibers.

Physical Properties

White powder, hexagonal graphite-like form or cubic crystal; cubic form similar to diamond in its crystal structure, and reverts to graphite form when heated above 1,700°C; density 2.18 g/cm^3; melts at 2,975°C (under nitrogen pressure); sublimes at 2,500°C at atmospheric pressure; insoluble in water and acid; attacked by hot alkalies and fused alkali carbonates; not wetted by most molten metals or glasses.

Thermochemical Properties

$\Delta H_f°$(cry)	–60.80	kcal/mol
$\Delta G_f°$ (cry)	–54.59	kcal/mol
$S°$ (cry)	3.54	cal/degree mol
C_ρ (cry)	4.71	cal/degree mol
$\Delta H_f°$(g)	154.8	kcal/mol
$\Delta G_f°$ (g)	146.9	kcal/mol
$S°$ (g)	50.74	cal/degree mol
C_ρ (g)	7.05	cal/degree mol

Preparation

Boron nitride is prepared by heating boric oxide with ammonia:

$$B_2O_3 + 2NH_3 \xrightarrow{heat} 2BN + 3H_2O$$

Alternatively, the compound can be prepared by heating boric oxide or boric acid with ammonium chloride or an alkali metal cyanide. Purified product can be obtained by high temperature reaction of boron halide with ammonia:

$$BCl_3 + NH_3 \xrightarrow{heat} BN + 3HCl$$

Boron nitride can also be made from the elements by heating boron and nitrogen at red heat.

BORON PHOSPHATE

[13308–51–5]
Formula: BPO_4; MW 105.784
Synonym: borophosphoric acid

Uses

Boron phosphate is used as an acid catalyst for dehydration of alcohols to olefins; isomemization of olefins; nitration of aromatic hydrocarbons; polymerization of aldehydes and other synthetic reactions. It also is used as a flux in silica–based porcelain and ceramics; special glasses; and acid cleaners.

Physical Properties

White infusible solid; density 1.873 g/mL; sublimates slowly above 1,450°C; soluble in water, decomposes to phosphoric acid and boric acid; pH of 1% solution is ~2.0.

Preparation

Boron phosphate is prepared by heating an equimolar mixture of boric acid and phosphoric acid at 1,000 to 1,200°C:

$$H_3BO_3 + H_3PO_4 \xrightarrow{1000^\circ C} BPO_4 + 3H_2O$$

Various preparative methods are adopted at nonstoichiometric formulations, incomplete dehydration or using oxide additives to obtain boron phosphate of varying purity for its catalytic applications. The compound also forms hydrates (tri– tetra–, penta–, and hexahydrates) which readily decompose in water to phosphoric acid and boric acid.

Analysis

Elemental composition: B 10.22% ; P 29.28% ; O 60.50%. A small, measured amount is dissolved in water and the solution is analyzed for orthophosphate by ion chromatography, or by molybdenum-blue colorimetric method (APHA, AWWA and WEF. 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th. ed. Washington, DC: American Public Health Association). Borate may be analyzed by ion chromatography, and elemental boron by AA or ICP spectrophotometry, following appropriate dilution of the solution (see Boron).

BORON TRICHLORIDE

[10294–34–5]
Formula: BCl_3; MW 117.17; planar geometry; Cl–B–Cl bond angle 120°C; a Lewis acid, an electron deficient compound.
Synonym: boron chloride

Uses

Boron trichloride is used as a catalyst in polymerization reactions. Other applications include refining of alloys; soldering flux; and as a component in certain fire extinguishers. It also is used to prepare boron fibers and other boron compounds including diborane, sodium borohydride and several adducts.

Physical Properties

Colorless gas (or fuming liquid); density 5.14 g/L; liquefies at 12.6°C; solidifies at –107°C; vapor pressure 470 torr at 0°C; critical temperature 182°C; critical pressure 38.2 atm; critical molar volume 239 cm^3/mol; reacts with water and ethanol; soluble in carbon tetrachloride.

Thermochemical Properties

$\Delta H_f°$ (l)	–102.1	kcal/mol
$\Delta H_f°$(g)	–96.5	kcal/mol
$\Delta G_f°$ (l)	–92	kcal/mol
$\Delta G_f°$ (g)	–92.9	kcal/mol
S° (l)	49.3	cal/degree mol
S° (g)	69.3	cal/degree mol
C_ρ (l)	25.5	cal/degree mol
C_ρ (g)	15.0	cal/degree mol
ΔH_{vap}	5.68	kcal/mol
ΔH_{fus}	0.50	kcal/mol

Preparation

Boron trichloride can be prepared by high temperature chlorination of boron trioxide, boric acid, metal borates or other boron compounds. Chlorine, hydrogen chloride, phosgene, silicon tetrachloride, metal chlorides, carbon tetrachloride, sulfuryl chloride and phosphorus tri- and pentachlorides are some of the common chlorinating agents. The reaction is carried out at temperatures varying between 400° to 1,400°C, depending on the reactants used. In commercial processes, carbon is generally used to reduce boron oxide during its chlorination. Some of the preparative reactions are outlined below:

$$B_2O_3 + 2PCl_3 \xrightarrow{800^\circ C} 2BCl_3 + P_2O_3$$

$$2B_2O_3 + 3CCl_4 \xrightarrow{800^\circ C} 4BCl_3 + 3CO_2$$

$$B_2O_3 + 3C + 3Cl_2 \xrightarrow{600^\circ C} 2BCl_3 + 3CO$$

$$2B(OH)_3 + 3C + 3Cl_2 \xrightarrow{>500^\circ C} 2BCl_3 + 3CO + 3H_2O$$

$$B_2O_3 + 3C + 6HCl \xrightarrow{>900^\circ C} 2BCl_3 + 3CO + 3H_2$$

$$Na_2B_4O_7 + 7C + 14HCl \xrightarrow{>900^\circ C} 4BCl_3 + 2NaCl + 7CO + 7H_2$$

$$2KBF_4 + 3MgCl_2 \xrightarrow{500^\circ - 1000^0 C} 2BCl_3 + 2KF + 3MgF_2$$

Boron trichloride may also be obtained by high temperature chlorination of boron:

$$2B + 3Cl_2 \xrightarrow{>500^\circ C} 2BCl_3$$

$$B + 3AgCl \xrightarrow[vacuum]{600^\circ C} BCl_3 + 3Ag$$

In the laboratory, boron trichloride may be made at ordinary temperatures by the reaction of boron trifluoride with aluminum chloride:

$$BF_3 + AlCl_3 \rightarrow BCl_3 + AlF_3$$

Reactions

Boron trichloride reacts with water forming boric acid and hydrogen chloride:

$$BCl_3 + 3H_2O \rightarrow B(OH)_3 + 3HCl$$

Similar reaction occurs with hydrogen sulfide:

$$BCl_3 + 3H_2S \rightarrow B(SH)_3 + 3HCl$$

Reaction with lower alcohols produces alkyl derivatives of boric acid with hydrogen chloride:

$$BCl_3 + 3CH_3OH \rightarrow B(OCH_3)_3 + 3HCl$$

However, tertiary alcohol gives alkyl chloride and no HCl is produced:

$$BCl_3 + 3(CH_3)_3COH \rightarrow B(OH)_3 + 3(CH_3)_3CCl$$

At low temperatures, donor-acceptor complexes are obtained with Lewis bases; for example, with ammonia and phosphine, the adducts are boron trichloride ammonia and boron trichloride phosphine, respectively:

$$BCl_3 + NH_3 \rightarrow BCl_3 \cdot NH_3$$
$$BCl_3 + PH_3 \rightarrow BCl_3 \cdot PH_3$$

Sodium, potassium, magnesium and other alkali and alkaline earth metals at elevated temperatures reduce boron trichloride to elemental boron:

$$2BCl_3 + 3Mg \xrightarrow{heat} 2B + 3MgCl_2$$

Hydrogen reduces the compound to diborane when heated at 350 to 500°C over aluminum:

$$2BCl_3 + 6H_2 \xrightarrow[Al]{350\text{–}500^\circ C} B_2H_6 + 6HCl$$

but at higher temperatures over 1,000°C, hydrogen decomposes boron trichloride forming boron fibers and HCl:

$$2BCl_3 + 3H_2 \xrightarrow{>1000^\circ C} 2B + 6HCl$$

Alkali metal hydrides reduce boron trichloride to diborane at ordinary temperatures:

$$2BCl_3 + 6NaH \xrightarrow[diglyme]{25^\circ C} B_2H_6 + 6NaCl$$

Boron trichloride undergoes several exchange reactions with diborane, other boron halides and trialkyl-, triaryl-, or triaryloxy boranes (Lower, L.D. 1978. Boron compounds (halides). In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd. ed. pp 129–135. New York: Wiley Interscience). The reactions occur at ambient or lower temperatures:

$$BCl_3 + B_2H_6 \rightarrow BHCl_2 + B_2H_5Cl$$

$$BCl_3 + BBr_3 \xrightarrow{<30^\circ C} BCl_2Br + BClBr_2$$

$$BCl_3 + 2B(C_2H_5)_3 \rightarrow 3(C_2H_5)_2BCl$$

Analysis

Elemental composition: B 9.23%, Cl 90.77%. The compound is slowly hydrolyzed (reaction may be vigorous to violent) and the solution is analyzed for boron by AA or ICP spectroscopy (see Boron), Also, other metals that may be present as impurities can be measured. The product, HCl in the aqueous solution, resulting from hydrolysis, may be analyzed by chloride ion-selective electrode or ion chromatography (at trace concentrations) with appropriate dilution.

Toxicity

Boron trichloride is highly toxic, causing severe irritation of eyes, skin and mucous membranes.

LC_{LO} inhalation (rat): 20 ppm/7hr.

BORON TRIFLUORIDE

[7637–07–2]
Formula: BF_3; MW 67.82; planar sp^2 hybridization; F–B–F angle 120°; an electron deficient compound (Lewis acid)
Synonym: boron fluoride

Uses

Boron trifluoride is used as a catalyst in esterification, polymerization and many other organic synthetic reactions. Other applications of this compound include measuring weak neutrons in ionization chambers and in devices to monitor radiation levels in the earth's atmosphere; and measuring depth for oil drilling. It also is used in fumigation; as a flux for soldering magnesium; to prepare diborane; and in gas brazing.

Physical Properties

Colorless gas; pungent suffocating odor; density 2.975 g/L; fumes in moist air; liquefies at –101°C; solidifies at –126.8°; vapor pressure at –128°C is 57.8 torr; critical temperature –12.2°C; critical pressure 49.15 atm; critical volume 115 cm^3/mol; soluble in water with partial hydrolysis; solubility in water at 0°C 332 g/100g; also soluble in benzene, toluene, hexane, chloroform and methylene chloride; soluble in anhydrous concentrated sulfuric acid.

Thermochemical Properties

$\Delta H_f°$	–271.5 kcal/mol
$\Delta G_f°$	–267.5 kcal/mol
S°	60.8 cal/degree mol
ΔH_{vap}	4.62 kcal/mol
ΔH_{fus}	1.004 kcal/mol

Preparation

Boron trifluoride is prepared by treating borax with hydrofluoric acid; or boric acid with ammonium bifluoride. The complex intermediate product is then treated with cold fuming sulfuric acid.

Reaction

Boron trifluoride is partially hydrolyzed when dissolved in water. The hydrolysis products are boric acid and fluoroboric acid:

$$4BF_3 + 3H_2O \rightarrow B(OH)_3 + 3HBF_4$$

The tetrafluoroborate, BF_4^- anion can form stable salts with pyridinium, tetraalkylammonium and other countercations.

Boron trifluoride is reduced to elemental boron when heated with alkali metals:

$$BF_3 + 3Na \xrightarrow{heat} B + 3NaF$$

The reaction is highly exothermic resulting in incandescence. Similar reduction occurs with alkaline earth metals except magnesium.

Being an electron deficient compound, boron trifluoride forms complexes with Lewis bases and compounds that have unshared pair(s) of electrons. With ammonia, it forms boron trifluoride ammonia. Similar coordination compounds are formed with monoethylamine, $BF_3–NH_2C_2H_5$; diethyl ether, $CH_3CH_2O(BF_3)CH_2CH_3$; and methanol, $BF_3–OHCH_3$. It forms a solid complex $HNO_3–2BF_3$ with concentrated nitric acid.

BORON TRIFLUORIDE ETHERATE

[109–63–7]
Formula: $(CH_3CH_2O)_2O \cdot BF_3$; MW 141.94;
Synonyms: boron fluoride etherate; boron fluoride ethyl ether

Uses

Boron trifluoride etherate is used as a catalyst in many organic reactions; namely, alkylation, polymerization and condensation reactions.

Physical Properties

Fuming liquid; stable at ambient temperatures but hydrolyzed on exposure to moist air; density 1.125 g/mL; refractive index 1.348; solidifies at –60.4°C; boils at 125.7°C; flash point (open cup) 147°F (68.8°C); decomposes in water.

Preparation

Boron trifluoride etherate is prepared by the reaction of vapors of boron trifluoride with that of anhydrous diethyl ether:

$$BF_3\ (g) + (C_2H_5)_2O\ (g) \rightarrow (C_2H_5)_2O \cdot BF_3$$

Toxicity

The compound is highly toxic by inhalation. Skin contact causes burns.

BROMIC ACID

[7789–31–3]
Formula: $HBrO_3$; MW 128.91

Uses

Bromic acid is used as an oxidizing agent; and also as intermediate in the preparation of dyes and pharmaceuticals .

Physical Properties

Unstable compound; stable only in dilute aqueous solutions; solution turns yellow on standing; decomposes when heated to 100°C.

Preparation

Bromic acid is prepared by adding sulfuric acid to barium bromate.

$$Ba(BrO_3)_2 + H_2SO_4 \rightarrow 2HBrO_3 + BaSO_4$$

The product is distilled and absorbed in water. A 50% solution may be obtained by slow evaporation of the dilute solution in vacuum at –12°C.

Toxicity

Contact with skin and eyes can cause severe irritation.

BROMINE

[7726–95–6]
Symbol Br; atomic number 35; atomic weight 79.904; a halogen group element; electron affinity 3.36359 eV; electronegativity 2.8; electron configuration [Ar] $3d^{10}4s^24p^5$; most stable valence states –1 and +5, less stable valence states +1 and +3; a diatomic molecule (Br_2) in liquid and vapor states over a wide range of temperature; two stable isotopes, Br–79 (50.57%) and Br–81 (49.43%).

Occurrence and Uses

Bromine occurs in nature as bromide in many natural brine wells and salt deposits. It also is found in seawater at a concentration of 85 mg/L. The element was discovered by A. J. Balard and C. Lowig, independently in 1826. Bromine is used in bleaching fibers and as a disinfectant for water purification. Other applications are in organic synthesis as an oxidizing or brominating agent; in the manufacture of ethylene dibromide, methyl bromide and other bromo compounds for dyes and pharmaceutical uses; as a fire retardant for plastics; and in chemical analysis. Ethylene dibromide is used in antiknock fluids in motor fuels. Over 80% of the bromine produced is consumed in the manufacture of this compound.

Physical Properties

Dark reddish-brown liquid; the only nonmetallic element that is a liquid at ambient temperatures; strong disagreeable odor; volatilizes; density 3.12 g/mL at 20°C; vapor density 7.59 g/L; refractive index 1.6475; boils at 58.8°C; solidifies at –7.2°C; vapor pressure 64 torr at 0°C and 185 torr at 22°C; critical temperature 315°C; critical pressure 102 atm; critical volume 127 cm^3/mol; surface tension 39.8 dynes/cm at 25°C; electrical resistivity 6.5 x 10^{10} ohm–cm at 25°C; sparingly soluble in water (2.31 g/100g at 0°C and 3.35 g/100g at 25°C); soluble in common organic solvents.

Thermochemical Properties

$\Delta H_f°$ (Br_2)	0.0 kcal/mol
$\Delta H_f°$ (g)	26.74 kcal/mol
$\Delta G_f°$ (g)	19.69 kcal/mol
S° (g)	41.82 cal/degree mol
C_ρ (g)	4.97 cal/degree mol
C_ρ (l)	8.56 cal/degree mol

Production

Bromine is obtained from natural brines, salt beds and seawater. The bromide salts extracted from these sources are oxidized by chlorine to yield bromine:

$$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2$$

The bromine vapors are swept out into current of air or stream from the reaction chamber and trapped in an alkaline or reducing solution. Chlorine is removed over a stripping column. Bromine is purified in a fractionating column.

Reactions

Most reactions of bromine are similar to other halogens. Its reactivity falls between chlorine and iodine. It readily attacks a number of metals including alkali and alkaline earth metals, palladium, platinum, aluminum, copper, antimony and tin, forming their bromides. These reactions can be vigorous to violent. It oxidizes a number of substances, including metal carbides, carbonyls, hydrides, and organic substances. It combines with hydrogen to form hydrogen bromide. Organic compounds, such as olefins, aromatics and alkanes undergo addition or substitution reactions yielding bromoderivatives. While the addition reaction with ethylene produces ethylene dibromide, bromination of benzene in the presence of iron as catalyst produces a substitution product, bromobenzene. Reaction with aqueous acetone and sodium chlorate at 40°C forms bromoacetone. Substitution reactions with alkanes yield alkyl bromides. Bromine combines with fluorine at room temperature forming bromine trifluoride, BrF_3. The reaction produces luminous flame. Diluted with nitrogen, bromine vapor and fluorine react on heating at 200°C to form bromine trifluoride, BrF_3, or the pentafluoride, BrF_5. Reaction with iodine produces iodine monobromide, IBr.

Bromine reacts with phosphorus to form phosphorus tribromide, PBr_3 or phosphorus pentabromide, PBr_5. The pentabromide forms in the presence of excess bromine. Bromine oxidizes hydrogen sulfide to sulfur:

$$Br_2 + H_2S \rightarrow S + 2HBr$$

Bromine liberates iodine from iodide solution:

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

Combination reactions occur with several nonmetals. With sulfur, it forms sulfur monobromide, S_2Br_2. With the addition of selenium, products are selenium monobromide, Se_2Br_2, and selenium tetrabromide, $SeBr_4$. It yields unstable tellurium monobromide, Te_2Br_2, and a stable tetrabromide, $TeBr_4$,with tellurium.

In aqueous solution, bromine hydrolyzes slightly, forming unstable hypobromous acid, HOBr, which decomposes to hydrobromic acid and oxygen, causing the bleaching action of bromine water. The decomposition is accelerated by light.

$$Br_2 + H_2O \rightarrow HOBr + HBr$$

$$HOBr \xrightarrow{light} HBr + O$$

Bromine water oxidizes aldose to lactones which hydrolyze to alfonic acids.

Bromine combines with rubidium and cesium bromides forming solid polybromo complexes that can be crystallized from aqueous solutions. The complexes are soluble in liquid bromine.

Bromine reacts with cold nitric oxide forming nitrosyl bromide, NOBr, and nitrosyl tribromide, $NOBr_3$.

Hazard

Most reactions of bromine are highly exothermic which can cause incandescence or sudden increase in pressure and rupture of reaction flasks. There are a number of cases of explosions documented in the literature. (NFPA. 1986. *Fire Protection Guide on Hazardous Materials*, 9th ed. Quincy, MA: National Fire Protection Association) Reactions of liquid bromine with most metals (or any metal in finely divided state), metal hydrides, carbonyls and nitrides can be explosive. Many oxides and halides of nonmetals, such as nitrogen triiodide or phosphorus trioxide, react explosively or burst into flame in contact with liquid bromine.

Bromine is moderately toxic by all routes of exposure. It is an irritant to the eye and respiratory tract. Inhalation can cause dizziness, headache, coughing and lacrimation. A short exposure to 1,000 ppm for 15 minutes can be fatal to humans. (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd edition. New York: John Wiley & Sons). Ingestion produces nausea, abdominal pain and diarrhea. The liquid is corrosive to skin.

BROMINE PENTAFLUORIDE

[7789–30–2]
Formula: BrF_5; MW 174.896

Uses

Bromine pentafluoride is used as an oxidizer in liquid rocket propellants; and as a fluorinating agent in the processing of uranium.

Physical Properties

Colorless to pale yellow liquid; fumes in air; density 2.466 g/mL at 25°C; boils at 40.8°C; decomposes above 460°C; solidifies at –60.5°C; reacts violently with water.

Thermochemical Properties

$\Delta H_f°$ (l)	–109.6 kcal/mol
$\Delta H_f°$ (g)	–102.5 kcal/mol
$\Delta G_f°$ (l)	–84.1 kcal/mol
S° (l)	53.8 cal/degree mol
S° (g)	76.5 cal/degree mol
C_ρ (g)	23.8 cal/degree mol
ΔH_{fus}	1.355 kcal/mol
ΔH_{vap} (at bp)	7.31 kcal/mol

Preparation

Bromine pentafluoride is prepared by fluorination of bromine at 200°C. The reaction is carried out in an iron or copper vessel. The halogens are diluted in nitrogen.

Hazard

Bromine pentafluoride is a highly reactive compound combining explosively or with ignition with most elements and their compounds. Spontaneous explosion or flaming can occur when mixed with water, organic compounds, metal powder, metal halides, metal oxides, metal sulfides and chlorine (upon warming) (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley).

The liquid is dangerously corrosive to skin. The vapors are highly irritating to eyes, skin and mucous membranes.

BROMINE TRIFLUORIDE

[7787–71–5]
Formula: BrF_3; MW 136.90

Uses

Bromine trifluoride is used as a fluorinating agent; and an electrolytic solvent for fluoride.

Physical Properties

Colorless liquid; hygroscopic; density 2.803 g/mL; boils at 125.8°C; solidifies at 8.8°C; vapor pressure 8 torr at 21°C; decomposes violently in water.

Thermochemical Properties

$\Delta H_f°$ (l)	–71.9 kcal/mol
$\Delta H_f°$ (g)	–61.1 kcal/mol
$\Delta G_f°$ (l)	–57.5 kcal/mol
$\Delta G_f°$ (g)	–54.8 kcal/mol
S° (l)	42.6 cal/degree mol
S° (g)	69.9 cal/degree mol
C_ρ (l)	29.78 cal/degree mol
C_ρ (g)	15.92 cal/degree mol
ΔH_{vap}	11.37 kcal/mol

Preparation

Bromine trifluoride may be prepared by fluorination of bromine at 80°C. The halogen mixtures may be diluted in nitrogen or an inert gas.

Hazard

Bromine trifluoride is a highly reactive compound. It ignites or explodes in contact with a wide array of substances including water, finely divided metals, metal oxides and salts and organics. See Bromine Pentafluoride.

Skin contact with liquid can burn tissues. Vapors can damage eyes, lungs and respiratory tract.

CADMIUM

[7440–43–9]
Symbol Cd; atomic number 48; atomic weight 112.41; a Group IIB (Group 12) metallic element; ionization potential 8.994eV; electron configuration $[Kr]4d^{10}5s^2$; valence state +2; standard electrode potential, E° –0.40V. The isotopes and their natural relative abundance are:

Cd–106	1.25%
Cd–108	0.89%
Cd–110	12.49%
Cd–111	12.80%
Cd–112	24.13%

Cd–113	12.22%
Cd–114	28.73%
Cd–116	7.49%

Occurrence and Uses

Cadmium was discovered by F. Stromeyer in 1817. In nature, it is mostly found in zinc deposits. The mineral, greenocktite (CdS) is found associated with the zinc ore, sphalerite (ZnS). Similarly zinc carbonate contains otavite ($CdCO_3$) in small amounts. Its abundance in the earth's crust is estimated to be 0.15 mg/kg and in sea water 0.11 µg/L.

Cadmium is used for electroplating to impart a protective coating on iron and steel. It provides resistance against caustic alkalis. Another major application is in the nickel–cadmium storage battery where it enhances long service life and a wide operating range. Cadmium alloys find wide applications in bearing metals, solders, fusible metals, electrical conductors, power transmission wires, and jewelry. Cadmium electrodes are used in photoelectric cells, cadmium vapor lamps and selenium rectifiers. Graphite impregnated with cadmium is used in electrical controller switches, oil–less bearings and busing lines. Cadmium rods are used in nuclear reactors to absorb low–energy neutrons. Many cadmium compounds have a number of commercial applications.

Physical Properties

Bluish–white lustrous soft metal; closed–packed hexagonal system; density 8.69 g/cm^3; Brinnel hardness 21; melts at 321.1°C; vaporizes at 767°C; vapor pressure 5 torr at 455°C; electrical resistivity 6.8 microhm-cm at 0°C; insoluble in water.

Thermochemical Properties

$\Delta H_f°$ (g)	26.72 kcal/mol
S° (s)	12.38 cal/degree mol
S° (g)	40.08 cal/degree mol
C_ρ (s)	6.21 cal/degree mol
C_ρ (g)	4.97 cal/degree mol
ΔH_{fus}	1.479 kcal/mol
ΔH_{vap}	23.87 kcal/mol
Co–eff. linear expansion (at 25°C)	$29.8x10^{-6}$/°C

Production

Cadmium is obtained as a byproduct in zinc recovery processes. The metal volatilizes during roasting of zinc concentrates and collected as dust or fume in bag houses or electrostatic precipitators. The dusts are mixed with coal (or coke) and zinc chloride and calcined. The cadmium chloride formed volatilizes upon calcination and thus separates out from zinc. The chloride then is treated with sulfuric acid in the presence of an oxidizing agent. This converts lead, present as impurity in cadmium ore, to lead sulfate which precipitates out. Cadmium is finally separated from copper by the addition of zinc dust and fractional precipitation.

Cadmium also may be recovered from zinc ores and separated from other metals present as impurities by fractional distillation. Alternatively, the cadmium dust obtained from the roasting of zinc ore is mixed with sulfuric acid. Zinc dust is added in small quantities to precipitate out copper and other impurities. The metal impurities are removed by filtration. An excess amount of zinc dust is added to the solution. A spongy cadmium–rich precipitate is formed which may be oxidized and dissolved in dilute sulfuric acid. Cadmium sulfate solution is then electrolyzed using aluminum cathodes and lead anodes. The metal is deposited at the cathode, stripped out regularly, washed and melted in an iron retort in the presence of caustic soda, and drawn into desired shapes. More than half of the world's production of cadmium is obtained by elecrolytic processes.

Reactions

The metal is oxidized slowly in moist air at ordinary temperatures, forming a protective coating of cadmium oxide, CdO. At ordinary temperatures, it is not oxidized in dry air. However, upon heating it readily forms cadmium oxide.

The element combines with many nonmetals upon heating, forming its binary salts. It combines with halogens when heated, forming the corresponding halides. Heating with phosphorus, sulfur, and tellurium produces phosphide, Cd_3P_2; sulfide, CdS; and telluride, CdTe salts, respectively.

The metal is attacked by mineral acids. It reacts with warm dilute hydrochloric acid or sulfuric acid liberating hydrogen:

$$Cd + 2\,HCl \rightarrow CdCl_2 + H_2$$

Reactions with hot dilute nitric acid give various oxides of nitrogen and hydrogen:

$$2Cd + 2HNO_3 \rightarrow 2CdO + 2NO_2 + H_2$$

$$4Cd + 2HNO_3 \rightarrow 4CdO + 2NO + H_2$$

$$Cd + 2HNO_3 \rightarrow CdO + N_2O_5 + H_2$$

Aqueous solutions of alkali hydroxides do not attack cadmium. Cadmium replaces elements that are less electropositive in the activity series from their salt solutions. The standard electrode potential:

$$Cd^{2+} + 2e^{-} \rightarrow Cd \qquad E^{\circ} = -0.4025V$$

Thus, cadmium can displace a number of metals that are less active, such as copper, lead, silver, mercury, tin, and antimony from their aqueous salt solutions:

$$Cu^{2+}(aq) + Cd(s) \rightarrow Cd^{2+}(aq) + Cu(s)$$

Analysis

Cadmium in acidified aqueous solution may be analyzed at trace levels by various instrumental techniques such as flame and furnace atomic absorption, and ICP emission spectrophotometry. Cadmium in solid matrices is extracted into aqueous phase by digestion with nitric acid prior to analysis. A much lower detection level may be obtained by ICP–mass spectrometry. Other instrumental techniques to analyze this metal include neutron activation analysis and anodic stripping voltammetry. Cadmium also may be measured in aqueous matrices by colorimetry. Cadmium ions react with dithizone to form a pink-red color that can be extracted with chloroform. The absorbance of the solution is measured by a spectrophotometer and the concentration is determined from a standard calibration curve (APHA, AWWA and WEF. 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington, DC: American Public Health Association). The metal in the solid phase may be determined nondestructively by x-ray fluorescence or diffraction techniques.

Toxicity

Cadmium is highly toxic to humans by both inhalation and ingestion. The acute poisoning effects are nausea, vomiting, diarrhea, headache, abdominal pain, muscular ache, salivation, and shock. In addition, inhalation of its dusts or fumes can cause cough, respiratory distress, congestion of lungs, and bronchopneumonia (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons). The LD_{50} (oral) in rat is in the range 250 mg/kg. The metal accumulates in the liver and kidneys, damaging these organs when exposure is chronic. Biological half–life in humans is estimated at 20–30 years (Manahan, S. 1989. *Toxicologial Chemistry*. Chelsea, MI: Lewis Publishers). Cadmium is listed by the US EPA as one of the priority pollutant metals.

CADMIUM ACETATE

[543–90–8]
Formula: $Cd(C_2H_3O_2)_2$; MW 230.50; also, a dihydrate of the compound $Cd(C_2H_3O_2)_2 \cdot 2H_2O$ [5743–04–4] is known.

Uses

Cadmium acetate is used for glazing ceramics and pottery; in electroplating baths; in dyeing and printing textiles; and as an analytical reagent for sulfur, selenium, and tellurium.

Physical Properties

The anhydrous salt occurs as a colorless crystal while the dihydrate is a white crystalline solid; faint odor of acetic acid; density 2.34 g/cm^3 (dihydrate

2.01 g/cm^3); melts at 255°C; dihydrate decomposes at 130°C; soluble in water and ethanol; pH of 0.2M aqueous solution 7.10.

Preparation

Cadmium acetate is prepared by treating cadmium oxide with acetic acid:

$$CdO + 2CH_3COOH \rightarrow (CH_3COO)_2Cd + H_2O$$

Also, the compound may be prepared by treating cadmium nitrate with acetic anhydride.

Analysis

Elemental composition: Cd 48.77%, C 20.84%, H 2.62%, O 27.77%. Aqueous solution may be analyzed for cadmium (see Cadmium) and the concentration of cadmium acetate can be estimated stoichiometrically.

CADMIUM BROMIDE

[7789–42–6]
Formula: $CdBr_2$; MW 272.22; also forms a tetrahydrate, $CdBr_2 \cdot 4H_2O$ [13464–92–1]

Uses

Cadmium bromide is used in lithography, engraving, and in the manufacture of photographic film.

Physical Properties

White to yellowish powder or flakes; hexagonal crystal system; hygroscopic; density 5.192g/cm^3; melts at 568°C; vaporizes at 844°C; soluble in water, alcohol, ether, acetone, and liquid ammonia.

Thermochemical Properties

$\Delta H_f°$	–75.53 kcal/mol
$\Delta G_f°$	–70.75 kcal/mol
S°	32.79 cal/degree mol
C_ρ	18.33 cal/degree mol
ΔH_{fus}	4.995 kcal/mol
ΔH_{vap}	27.49 kcal/mol

Preparation

Cadmium bromide is prepared by heating cadmium with bromine vapor. Also the compound can be prepared by the treatment of dry cadmium acetate with glacial acetic acid and acetyl bromide. Alternatively, it may be obtained by dissolving cadmium or cadmium oxide in hydrobromic acid and evaporating the solution to dryness under helium in an inert atmosphere.

Analysis

Elemental composition: Cd 41.29%, Br 58.71%. The salt is dissolved in water and the aqueous solution is analyzed by AA or ICP spectrophotometry. The bromide anion in the aqueous solution may be measured by ion chromatography. Appropriate dilution may be needed for analysis

CADMIUM CYANIDE

[542–83–6]
Formula: $Cd(CN)_2$; MW 164.45

Uses

Cadmium cyanide is used as an electrolyte for electrodeposition of thin metallic cadmium coatings on metals to protect against corrosion.

Physical Properties

White, cubic crystal or powder; density 2.226 g/cm^3; sparingly soluble in water 1.71g/100mL (at 15°C); slightly soluble in alcohol; dissolves in alkali, metal cyanides, and hydroxides.

Preparation

Cadmium cyanide may be prepared by treating a concentrated aqueous solution of cadmium chloride or cadmium nitrate with potassium cyanide or sodium cyanide. The white precipitate obtained is filtered, washed and dried.

$$CdCl_2 + 2KCN \rightarrow Cd(CN)_2 + 2KCl$$

Reactions

Cadmium cyanide reacts with dilute mineral acids, evolving hydrogen cyanide:

$$Cd(CN)_2 + 2HCl \rightarrow CdCl_2 + 2HCN$$

With organic acids, the reaction is slow. Reactions with sodium cyanide or potassium cyanide in aqueous solutions yield complex metal cyanide. For example, with potassium cyanide, the product is potassium tetracyanocadmate:

$$Cd(CN)_2 + 2KCN \rightarrow K_2Cd(CN)_4$$

Analysis

Elemental composition: Cd 68.36%, C 14.61%, N 17.04%

Cadmium may be measured by various instrumental analysis (see cadmium). Cyanide may be extracted by distilling an acidified solution of cadmium cyanide and then purging the liberated hydrogen cyanide with air, passing it into a scrubbing solution of caustic soda. Cyanide in the scrubbing solution is then measured by titration, or by colorimetry. In titrimetry, the distillate is titrated against silver nitrate standard solution using ρ–dimethylaminobenzalrhodamine indicator, while for colorimetric measurement, a color-forming reagent such as pyridine-barbituric acid or pyridine-pyrazolone may be used (Patnaik, P. 1997. *Handbook of Environmental Analysis*. Boca Raton, FL: Lewis Publishers.

CADMIUM CHLORIDE

[10108–64–2]
Formula: $CdCl_2$; MW 183.306; also forms a hemipentahydrate.

Uses

Cadmium chloride is used in metal finishing bath for cadmium plating. Also, it is used in photocopying, dyeing and printing.

Physical Properties

Colorless powder or crystal; hexagonal crystal system; hygroscopic; density 4.047 g/cm^3; melts at 560°C; vaporizes at 960°C; highly soluble in water (140 g/100g at 20°C), also soluble in acetone; slightly soluble in alcohol; insoluble in ether.

Thermochemical Properties

$\Delta H_f°$	–93.57 kcal/mol
$\Delta G_f°$	–82.21 kcal/mol
S°	27.55 cal/degree mol
C_ρ	17.85 cal/degree mol

Preparation

Cadmium chloride may be prepared by heating the metal with chlorine or hydrogen chloride gas. In the solution, it is formed by treating the metal or its salts, such as oxide, hydroxide, carbonate, or sulfide with hydrochloric acid:

$$Cd + 2HCl \rightarrow CdCl_2 + H_2$$

$$CdO + 2HCl \rightarrow CdCl_2 + H_2O$$

$$CdCO_3 + 2HCl \rightarrow CdCl_2 + H_2O + CO_2$$

The solution is evaporated and crystallized to yield a hydrated salt. The hydrated salt yields anhydrous cadmium chloride upon heating under hydrogen chloride or when refluxed with thionyl chloride.

Cadmium chloride also may be prepared by adding dry cadmium acetate to acetyl chloride in glacial acetic acid.

CADMIUM CARBONATE

[513–78–0]
Formula: $CdCO_3$; MW 172.41

Uses

Cadmium carbonate occurs in nature as the mineral otavite. The commercial applications of this compound are limited. It is used as a catalyst in organic synthesis and as a starting material to prepare other cadmium salts.

Physical Properties

White powdery solid; density 4.258 g/cm^3; decomposes on heating below 500°C; insoluble in water and liquid ammonia; soluble in acid (with reaction).

Thermochemical Properties

$\Delta H_f°$	–179.4 kcal/mol
$\Delta G_f°$	–160.0 kcal/mol
S°	22.1 cal/degree mol

Preparation

Cadmium carbonate is precipitated by adding excess ammonium carbonate to a solution of cadmium chloride:

$$CdCl_2 + (NH_4)_2CO_3 \rightarrow CdCO_3 + 2NH_4Cl$$

The precipitate is filtered and dried at 100°C. If an alkali metal carbonate is used instead of ammonium carbonate, a hydrated basic carbonate is obtained which upon heating with ammonium chloride at 150°C in the absence of air produces anhydrous carbonate.

Cadmium carbonate also may be obtained by slow absorption of cadmium oxide with carbon dioxide.

Reactions

Cadmium carbonate decomposes to cadmium oxide and carbon dioxide at 357°C. The compound dissolves in mineral acids forming their cadmium salts and carbon dioxide:

$$CdCO_3 + 2HCl \rightarrow CdCl_2 + CO_2 + H_2O$$

Cadmium carbonate forms a cyanide complex ion, $Cd(CN)_4^{2+}$ in cyanide solutions. It dissolves in concentrated aqueous solutions of ammonium salts forming ammonium complexes.

Analysis

Elemental composition: Cd 65.20%, C 6.97%, O 27.84%. See Cadmium.

CADMIUM FLUORIDE

[7790–79–6]
Formula: CdF_2; MW 150.41

Uses

Cadmium fluoride is used in electronics and optics; to produce crystals for lasers; in the manufacture of phosphors and glass; in high temperature dry-film lubricants; and as a catalyst in organic reactions.

Physical Properties

Colorless cubic crystal; density 6.33 g/cm^3; melts at 1,110°C; vaporizes at 1,748°C; vapor pressure 5 torr at 1,231°C; moderately soluble in water, 4.35 g/100mL at 25°C; soluble in hydrofluoric and other mineral acids; practically insoluble in alcohol and liquid ammonia.

Thermochemical Properties

$\Delta H_f°$	–167.4 kcal/mol
$\Delta G_f°$	–154.8 kcal/mol
S°	18.5 cal/degree mol
ΔH_{fus}	5.4 kcal/mol
ΔH_{vap}	55.9 kcal/mol

Preparation

Cadmium fluoride is prepared by the reaction of gaseous fluorine or hydrogen fluoride with cadmium metal or its salt, such as chloride, oxide or sulfide:

$$Cd + F_2 \rightarrow CdF_2$$

$$Cd + 2HF \rightarrow CdF_2 + H_2$$

$$CdO + 2HF \rightarrow CdF_2 + H_2O$$

It also may be obtained by dissolving cadmium carbonate in 40% hydrofluoric acid solution, evaporating the solution and drying in vacuum at 150°C:

$$CdCO_3 + 2HF \rightarrow CdF_2 + H_2O + CO_2$$

It also may be prepared by mixing cadmium chloride and ammonium fluoride solutions, followed by crystallization.

Analysis

Elemental composition: Cd 74.74%, F 25.26%. The metal may be analyzed by various instrumental techniques (see Cadmium). Fluoride may be determined by ion chromatography or by using a fluoride ion–selective electrode.

CADMIUM HYDROXIDE

[21041–95–2]
Formula: $Cd(OH)_2$; MW 146.43

Uses

Cadmium hydroxide is used in storage battery anodes, in nickel-cadmium and silver-cadmium storage batteries, and in cadmium plating. It also is used to prepare other cadmium salts.

Physical Properties

White powder or crystal; trigonal or hexagonal crystal system; density 4.79 g/cm^3; decomposes slowly at 130°C; dehydration completes at 300°C; insoluble in water (2.6 mg/L at 20°C); soluble in dilute acids.

Thermochemical Properties

$\Delta H_f°$	–134.0 kcal/mol
$\Delta G_f°$	–113.2 kcal/mol
S°	22.94 cal/degree mol

Preparation

Cadmium hydroxide may be precipitated by adding any cadmium salt solution to a boiling solution of caustic soda or caustic potash:

$$CdCl_2 + 2NaOH \rightarrow Cd(OH)_2 + 2NaCl$$

Reactions

Cadmium hydroxide loses water on heating producing cadmium oxide:

$$Cd(OH)_2 \xrightarrow{heat} CdO + H_2O$$

Decomposition commences at 130°C and is complete at 300°C.

Cadmium hydroxide is more basic than zinc hydroxide. It forms anionic complex $Cd(OH)_4^{2-}$ when treated with concentrated caustic soda solution. It forms complexes with cyanide, thiocyanate and ammonium ions when added to the solutions of these ions.

Reactions with mineral acids produce their cadmium salts. With hydrochloric acid, sulfuric acid and nitric acid, the products are cadmium chloride, cadmium sulfate and cadmium nitrate, respectively:

$$Cd(OH)_2 + 2HNO_3 \rightarrow Cd(NO_3)_2 + 2H_2O$$

Hydrated salts, such as $Cd(NO_3)_2 \cdot 4H_2O$ or $2CdCl_2 \cdot 5H_2O$, crystallize upon evaporation.

Analysis

Elemental composition: Cd 76.77%, H 1.38%, O 21.85%. The compound may be identified non-destructively by x-ray techniques (see Cadmium).

CADMIUM IODIDE

[7790–80–9]
Formula: CdI_2; MW 366.22

Uses

Cadmium iodide is used in lithography, process engraving, photography, electroplating, and in the manufacture of phosphors.

Physical Properties

White, hexagonal flakes or crystals; slowly turns yellow upon exposure to air or light; occurs in two allotropic forms, the alpha and beta forms; density 5.67 g/cm^3; melts at 387°C (alpha form) and 404°C (beta form); vaporizes at 742°C; vapor pressures 1 and 5 torr at 416 and 481°C, respectively; soluble in water (86 g/100 mL at 25°C), ethanol, acetone, ether, and ammonia.

Thermochemical Properties

$\Delta H_f°$ (alpha–)	–48.59 kcal/mol
$\Delta G_f°$ (alpha–)	–48.14 kcal/mol
S° (alpha–)	38.50 cal/degree mol
C_ρ (alpha–)	19.12 cal/degree mol
ΔH_{fus} (alpha–)	8.0 kcal/mol
ΔH_{vap} (alpha–)	25.33 kcal/mol

Preparation

Cadmium iodide is prepared by the addition of cadmium metal, or its oxide, hydroxide, nitrate or carbonate to hydriodic acid:

$$CdO + 2HI \rightarrow CdI_2 + H_2O$$

Also, the compound can be made by heating cadmium with iodine:

$$Cd + I_2 \xrightarrow{heat} CdI_2$$

A brownish crystalline β–form of the salt may be obtained by slow crystallization from solutions or fused salt mixtures.

Reactions

In acid medium, cadmium iodide solution should exhibit the reduction reactions of I^- anion. Iodide anion is a fairly strong reducing agent which can reduce many metal ions in their higher oxidation states:

$$Fe + 2I^{-} \rightarrow 2Fe^{2+} + I_2(s)$$

It undergoes double decomposition reactions in aqueous solution forming precipitates of insoluble products:

$$CdI_2 + AgNO_3 \rightarrow 2AgI + Cd(NO_3)_2$$

When heated with hydrogen, it is reduced to cadmium metal and hydrogen iodide:

$$CdI_2 + H_2 \xrightarrow{\text{elevated temperataure}} Cd + 2HI$$

Analysis

Elemental composition: Cd 30.69%, I 69.31%. A small amount of salt is weighed accurately, dissolved in water, appropriately diluted, and analyzed by AA or ICP spectrophotometry. Iodide anion at similar trace concentrations may be analyzed by ion chromatography. I^{-} anion may be identified by adding a few drops of 6*M* HNO_3 to a few drops of the aqueous solution of the salt, followed by the addition of 1mL 0.1 *M* $FeCl_3$ solution and 1mL methylene chloride. A purple or pink bottom layer after shaking indicates the presence of iodide.

CADMIUM NITRATE

[10325–94–7]
Formula: $Cd(NO_3)_2$; MW 236.42; also forms a tetrahydrate, $Cd(NO_3)_2 \cdot 4H_2O$ [10022–68–1]

Uses

Cadmium nitrate is used for coloring glass and porcelain; (historically) as a flash powder in photography; and in the manufacture of many other cadmium salts.

Physical Properties

White crystal or amorphous powder; hygroscopic; density 3.60 g/cm^3; melts at 350°C; very soluble in water, also soluble in alcohols.

Preparation

Cadmium nitrate is prepared by dissolving cadmium metal or its oxide, hydroxide, or carbonate, in nitric acid followed by crystallization:

$$CdO + 2HNO_3 \rightarrow Cd(NO_3)_2 + H_2O$$

Reactions

Thermal dissociation at elevated temperatures produces cadmium oxide and oxides of nitrogen. When hydrogen sulfide is passed through an acidified solution of cadmium nitrate, yellow cadmium sulfide is formed. A red modification of the sulfide is formed under boiling conditions.

When mixed with caustic soda solution, cadmium oxide forms precipitate of cadmium hydroxide. Many insoluble cadmium salts are obtained by such precipitation reactions. For example, mixing aqueous solutions of cadmium nitrate with ammonium tungstate results in precipitation of cadmium tungstate.

Analysis

Elemental composition: Cd 47.55%, N 11.85%, O 40.60%. The metal may be analyzed in its acidified aqueous solution by various instrumental techniques (see Cadmium). Nitrate ion in the aqueous solution may be determined by ion chromatography or by using a nitrate ion-selective electrode.

Toxicity

Cadmium nitrate is moderately toxic by ingestion, and possibly other routes of exposure.

LD_{50} oral (rat): 300 mg/kg

The compound also is a confirmed human carcinogen.

CADMIUM OXIDE

[1306–19–0]
Formula CdO; MW 128.41

Uses

Cadmium oxide is used in storage battery electrodes. Its solution, mixed with sodium cyanide, is used in electroplating baths. Other uses are in PVC heat stabilizers; as an additive to nitrile rubbers and plastics to improve heat resistance; and in ceramic glazes and phosphors.

Physical Properties

Occurs in two forms, alpha form—a colorless amorphous powder, and beta form—a reddish-brown crystal; density 6.95 g/cm^3 (alpha form) and 8.15 g/cm^3 (beta form); decomposes on rapid heating at 900°C; sublimation temperature 1,559°C; insoluble in water and alkalis; dissolves in mineral acids.

Thermochemical Properties

$\Delta H_f°$	–61.76 kcal/mol
$\Delta G_f°$	–54.66 kcal/mol
S°	13.10 cal/degree mol
C_ρ	10.37 cal/degree mol

Preparation

Cadmium oxide is prepared by the reaction of cadmium vapor with oxygen. The metal is first melted in a steel retort and transported into a heated chamber where it is vaporized. The vapor is reacted with air, and the cadmium oxide formed is collected in a bag house. The particle size of the product depends on the ratio of air to cadmium vapor. The oxide may be further purified and particles of uniform size may be obtained by calcination at low red heat.

Cadmium oxide also may be prepared by several other routes starting with various cadmium salts. The compound can be made by thermal decomposition of cadmium carbonate or cadmium hydroxide:

$$CdCO_3 \xrightarrow{heat} CdO + CO_2$$

$$Cd(OH)_2 \xrightarrow{heat} CdO + H_2O$$

Similar thermal decomposition of cadmium nitrate or sulfate would yield the oxide.

Cadmium oxide also may be made by high temperature oxidation of cadmium sulfide:

$$2CdS + 3O_2 \xrightarrow{heat} 2CdO + 2SO_2$$

Finely divided oxide may be obtained by pyrolysis of cadmium salts of carboxylic acids, such as cadmium formate or oxalate:

$$(COOH)_2Cd \xrightarrow{pyrolysis} CdO + H_2O + 2CO$$

$$(COO)_2Cd \xrightarrow{pyrolysis} CdO + CO_2 + CO$$

Reactions

Reactions with reducing agents at elevated temperatures convert the oxide to metal:

$$CdO + H_2 \xrightarrow{heat} Cd + H_2O$$

$$CdO + CO \xrightarrow{heat} Cd + CO_2$$

Cadmium oxide reacts with mineral acids forming their cadmium salts:

$$CdO + 2HCl \rightarrow CdCl_2 + H_2O$$

$$CdO + H_2SO_4 \rightarrow CdSO_4 + H_2O$$

Similar reactions occur with carboxylic acids producing corresponding carboxylates of cadmium.

Heating a mixture of cadmium oxide and sulfur produces cadmium sulfide:

$$2CdO + S \xrightarrow{\text{heat}} 2CdS + O_2$$

CdO slowly absorbs carbon dioxide forming cadmium carbonate, $CdCO_3$.

Reaction with amorphous silicon at 900°C, catalyzed by steam produces cadmium orthosilicate, Cd_2SiO_4. The same product also is obtained by reaction with silica. Finely divided oxide reacts with dimethyl sulfate forming cadmium sulfate. Cadmium oxide, upon rapid heating with oxides of many other metals, such as iron, molybdenum, tungsten, titanium, tantalum, niobium, antimony, and arsenic, forms mixed oxides. For example, rapid heating with ferric oxide at 750°C produces cadmium ferrite, $CdFe_2O_4$:

$$CdO + Fe_2O_3 \xrightarrow{750^\circ C} CdFe_2O_4$$

Analysis

Elemental composition: Cd 87.54%, O 12.46%. CdO may be identified nondestructively by various x-ray techniques. Cadmium may be analyzed in aqueous phase by AA or ICP spectrophotometry following acid digestion. The oxide also can be analysed by various x-ray techniques.

CADMIUM SULFATE

[10124–36–4]

Formula: $CdSO_4$; MW 208.48; also forms two hydrates, cadmium sulfate monohydrate, $CdSO_4 \cdot H_2O$ [7790–84–3] and cadmium sulfate octahydrate, $CdSO_4 \cdot 8H_2O$ [15244–34–6].

Uses

Cadmium sulfate is used as electrolyte in standard cells and electroplating baths. Also, it is used in pigments and fluorescent screens.

Physical Properties

Colorless orthogonal crystal; the hydrates have monoclinic crystal system; density 4.69 g/cm^3 (density of mono-, and octahydrates is 3.79 and 3.08 g/cm^3, respectively); melts at 1,000°C (octahydrate decomposes at 40°C); soluble in water, insoluble in ethanol.

Thermochemical Properties

$\Delta H_f°$	–223.1 kcal/mol
$\Delta G_f°$	–196.6 kcal/mol
S°	29.4 cal/degree mol
C_ρ	23.8 cal/degree mol

Preparation

Cadmium sulfate is prepared by the reaction of cadmium metal or its oxide or hydroxide with dilute sulfuric acid:

$$CdO + H_2SO_4 \rightarrow CdSO_4 + H_2$$

$$CdO + H_2SO_4 \rightarrow CdSO_4 + H_2O$$

$$Cd(OH)_2 + H_2SO_4 \rightarrow CdSO_4 + 2H_2O$$

Analysis

Elemental composition: Cd 53.92%, O 30.70%, S 15.38%. $CdSO_4$ is dissolved in water and cadmium is analysed by atomic absorption or emission spectrophotometry, following appropriate dilution (see Cadmium). Sulfate ion in the solution may be determined by ion–chromatography or by gravimetry following treatment with barium chloride solution.

CADMIUM SULFIDE

[1306–23–6]
Formula: CdS; MW 144.48

Occurrence and Uses

Cadmium sulfide occurs in nature as the mineral greenoktite. The compound is widely used in pigments for paints, baking enamels, ceramics and plastics. It imparts bright yellow to maroon, with strong retention of color and resistance to alkalis. It also is used in inks, phosphors, and fluorescent screens. Other applications of this compound are in photovoltaic and solar cells (for converting solar energy to electrical energy), photoconductors (in xerography), thin film transistors and diodes, rectifiers, scintillation counters, pyrotechnics, and smoke detectors.

Physical Properties

Yellow to orange crystal; occurs as two polymorphs, hexagonal alpha form and cubic beta form; exhibits stable wurtzite structure at lower temperature, and zinc blende type structure at higher temperatures; the beta form converts to alpha form when heated at 750°C in sulfur atmosphere; sublimes at 980°C; practically insoluble in water (1.3 mg/L at 20°C); K_{sp} 3.6×10^{-29}; dissolves in dilute mineral acids on heating or concentrated acids at ordinary temperatures (decomposes with liberation of H_2S).

Thermochemical Properties

$\Delta H_f°$	–38.70 kcal/mol
$\Delta G_f°$	–37.40 kcal/mol
S°	15.51 cal/degree mol

Preparation

Cadmium sulfide may be prepared by precipitation from an aqueous solution of its soluble salts such as cadmium chloride or cadmium nitrate by passing hydrogen sulfide. The reactions may be carried out in acidic, neutral or alkaline solutions using various cadmium salts to obtain different crystal modifications as shown in the table below.

Reaction of H_2S with Cadmium Salts under Varying Conditions

Aqueous Solution of Cd Salt	Reaction Conditions	CdS Color
$CdCl_2$	neutral pH; ordinary temperature	yellow crystal
$CdCl_2$	acidic pH; boiling solution	red crystal
$Cd(NO_3)_2$	neutral pH; ordinary temperature	yellow crystal
$Cd(NO_3)_2$	acidic pH; boiling solution	red crystal
$CdSO_4$	neutral pH; ordinary temperature	yellow crystal
$CdSO_4$	acidic pH, boiling solution	red crystal,
$Cd(C_2H_4O_2)_2$	acidic pH; ordinary temperature	yellow crystal
$Cd(C_2H_4O_2)_2$	alkaline ammoniacal solution	red solution
$Cd(ClO_4)_2$	acidic pH; warm solution	yellow crystal

Cadmium sulfide also may be obtained by treatment of sodium or other alkali metal sulfide solution with that of a soluble cadmium salt. The compound also may be prepared by heating a mixture of cadmium or its oxide with sulfur at 800°C; or by the reaction of H_2S with cadmium vapor at 800°C.

Analysis

Elemental composition: Cd 77.81%, S 22.91%. In crystalline state, it may be identified by x-ray diffraction measurement. In aqueous acid extract following digestion with nitric acid, cadmium may be measured by various instrumental techniques. (see Cadmium). Warming with dilute mineral acids liberates H_2S, which may be identified by its odor or by browning of a white paper soaked in lead acetate solution.

Toxicity

Cadmium sulfide is moderately toxic to experimental animals by all routes of exposure. Toxicity in humans is low. It is, however, carcinogenic to humans.

CALCIUM

[7440–70–2]
Symbol: Ca; atomic number 20; atomic weight 40.078; a Group IIA (Group 2) alkaline–earth metallic element; ionic radius 1.06 Å (Ca^{2+}); electron configuration $[Ar]4s^2$; valence state +2; standard electrode potential, E° = –2.87V; stable isotopes and their abundance: Ca–40 (97.00%), Ca–44 (2.06%); Ca–42 (0.64%), Ca–48 (0.18%), Ca–43 (0.145%), and Ca–46 (0.003%); also the element has six unstable isotopes of which Ca–41 has the longest half–life, 1.1×10^5 yr (decay mode: electron capture), and Ca–38 has shortest half life 0.66 sec (β–decay).

Occurrence and Uses

A few calcium compounds, such as calcium oxide and calcium carbonate have been known since ancient times. The metal was isolated by Davy in 1808. Earlier its amalgam was prepared by Berzelius and Pontin. Calcium is the fifth most abundant element in the earth's crust, constituting 4.15 % by weight. Its concentration in sea water is 412 mg/L. Calcium is a highly reactive metal and is never found in free elemental form. Its compounds, however,are widely distributed in nature. Some of its common ores are limestone ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$), fluorite (CaF_2), anorthite ($CaAl_2Si_2O_8$) and apatite ($Ca_5FP_3O_{12}$). It also occurs in living matter, as an essential element in bones, teeth, shell, corals, and plant leaves. It constitutes about 2% of body weight, found mostly in bones and teeth. Its concentration in the blood is about 100 mg/L, found in blood proteins and serum.

The few limited applications of calcium are mostly in metallurgy. It is used to produce alloys with aluminum, lead, beryllium, copper, silicon, and other metals; as a desulfurizer, decarburizer, and deoxidizer for ferrous and nonferrous alloys; for removal of bismuth from lead; and as a reducing agent for zirconium, uranium, thorium, and other metals. Minor, non-metallurgical applications include dehydration of organic solvents; purification of helium, argon, and other inert gases to remove nitrogen and other impurities; and as a "getter" for residual gases in vacuum tubes. Calcium compounds have numerous applications (see individual compounds).

Physical Properties

Bright, silvery-white metal; face-centered cubic crystal structure (α = 0.5582 nm) at ordinary temperatures, transforming to body-centered cubic form ($\alpha = 0.4407$) at 430°C; density 1.54 g/cm^3 at 20°C; hardness 2 Mohs, 17 Brinnel (500 kg load); melts at 851°C; vaporizes at 1,482°C; electrical resistivity 3.43 and 4.60 microhm–cm at 0° and 20°C, respectively; modulus of elasticity $3–4 \times 10^6$ psi; mass magnetic susceptibility $+1.10 \times 10^{-6}$ cgs; surface tension 255 dynes/cm; brick-red color when introduced to flame (flame test); standard reduction potential E° = –2.87V

Manufacture

Calcium may be obtained by electrolytic or thermal reduction of its salts.

Electrolytic reduction involves electrolysis of partially molten calcium chloride at 780° to 800°C in a graphite lined steel vessel. The method requires precise control of temperature and current. The solid deposit of metal produced may contain entrapped salt and impurities such as chlorine and nitrogen. It is re-melted to reduce impurity levels.

Currently, thermal reduction processes have replaced the electrolysis method. The starting material in these methods is limestone, which is calcined to produce calcium oxide. The latter is ground, mixed and compacted with aluminum, and reduced at temperatures between 1,000° to 1,200°C under vacuum. Calcium vapors formed in low yield under such thermodynamic conditions are transferred from the reactor and condensed in cool zones, thus shifting the equilibrium to allow formation of more calcium vapors. The reactions are as follows:

$$4Ca + 2Al \rightarrow CaO \cdot Al_2O_3 + 3Ca \quad \text{(vapor)}$$

$$6Ca + 2Al \rightarrow 3CaO \cdot Al_2O_3 + 3Ca \quad \text{(vapor)}$$

Reactions

Calcium forms divalent compounds. At ordinary temperatures it does not oxidize readily in dry air. However, at 300°C the reaction is rapid in dry oxygen. The oxidation can occur at ambient temperatures in moist air. Reaction with hydrogen at 400°C gives calcium hydride, CaH_2. Ca metal reacts with a number of nonmetallic elements forming their corresponding binary compounds. While the reaction with fluorine occurs at ambient temperatures, other elements combine only at elevated temperatures in the range 300–900°C. Calcium combines with chlorine, bromine and iodine at 400°C and nitrogen at 900°C forming calcium halides or nitride. With sulfur, phosphorus, carbon and boron, the products are the sulfide CaS, phosphide Ca_3P_2, carbide CaC_2, and boride Ca_3B_2, respectively.

Calcium reacts vigorously with water at ordinary temperatures with the evolution of hydrogen:

$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$$

Violent reactions occur in dilute mineral acids with evolution of hydrogen. Ca reacts with carbon dioxide on heating, forming calcium oxide and calcium carbide:

$$5Ca + 2CO_2 \rightarrow 4CaO + CaC_2$$

Calcium combines with a number of metals at elevated temperatures forming alloys and intermetallic compounds.

Calcium is a strong reducing agent and can reduce most metal oxides and halides into their metals at elevated temperatures. It can reduce all the lower electropositive metals; e.g.

$$Ca + ZnCl_2 \rightarrow Zn + CaCl_2$$

Analysis

Calcium may be analyzed by several instrumental techniques such as atomic absorption and emission spectrophotometry, ICP–MS, neutron activation, and x-ray fluorescence and diffraction methods. For all these techniques, except the x-ray methods, the compounds of calcium must be digested in aqueous medium and diluted sufficiently prior to analysis. The metal may be measured at the wavelength 422.7nm by flame-AA or 317.93 or 315.89nm by ICP-AES. Soluble calcium compounds in water also may be measured by EDTA complexometric titration using Eriochrome Black or Calmagite indicator. Magnesium interferes with this test.

Hazard

Calcium is nontoxic. It can be handeled safely. However, contact with acids, oxidizing agents or oxidizable substances can progress to explosive reactions.

CALCIUM CARBONATE

[471–34–1]
Formula: $CaCO_3$; MW 100.09

Occurrence and Uses

Calcium carbonate occurs in nature as limestone in various forms, such as marble, chalk, and coral. It is probably the most widely-used raw material in the chemical industry. It has numerous applications, primarily to produce cement, mortars, plasters, refractories, and glass as building materials. It also is used to produce quicklime, hydrated lime and a number of calcium compounds. It is produced either as powdered or precipitated calcium carbonate. The latter consists of finer particles of greater purity and more uniform size. They also have many important commercial applications. Various grades of precipitated calcium carbonate are used in several products, such as textiles, papers, paints, plastics, adhesives, sealants, and cosmetics.

Physical Properties

Calcium carbonate occurs in two forms—hexagonal crystal known as calcite, and orthorhombic form, aragonite. Calcite decomposes on heating at 825°C, aragonite melts at 1,339°C (at 102.5 atm). Density 2.71 g/cm^3 (calcite), 2.83 g/cm^3 (aragonite); insoluble in water (15mg/L at 25°C); Ksp 4.8×10^{-9}; soluble in dilute mineral acids.

Thermochemical Properties

$\Delta H_f°$	–288.6 kcal/mol
$\Delta G_f°$	–269.9 kcal/mol
S°	21.92 cal/degree mol
C_ρ	19.9 cal/degree mol

Production

Calcium carbonate is obtained from natural limestone deposits. The purified compound, known as precipitated calcium carbonate, is synthesized from limestone. Limestone is calcined to calcium oxide and carbon dioxide in a kiln. The products are recombined after purification. Calcium oxide is hydrated with water to give a slurry called milk of lime, which is then carbonated by bubbling CO_2 through it. The reactions involved in the process are as follows:

$$CaCO_3 \xrightarrow{\text{heat}} CaO + CO_2$$

$$CaO + H_2O \xrightarrow{\text{slaking}} Ca(OH)_2$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

The crystal sizes required for various commercial applications may be controlled by temperature, pH, concentrations, and mixing rate.

Calcium carbonate also may be precipitated by mixing solutions of calcium chloride and sodium carbonate.

Reactions

Calcium carbonate decomposes to calcium oxide and CO_2 on heating. Treatment with dilute mineral acids produces corresponding calcium salts with liberation of CO_2:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

In the presence of CO_2 it dissolves in water with the formation of bicarbonate:

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^-$$

It is reduced to calcium carbide when heated with coke or anthracite in an electric furnace:

$$2CaCO_3 + 5C \xrightarrow{\text{high temperature}} 2CaC_2 + 3CO_2$$

Analysis

Elemental composition: Ca 40.04%, C 12.00%, O 47.96%. $CaCO_3$ dissolves in water in the presence of a few drops of HCl. The solution is analyzed for calcium by AA or ICP spectroscopy or by treatment with ammonium oxalate followed by titration with potassium permanganate.

CALCIUM CARBIDE

[75–20–7]
Formula: CaC_2; MW 64.100

Uses

The most important application of calcium carbide is the production of acetylene. It also is used to produce calcium cyanamide, $CaCN_2$, a nitrogen fertilizer and a source of ammonia.

Physical Properties

Grayish-black orthorhombic crystal; density 2.22 g/cm^3; melts at 2,200°C; reacts with water.

Thermochemical Properties

$\Delta H_f°$	–14.29 kcal/mol
$\Delta G_f°$	–15.51 kcal/mol
S°	16.73 cal/degree mol
C_ρ	14.99 cal/degree mol

Preparation

Calcium carbide is produced by the reaction of calcium oxide with carbon in an electric furnace at temperatures in the range 1,800° to 2,100°C:

$$CaO + 3C \xrightarrow{1,800C} CaC_2 + CO$$

Reactions

Calcium carbide reacts with water producing acetylene:

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$$

Reaction with nitrogen at elevated temperatures produces calcium cyanamide, used as a fertilizer:

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

Analysis

Elemental composition: Ca 62.53%, C 37.48%. The compound can be determined by various x-ray techniques.

Hazard

Contact with water can be hazardous due to the formation of acetylene which is highly flammable.

CALCIUM CHLORIDE

[10043–52–4]

Formula: $CaCl_2$; MW 110.99; also forms mono-, di-, tetra- and hexahydrates; $CaCl_2 \cdot H_2O$ [22691–02–7], $CaCl_2 \cdot 2H_2O$ [10035–04–8], $CaCl_2 \cdot 4H_2O$ [25094–02–4] and $CaCl_2 \cdot 6H_2O$ [7774–34–7], respectively.

Occurrence and Uses

Calcium chloride may be found in nature as the mineral tachhydrite, $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$. It also is found in other minerals. Its concentration in sea water is about 0.15%.

Calcium chloride has several industrial applications. The major applications of this compound are in deicing of roads, dust control, imparting stability to roads and buildings, and to improve traction in tractor tires. It is mixed with ice to make freezing mixtures. Hexahydrate mixed with crushed ice can lower the temperature of the cooling bath to below –50°C. It also is used as a desiccant for dehydrating gases and liquids. It is added to cement in various proportions to manufacture different types of concrete. Other uses are in adhesives, to lower gel temperatures, and as a calcium source in liquid feed supplements for dairy cattle. Also, the compound is used to control particle size development and reduce coalescence in plastics.

Physical Properties

White crystal, powder or flake; highly hygroscopic; the compound and its solutions absorb moisture from the air at various rates depending on calcium chloride concentrations, relative humidity and vapor pressure of water in the air, temperature, surface area of exposed material, and the rate of air circulation; at 40% and 95% relative humidity and 25°C, one gram anhydrous calcium chloride may absorb about 1.4 g and 17 g water, respectively. (Shearer, W. L. 1978 . In *Kirk–Othmer Encyclopedia of Chemical Technology*, 3rd ed., vol. 4, pp. 432–6. New York: Wiley Interscience); density 2.15, 2.24, 1.85, 1.83 and 1.71 g/cm^3 for the anhydrous salt and its mono-, di-, tetra- and hexahydrates, respectively; anhydrous salts melts at 772°C, while the mono-, di-, tetra- and hexahydrates decompose at 260°, 175°, 45.5° and 30°C, respectively; the anhydrous salt vaporizes at 1,935°C; highly soluble in water, moderate to high solubility in alcohol.

Thermochemical Properties

ΔH_f° ($CaCl_2$)	–190.11 kcal/mol
ΔH_f° ($CaCl_2 \cdot H_2O$)	–265.53 kcal/mol
ΔH_f° ($CaCl_2 \cdot 2H_2O$)	–335.56 kcal/mol
ΔH_f° ($CaCl_2 \cdot 4H_2O$)	–480.40 kcal/mol
ΔH_f° $CaCl_2 \cdot 6H_2O$)	–623.33 kcal/mol
ΔG_f° ($CaCl_2$)	–178.97 kcal/mol
S° ($CaCl_2$)	25.91 cal/degree mol
C_ρ ($CaCl_2$)	17.42 cal/degree mol
C_ρ ($CaCl_2 \cdot H_2O$)	25.39 cal/degree mol
C_ρ ($CaCl_2 \cdot 2H_2O$)	41.33 cal/degree mol
C_ρ ($CaCl_2 \cdot 4H_2O$)	60.03 cal/degree mol
C_ρ ($CaCl_2 \cdot 6H_2O$)	71.87 cal/degree mol
ΔH_{fus} ($CaCl_2$)	6.82 kcal/mol
ΔH_{fus} ($CaCl_2 \cdot H_2O$)	4.13 kcal/mol
ΔH_{fus} ($CaCl_2 \cdot 2H_2O$)	3.09 kcal/mol
ΔH_{fus} ($CaCl_2 \cdot 4H_2O$)	7.13 kcal/mol
ΔH_{fus} ($CaCl_2 \cdot 6H_2O$)	10.94 kcal/mol
*ΔH_{soln} ($CaCl_2$)	–174 kcal/mol
*ΔH_{soln} ($CaCl_2 \cdot H_2O$)	–96.8 kcal/mol
*ΔH_{soln} ($CaCl_2 \cdot 2H_2O$)	–72.8 kcal/mol

*ΔH_{soln} ($CaCl_2 \cdot 4H_2O$)	–14.2 kcal/mol
*ΔH_{soln} ($CaCl_2 \cdot 6H_2O$)	17.2 kcal/mol

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* to infinite dilution in water.

Preparation

Calcium chloride is obtained as a by-product in the manufacture of sodium carbonate (soda ash) by ammonia-soda (Solvay) process. The process involves the reaction of sodium chloride with calcium carbonate and ammonia. Calcium chloride is currently produced in bulk amounts by evaporation of natural underground brines. In the laboratory, calcium chloride can be prepared by treating limestone with hydrochloric acid followed by evaporation of solution to obtain crystals. The crystals are dehydrated to obtain anhydrous salt. Calcium oxide or hydroxide may be used instead of carbonate.

Reactions

In aqueous solutions, calcium chloride undergoes double decomposition reactions with a number of soluble salts of other metals to form precipitates of insoluble calcium salts. For example, mixing solutions of calcium chloride with sodium carbonate, sodium tungstate and sodium molybdate solutions precipitates the carbonates, tungstates, and molybdates of calcium, respectively. Similar precipitation reactions occur with carboxylic acids or their soluble salt solutions. $CaCl_2$ forms calcium sulfide when H_2S is passed through its solution. Reaction with sodium borohydride produces calcium borohydride, $Ca(BH_4)_2$. It forms several complexes with ammonia. The products may have compositions $CaCl_2 \cdot 2NH_3$, $CaCl_2 \cdot 4NH_3$, and $CaCl_2 \cdot 8NH_3$.

Analysis

Elemental composition: Ca 36.11%, Cl 63.89%. An aqueous solution of the compound may be acidified and analyzed for calcium by AA or ICP methods (see Calcium). The solution may be analyzed for chloride ion by ion selective electrode, ion chromatography or by argentometric titration.

CALCIUM CYANAMIDE

[156–62–7]
Formula: $CaCN_2$; MW 80.11; cyanamide ion is linear and structurally similar to CO_2; Structure $N \equiv CN = Ca$
Synonyms: calcium carbimide; lime nitrogen; nitrolime

Uses

Calcium cyanamide is used primarily as a fertilizer. It also is used as a defoliant and pesticide. Other major applications of this compound are in hardening iron and steel, and in preparation of calcium cyanide and melamine.

Physical Properties

Pure product is a colorless, hexagonal crystal or white powder. Commercial grade material may be grayish-black powder or lump (the color is due to presence of calcium carbide and other impurities); density 2.29 g/cm^3; melts around 1,340°C; sublimes around 1,150 to 1,200°C on rapid heating; reacts with water.

Preparation

Calcium cyanamide is prepared from calcium carbide. The carbide powder is heated at about 1,000°C in an electric furnace into which nitrogen is passed for several hours. The product is cooled to ambient temperatures and any unreacted carbide is leached out cautiously with water.

$$CaC_2 + N_2 \xrightarrow{\text{elecric furnace}} CaCN_2 + C \qquad (\Delta H_f^\circ = -69.0 \text{ kcal/mol at } 25°C)$$

Reactions

Calcium cyanamide partially hydrolyzes to calcium hydrogen cyanamide, $CaHCN_2$. The final hydrolysis products are calcium carbonate and ammonia. The reaction is slow, occurring in moist soil:

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$$

When heated at elevated temperatures in oxygen (or air) it oxidizes to calcium oxide, carbon dioxide and oxides of nitrogen.

Analysis

Elemental composition: Ca 50.03%, C 14.99%, N 34.98. A measured amount of the compound is hydrolyzed with water. The product $CaCO_3$ is filtered, dried and determined by gravimetry. Calcium carbonate or the parent calcium cyanamide may be digested with nitric acid, diluted appropriately, and analyzed for Ca by AA or ICP spectroscopy. The hydrolysis product in solution, ammonia, may be measured by ammonium ion selective electrode, or by colorimetry followed by Nesslerization.

CALCIUM FLUORIDE

[7789–75–5]
Formula: CaF_2; MW 78.075

Occurrence and Uses

Calcium fluoride occurs in nature as the mineral fluorspar or fluorite. It is used as a flux in ferrous metallurgy to enhance the fluidity of the slag. An important application of this compound is in the manufacture of fluorine and hydrofluoric acid, starting materials for producing many fluoroorganics. It also is used in glass and ceramics. Pure crystals are used in lasers, optics, and electronics. Other applications are in high temperature, dry-film lubricants;

catalysis, and fluoridation of drinking water.

Physical Properties

White cubic crystal or powder; refractive index 1.434; density 3.18 g/cm^3; hardness 4 Mohs; melts at 1,418°C; vaporizes at 2,533°C; insoluble in water (16 mg/L at 20°C); K_{sp} 3.9×10^{-11}; slightly soluble in dilute mineral acid; soluble in concentrated acids (with reaction).

Thermochemical Properties

$\Delta H_f°$	–293.5 kcal/mol
$\Delta G_f°$	–281.0 kcal/mol
S°	16.37 cal/degree mol
C_ρ	16.01 cal/degree mol
ΔH_{fus}	7.1 kcal/mol

Production

The commercial product is obtained from naturally occurring mineral fluorspar, which is purified and powdered. Also, it may be precipitated by mixing a solution of sodium fluoride with a soluble calcium salt:

$$Ca(NO_3)_2 + 2NaF \rightarrow CaF_2 + NaNO_3$$

Alternatively, it may be obtained by treating calcium carbonate with hydrofluoric acid:

$$CaCO_3 + 2HF \rightarrow CaF_2 + CO_2 + H_2O$$

Reactions

Reaction with concentrated sulfuric acid yields hydrogen fluoride and calcium sulfate:

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4$$

Similar HF liberation occurs with other concentrated mineral acids.

Analysis

Elemental composition: Ca 51.33%, F 48.67%. The compound may be analysed nondestructively by x-ray techniques. Calcium may be measured in acid extract by AA or ICP spectrophotometry. The insoluble salt is digested in concentrated nitric acid and the acid extract diluted for analysis.

CALCIUM HYDRIDE

[7789–78–8]
Formula: CaH_2; MW 42.094

Uses

Calcium hydride is used as a source of hydrogen, liberating hydrogen either on heating or shaking in water. When mixed in water, 1 g calcium hydride would release 1.16 L hydrogen at NTP or about twice the volume of hydrogen generated from equivalent mass of calcium metal in water. Other applications are in organic synthesis as a reducing agent to reduce metal oxides to metals, and as a drying agent.

Physical Properties

Grayish orthorhombic crystal or powder; stable at ambient temperature; density 1.70 g/cm^3; melts at 816°C; reacts with water and alcohol.

Thermochemical Properties

$\Delta H f°$	–43.38 kcal/mol
$\Delta G_f°$	–34.06 kcal/mol
S°	9.89 cal/degree mol
C_ρ	9.80 cal/degree mol

Preparation

Calcium hydride may be prepared from its elements by direct combination of calcium and hydrogen at 300 to 400°C. It also can be made by heating calcium chloride with hydrogen in the presence of sodium metal:

$$CaCl_2 + H_2 + 2Na \xrightarrow{heat} CaH_2 + NaCl$$

Alternatively, calcium hydride may be prepared by the reduction of calcium oxide with magnesium in the presence of hydrogen:

$$CaO + Mg + H_2 \rightarrow CaH_2 + MgO$$

Reactions

Calcium hydride reacts with water, evolving hydrogen:

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$$

Similar reaction occurs with lower alcohols and carboxylic acids:

$$CaH_2 + 2C_2H_5OH \rightarrow (C_2H_5O)_2Ca + H_2$$

$$CaH_2 + 2CH_3COOH \rightarrow (CH_3COO)_2Ca + 2H_2$$

Calcium hydride is a strong reducing agent. It reduces most metal oxides to metals:

$$CaH_2 + 2CuO \rightarrow 2Cu + Ca(OH)_2$$

$$3CaH_2 + 2Al_2O_3 \rightarrow 4Al + Ca(OH)_2$$

When heated with chlorine, bromine or iodine, the reaction goes to incandescence with the formation of calcium halide and hydrogen halide:

$$CaH_2 + 2Cl \xrightarrow{heat} CaCl_2 + 2HCl$$

Analysis

Elemental composition: Ca 95.41%; H 4.79%. A measured amount of the solid is carefully treated with water and the volume of evolved hydrogen is measured using a manometer (1g liberates 1.16 L H_2 at NTP). The solution is then acidified with nitric acid and diluted for the measurement of calcium by AA or ICP spectrophotometry, or by a wet method (see Calcium). The liberated hydrogen gas may be analyzed by GC using a TCD. Many packed and capillary GC columns are commercially available.

Hazard

Calcium hydride ignites in air on heating and can explode violently if mixed and rubbed with a strong oxidizing agent such as perchlorate or bromate. Contact with water produces hydrogen which can create a fire hazard in a confined space.

CALCIUM HYDROXIDE

[1305–62–0]
Formula: $Ca(OH)_2$; MW 74.093
Synonyms: hydrated lime; slaked lime; calcium hydrate

Uses

Calcium hydroxide has wide industrial applications. It is used to make cement, mortar, plaster, and other building materials. It also is used in water soluble paints, and for fireproofing coatings and lubricants. Other applications are in the manufacture of paper pulp; as a preservative for egg; in vulcanization of rubber; as a depilatory for hides; and in preparation of many calcium salts.

Physical Properties

Soft white crystalline powder; hexagonal; density 2.34 g/cm^3; slightly bitter taste; loses water when heated at elevated temperatures (580°C); slightly soluble in water; K_{sp} 1.2×10^{-14}; aqueous solution alkaline; soluble in glycerol and acids; insoluble in alcohol.

Thermochemical Properties

$\Delta H_f°$	–235.47 kcal/mol
$\Delta G_f°$	–214.51 kcal/mol
S°	19.93 cal/degree mol
C_ρ	20.90 cal/degree mol

Production

Calcium hydroxide is produced commercially by treating lime with water:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

In the laboratory it may be prepared by treating an aqueous solution of any calcium salt with an alkali.

Reactions

Calcium hydroxide on heating at 580°C loses its water, forming calcium oxide (CaO). $Ca(OH)_2$ forms calcium carbonate by absorbing CO_2 from air or when CO_2 is passed through a suspension in water. Reaction with sulfuric acid yields calcium sulfate dihydrate:

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O$$

Mixing with other mineral acids following crystallization or evaporation of solution produces corresponding calcium salts.

It combines with sulfur dioxide to form calcium sulfite hemihydrate, $CaSO_3 \cdot ½H_2O$ which can oxidize in air in the presence of moisture to give calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$. However, when SO_2 is passed through a solution of calcium hydroxide, calcium bisulfite, $Ca(HSO_3)_2$ is obtained. The solution is yellowish when it contains bisulfite in aqueous SO_2.

When heated with carbon monoxide under pressure, the product is calcium formate, $Ca(HCOO)_2$:

$$Ca(OH)_2 + 2CO \xrightarrow[\text{pressure}]{\text{heat}} Ca(HCOO)_2$$

Hot aqueous solution of calcium hydroxide and iodine react in the presence of chlorine to form calcium iodate, $Ca(IO_3)_2$.

Analysis

Elemental composition: Ca 54.09%, H 2.72%, O 43.19%. Calcium may be measured by atomic absorption or emission spectroscopy (see Calcium). Its concentration in its alkaline aqueous solution may be measured by acid-base titration.

CALCIUM HYPOCHLORITE

[7778–54–3]
Formula: $Ca(OCl)_2$; MW 142.99
Synonym: calcium oxychloride

Uses

Calcium hypochlorite is used as a disinfectant and bactericide. It also is used as a fungicide; a deodorant; an oxidizing agent; and as a bleaching agent for paper and textiles. Some other applications of this compound are in refining sugar and producing chlorine.

Physical Properties

White crystalline solid; density 2.35 g/cm^3; decomposes when heated to 100°C; soluble in water and alcohol (with decomposition).

Preparation

Calcium hypochlorite may be prepared by passing chlorine into a slurry of lime and sodium hydroxide. Alternatively, chlorine is passed into a solution of hydrated lime to produce bleaching powder, $CaCl(OCl) \cdot H_2O$:

$$Ca(OH)_2 + Cl_2 \rightarrow CaCl(OCl) \cdot H_2O$$

The bleaching powder solution is then treated with sodium chloride to salt out calcium hypochlorite. The product obtained in its dihydrate form is dried under vacuum.

The commercial grade material usually contains 50 to 70% calcium hypochlorite.

Reactions

Calcium hypochlorite is an oxidizing agent. It undergoes vigorous to violent reactions with reducing agents and organics. In aqueous solution, it dissociates to calcium and hypochlorite ions. The hypochlorite ions form hypochlorous acid and molecular chlorine, which coexist in equilibrium.

Analysis

Elemental composition: Ca 28.03%, Cl 49.59%, O 22.38%. Calcium can be measured by various instrumental techniques or wet methods (see Calcium). Hypochlorite ion may be analyzed by ion chromatography. Free chlorine (as Cl_2) in the aqueous solution may be measured by DPD colorimetry or by iodometric titration (see Chlorine).

CALCIUM NITRATE

[10124–37–5]
Formula: $Ca(NO_3)_2$; MW 164.09; also forms a tetrahydrate, $Ca(NO_3)_2 \cdot 4H_2O$ [13477–34–4]
Synonyms: lime nitrate; lime saltpeter; Norwegian saltpeter, nitrocalcite

Uses

Calcium nitrate is used in explosives, matches and pyrotechnics. Other applications are in the manufacture of incandescent mantle; and as an additive to diesel fuel for corrosion inhibition.

Physical Properties

White cubic crystal; hygroscopic; density 2.50g/cm³; melts at 561°C; highly soluble in water; also dissolves in alcohols and acetone.

Thermochemical Properties

$\Delta H_f°$	–244.24 kcal/mol
$\Delta G_f°$	–177.53 kcal/mol
S°	46.18 cal/degree mol
C_ρ	35.71 cal/degree mol

Preparation

Calcium nitrate may be prepared by the reaction of nitric acid with calcium carbonate or calcium sulfide:

$$CaCO_3 + 2HNO_3 \xrightarrow{heat} Ca(NO_3)_2 + CO + H_2O$$

$$CaS + 2HNO_3 \xrightarrow{heat} Ca(NO_3)_2 + H_2S$$

Analysis

Elemental composition: Ca 24.42%, N 17.07%, O 58.50%. Calcium ion in its aqueous solution may be measured by various instrumental techniques or titrimetry (see Calcium). Nitrate ion can be measured by ion–chromatography or using a nitrate ion-selective electrode. The aqueous solutions must be diluted appropriately for such measurements.

Hazard

Calcium nitrate is a strong oxidizing agent. Mixing with organic substances such as fuel oil or hydrocarbons or other oxidizable compounds can cause explosion.

CALCIUM OXIDE

[1305–78–8]
Formula: CaO; MW 56.077
Synonyms: quicklime; lime; burnt lime; unslaked lime; fluxing lime

Uses

Calcium oxide is one of the most important industrial chemicals. It is used in the manufacture of building and construction materials, including bricks, mortar, stucco and plaster. It also is used as a flux in the manufacture of steel.

Other important products made from application of calcium oxide in their manufacturing processes include glass, pulp and paper, aluminum and magnesium. Some other major applications of this compound are in flotation of non-ferrous ores; removal of phosphate and pH control in sewage treatment; neutralization of acid waste effluents; depilatory for hides; drilling fluids; refining cane and beet sugar; in pesticides and fungicides; and as an absorbent for carbon dioxide in the form of soda-lime (a mixture with caustic soda). Also, calcium oxide is used to produce sodium carbonate (Solvay process) and many calcium compounds. Its slaked form, known as slaked lime, $Ca(OH)_2$ has numerous industrial applications (see Calcium Hydroxide).

Before the advent of electricity, calcium oxide was used to produce the so-called "lime light" to spotlight or illuminate the stage. When heated by an oxy-hydrogen flame, it incandesces emitting bright white light.

Physical Properties

Gray-white granular powder or lumps; cubic crystals; density 3.34 g/cm^3; melts at 2,572°C; becomes incandescent when heated to its melting point; vaporizes at 2,850°C; soluble in water forming slaked lime; also soluble in acids with decomposition; practically insoluble in alcohol.

Thermochemical Properties

$\Delta H_f°$	–151.74 kcal/mol
$\Delta G_f°$	–144.19 kcal/mol
S°	9.11 cal/degree mol
C_ρ	10.04 cal/degree mol
ΔH_{fus}	14.1 kcal/mol

Production

Calcium oxide is commercially obtained from limestone. The carbonate is roasted in a shaft or rotary kiln at temperatures below 1,200°C until all CO_2 is driven off. The compound is obtained as either technical, refractory or agricultural grade product. The commercial product usually contains 90 to 95% free CaO. The impurities are mostly calcium carbonate, magnesium carbonate, magnesium oxide, iron oxide and aluminum oxide.

Reactions

Calcium oxide reacts with water forming calcium hydroxide:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

The reaction is highly exothermic, with powdered material.

CaO absorbs CO_2 forming calcium carbonate:

$$CaO + CO_2 \rightarrow CaCO_3$$

With sulfur dioxide, calcium sulfite is the product which slowly oxidizes to calcium sulfate:

$$CaO + SO_2 \rightarrow CaSO_3 \ ;$$

and with hydrogen sulfide the product is calcium sulfide:

$$CaO + H_2S \rightarrow CaS + H_2O$$

Reactions with acids give corresponding calcium salts:

$$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O$$

and with hydrogen halides or their acids, calcium halide is formed:

$$CaO + 2HF \rightarrow CaF_2 + H_2O$$

When pulverized calcium oxide is heated with carbon (crushed coke or anthracite) in an electric furnace, calcium carbide is produced:

$$CaO + 3C \xrightarrow{\text{elevated temperatures}} CaC_2 + CO$$

Analysis

Elemental composition: Ca 71.47%, O 28.53%. Acidified CaO solution may be analyzed for Ca by flame AA or ICP spectrometry (see Calcium). The oxide may be determined by x-ray techniques. The compound may be identified by adding a small quantity slowly and carefully to water (reaction may be violent) and testing the pH (pH should be alkaline). Passage of CO_2 into its clear solution should turn the solution milky due to formation of $CaCO_3$.

Hazard

Skin contact of the powder can cause severe irritation. Mixing the powder form of the compound with water can produce explosive reactions with liberation of large quantities of heat. The reaction occurs after a few minutes delay (Mellor, J. W. 1941. *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 3, pp. 673. London: Longmans Green). The presence of moisture in storage containers or bottles may produce an explosion hazard. Hydration of granular lumps, however, is slow and smooth.

CALCIUM PHOSPHATE, DIBASIC

[7757–93–9]

Formula: $CaHPO_4$; MW 136.06; also occurs as dihydrate $CaHPO_4 \cdot 2H_2O$ [7789–77–7] known as brushite.

Synonyms: calcium hydrogen phosphate; secondary calcium phosphate; bicalcium phosphate

Uses

Dibasic calcium phosphate is found in nature as the mineral monetite. It is used as a food supplement and source of calcium, both in human food and animal feed. It is used in dough conditioner; in several dental products and in medicine. Other applications are in fertilizers, plastics and in the manufacture of glass.

Physical Properties

White triclinic crystal; density 2.92 g/cm^3 (anhydrous) and 2.31 g/cm^3 (dihydrate); hardness 3.5 Mohs; decomposes on heating; inosluble in water and alcohol; K_{SP} 2.7x10^{-7}; soluble in dilute mineral acid.

Preparation

Dibasic calcium hydrogen phosphate may be prepared by several methods. It is precipitated by mixing solutions of calcium chloride and disodium hydrogen phospate:

$$CaCl_2 + Na_2HPO_4 \rightarrow CaHPO_4 + 2NaCl$$

It also is prepared by treating phosphoric acid with lime water (suspension of calcium hydroxide in water). Also, it is obtained as a by-product in the preparation of hydroxypatite. The preparation involves the reaction of phosphoric acid with calcium phosphate.

$$H_3PO_4 + Ca_3(PO_4)_2 \rightarrow 3CaHPO_4$$

Analysis

Elemental composition: Ca 29.46%, H 0.74%, P 22.77%, O 47.04%. The compound may be identified by x-ray analysis. Calcium may be analyzed by AA or ICP spectrometry in aqueous matrix following acid digestion. Phosphorus in the aqueous solution may be determined by colorimetry (see Phosphorus).

CALCIUM PHOSPHATE, MONOBASIC

[7758–23–8]
Formula: $Ca(H_2PO_4)_2$;
MW 234.06; readily forms monohydrate, $Ca(H_2PO_4)_2 \cdot H_2O$
Synonyms: monocalcium orthophosphate; calcium biphosphate; primary calcium phospate, calcium dihydrogen phosphate.

Uses

Monobasic calcium phosphate is primarily used in fertilizers. It also is used in baking powders; as a mineral supplement in food; as a buffer for pH control; and as a stabilizer for plastics.

Physical Properties

Colorless shiny crystals, granules or powder; the impure material is hygroscopic due to the presence of trace phosphoric acid and other impurities; acid taste; density (monohydrate 2.22 g/cm^3); monohydrate loses water at 100°C; decomposes at 200°C; moderately soluble in water; aqueous solution acidic; soluble in dilute mineral acids and acetic acid.

Preparation

Monobasic calcium phosphate may be prepared in the laboratory by the reaction of calcium carbonate with phosphoric acid:

$$CaCO_3 + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + CO_2 + H_2O$$

Fertilizer grade product is obtained by pulverized phosphate rock (tricalcium phosphate) in phosphoric or sulfuric acid and evaporating the solution.

Analysis

Elemental composition: Ca 17.12%, H 1.72%, P 26.47%, O 54.69%

Calcium may be analyzed by AA or ICP spectrophotometry. Its aqueous solution may be analyzed for phosphorus by colorimetry (see Phosphorus).

CALCIUM PHOSPHATE, TRIBASIC

[7758–87–4]
Formula: $Ca_3(PO_4)_3$; MW 310.20
Synonyms: calcium orthophosphate; calcium phosphate; tricalcium phosphate; tertiary calcium phosphate; precipitated calcium phosphate; bone ash (technical product).

Occurrence and Uses

Tribasic calcium phosphate occurs in nature as minerals, oxydapatite, whitlockite, voelicherite, apatite, phosphorite. It has many industrial applications. Some are similar to the monobasic and dibasic salts. It is used in fertilizers, dental products, ceramics and polishing powder. Some other important applications are in plastics as a stabilizer; as an anticaking agent; as a nutrient supplement in cattle food; for clarifying sugar syrup; as a mordant in dyeing textiles; and as a buffer to control pH.

Physical Properties

White amorphous powder; refractive index 1.63; density 3.14 g/cm^3; melts at 1,670°C; insoluble in water; K_{SP} 1.0×10^{-25}; soluble in acids.

Thermochemical Properties

$\Delta H_f°$	–984.9 kcal/mol
$\Delta G_f°$	–928.5 kcal/mol
S°	56.4 cal/degree mol
C_ρ	54.4 cal/degree mol

Preparation

Tribasic calcium phosphate is obtained from naturally occurring minerals for fertilizer applications. The compound may be prepared in the laboratory by the reaction of sodium phosphate with calcium chloride with excess of ammonia. Also, it can be prepared by treatment of calcium hydroxide with phosphoric acid:

$$2H_3PO_4 + 3Ca(OH)_2 \rightarrow Ca_3(PO_4)_2 + 6H_2O$$

Analysis

Elemental composition: Ca 38.76%, P 19.97%, O 41.26%. Calcium may be analyzed by AA, and ICP, or x-ray methods (see Calcium). The orthophosphate anion may be analyzed by colorimetry (see Phosphorus). For colorimetric analysis the insoluble tribasic phosphate must be brought into aqueous phase by dissolving in dilute sulfuric acid.

CALCIUM SULFATE

[7778–18–9]
Formula: $CaSO_4$; MW 136.14; also forms hemihydrate, $CaSO_4 \cdot ½H_2O$ [10034–76–1] and the dihydrate, $CaSO_4 \cdot 2H_2O$ [10101–41–4].

Synonyms: *anhydrous calcium sulfate*-anhydrite; muriacite; karstenite; anhydrous gypsum; anhydrous sulfate of lime *hemihydrate*-plaster of Paris; annalin; dried gypsum; dried calcium sulfate *dihydrate*-gypsum; alabaster; satin spar; mineral white; terra alba; satinite; light spar; selenite; precipitated calcium sulfate; native calcium sulfate

Occurrence

Both the anhydrous calcium sulfate and dihydrate occur in nature, the former as the mineral, anhydrite, and the latter as gypsum. Gypsum is widely distributed in nature. It has been known since ancient times.

Uses

All three forms of calcium sulfate have many important commercial applications. The anhydrous salt, as insoluble anhydrite, is used in cement and as a paper filler. The soluble anhydrite, highly efficient in absorbing moisture, is commonly used as a desiccant for drying gases and liquids. It is known under the trade name Drierite. The most useful form of calcium sulfate, however, is gypsum. It is used in Portland cement, plaster for walls (gypsum plasters), wall boards, blocks, and mortars. It also is used in agriculture for conditioning soil. Gypsum also is used to produce other calcium compounds.

Hemihydrate is commonly used as plaster of Paris in numerous applications. It is used to make gypsum wallboards, molding plasters and pottery plasters. Pottery plasters are used in ceramics, pottery, and artworks.

Plasters made from hemihydrate also find applications in many orthopedic and dental materials and sanitary wares.

Physical Properties

Anhydrous calcium sulfate is a crystalline substance; orthorhombic; the color may vary as white, gray, blue or brick-red; occurs as insoluble anhydrite or porous soluble anhydrite; density 2.96 g/cm^3; hardness 3.5 Mohs; insoluble anhydrite is practically insoluble in water (0.21% at 20°C); soluble anhydrite readily absorbs moisture and is soluble in water.

Hemihydrate is a white fine powder; sparingly soluble in water (3g/L at 25°C); combines with water, setting to a hard mass.

Dihydrate may occur as lumps or powder; density 2.32 g/cm^3; partially loses water on heating at 100°C; slightly soluble in water (2.4 g/L at 25°C); $K_{SP} = 2.4 \times 10^{-5}$; almost insoluble in organic solvents.

Thermochemical Properties

$\Delta H_f°$ (anhydrite)	–342.76 kcal/mol
$\Delta G_f°$ (anhydrite)	–315.93 kcal/mol
S° (anhydrite)	25.50 cal/degree mol
C_ρ (anhydrite)	23.82 cal/degree mol
$\Delta H_f°$ (hemihydrate)	–376.85 kcal/mol
$\Delta G_f°$ (hemihydrate)	–343.41 kcal/mol
S° (hemihydrate)	31.20 cal/degree mol
C_ρ (hemihydrate)	28.54 cal/degree mol
$\Delta H_f°$ (dihydrate)	–483.42 kcal/mol
$\Delta G_f°$ (dihydrate)	–429.60 kcal/mol
S° (dihydrate)	46.40 cal/degree mol
C_ρ (dihydrate)	44.46 cal/degree mol

Manufacture

Gypsum may be produced from the natural mineral by surface quarrying or mining from natural deposits. Natural gypsum is generally found to contain both the anhydrous and dihydrate forms together. Also, it contains a number of impurities, such as, clay, silica, limestone, and magnesium carbonate. The rock is crushed to size as required and calcined. The dihydrate is dehydrated to hemihydrate or anhydrite. The calcination usually is done in a steel cylindrical vessel known as a kettle for several hours under hot air flow at temperatures ranging between 100 to 125°C. Calcination may be carried out under steam pressure. Soluble anhydrite may be produced by further heating the calcined product at temperatures between 200 to 220°C, and may be obtained in fine powder or granule form. Insoluble anhydrite may be produced in a similar manner, however, by calcination over a longer time period. Temperature controls and rate of heatng are crucial factors in the manufacture of various forms of calcium sulfate.

Calcium sulfate also is manufactured by various synthetic reactions. The products, generally known as synthetic gypsums, may be obtained as dihydrate or hemihydrate. Many commercial plants operate on synthetic routes to produce calcium sulfate. It is produced by the reaction of a calcium salt with sulfuric acid or sulfur dioxide:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 3CaSO_4 \cdot 2H_2O + 2H_3PO_4$$

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O$$

$$Ca(OH)_2 + SO_4 \rightarrow CaSO_4 + 2H_2O$$

$$2CaSO_3 + O_2 \rightarrow 2CaSO_4$$

Reactions

Calcium sulfate exhibits high thermal stability. At elevated temperatures, it occurs in anhydrous form. The dihydrate loses its water molecules upon strong heating. When ignited with charcoal, it is reduced to calcium sulfide:

$$CaSO_4 + 2C \xrightarrow{\text{elevated temperature}} CaS + 2CO_2$$

In aqueous solution, the dihydrate, $CaSO_4 \cdot 2H_2O$ (soluble in water) undergoes double decomposition reactions with other soluble salts, precipitating out insoluble salts:

$$CaSO_4 + 2AgNO_3 \rightarrow Ca(NO_3)_2 + Ag_2SO_4$$

Analysis

Elemental composition: Ca 29.44%, S 23.55%, O 47.01%. The compound may be digested with nitric acid and the acid extract may be analyzed for Ca by AA or ICP spectrophotometry. Various x-ray techniques may be applied for the nondestructive identification of the compound. Water of crystallization may be determined by gravimetry following high temperature heating to expel all water from the hydrated crystals.

CALCIUM SULFIDE

[20548–54–3]
Formula: CaS; MW 72.144

Occurrence and Uses

Calcium sulfide occurs in nature as the mineral oldhamite. It has several applications. The ‘luminous’ calcium sulfide is used in phosphors, luminous paints and varnishes. Calcium sulfide also is used as an additive to lubricants; and as a flotation agent in ore extraction.

Physical Properties

Pure compound is white cubic crystal or powder; impure or luminous calcium sulfide is pale yellow to light gray; bitter taste; odor of H_2S in moist air; hygroscopic; refractive index 2.137; hardness 4.0 Mohs; density 2.59 g/cm^3; melts at 2,525°C; slightly soluble in water; insoluble in alcohol; soluble in acids with decomposition.

Thermochemical Properties

$\Delta H_f°$	–115.30 kcal/mol
$\Delta G_f°$	–114.10 kcal/mol
S°	13.50 cal/degree mol
C_ρ	11.33 cal/degree mol

Preparation

Crude calcium sulfide may be obtained by ignition of pulverized calcium sulfate with charcoal. The products also may contain calcium carbonate, sulfite, carbonaceous ash and unreacted calcium sulfate. In the laboratory, pure calcium sulfide may be prepared by heating pure calcium carbonate with hydrogen sulfide and hydrogen at 1,000°C:

$$CaCO_3 + H_2S + H_2 \xrightarrow{1,000°C} CaS + CO + 2H_2O$$

Luminous calcium sulfate is prepared by the ignition of calcium carbonate with sulfur in the presence of small quantities of manganese or bismuth salts.

Reactions

When heated in dry air or oxygen, the compound is oxidized to calcium sulfite and then to the sulfate, $CaSO_4$:

$$CaS + 2O_2 \xrightarrow{heat} CaSO_4$$

Partial decomposition occurs in hot water with the evolution of H_2S:

$$CaS + H_2O \xrightarrow{heat} Ca(OH)_2 + H_2S$$

Reactions with acids evolve H_2S; evaporation and crystallization of the solutions give corresponding calcium salts:

$$CaS + 2HCl \rightarrow CaCl_2 + H_2S$$

Vigorous to violent reactions can occur with oxidizing agents, such as potassium chlorate, potassium nitrate or lead dioxide.

Analysis

Elemental composition: Ca 55.56%, S 44.44%. The compound may be identified from the odor of H_2S evolved when mixed with dilute acids. A paper moistened with lead acetate solution and exposed to liberated H_2S turns black. This is a qualitative test for sulfide. Calcium may be analysed by various instrumental techniques, such as AA or ICP spectroscopy and x-ray techniques. (see Calcium).

CALIFORNIUM

[7440–71–3]
Symbol: Cf; atomic number 98; atomic weight 251 (the principal isotope); californium is a transuranium radioactive actinide element; electron configuration [Rn]$5f^{10}7s^2$; valence state +3; most stable isotope ${}^{251}_{98}$Cf, half-life 800 years; isotope properties are presented below:

isotopes	half–life	decay mode
californium–244	25 min	α –emission
californium–245	44 min	orbital electron capture α –emission
californium–246	35.7 hr.	α –emission
californium–247	2.4 hr.	orbital electron capture
californium–248	350 days	α –emission spontaneous fission
californium–249	360 yr.	α –emission
californium–250	10 yr.	α –emission spontaneous fission
californium–251	800 yr.	α –emission
californium–252	2.55 yr.	α –emission spontaneous fission
californium–253	19 days	positron decay
californium–254	60 days	spontaneous fission

History, Occurrence and Uses

The element was synthesized in 1950 by S. G. Thompson, A. Ghiorso, K. Street, and Glen T. Seaborg, It was named after the state of California. Californium does not occur in nature. It can be synthesized only in microgram amounts in a nuclear reactor. The principal compounds of the element that have been synthesized are the californium trifluoride, CfF_3; californium trichloride, $CfCl_3$; californium oxide, Cf_2O_3; californium oxychloride $Cf(OCl)_3$; and californium hydroxide $Cf(OH)_3$. The element has not yet been obtained in metallic state.

The isotope californium–252 undergoes spontaneous fission generating neutrons. It serves as a convenient source of neutrons for neutron activation analysis, neutron moisture gages, and in the determination of water and oil-bearing layers in well-logging. It is expected to have many other potential applications, including synthesis of other heavy isotopes.

Production

Isotopes of californium may be produced in a cyclotron by neutron irradiation or charged particle bombardment. Lighter isotopes of californium may be produced by bombardment of curium–242 or curium–244 with alpha particles having 35.5 MeV energy:

$$^{242}_{96}\text{Cm} + ^{4}_{2}\text{He} \rightarrow ^{245}_{98}\text{Cf} + 2\,^{1}_{0}n$$

$$^{244}_{96}\text{Cm} + ^{4}_{2}\text{He} \rightarrow ^{247}_{98}\text{Cf} + ^{1}_{0}n$$

The above method was used for producing californium–245 during its first ever synthesis. Heavier isotopes of californium may be obtained by intense neutron irradiation:

$$^{249}_{98}\text{Cf} \xrightarrow{^{1}_{0}n} ^{250}_{98}\text{Cf} + \gamma \xrightarrow{^{1}_{0}n} ^{251}_{98}\text{Cf} + \gamma \xrightarrow{^{3}_{0}n} \ldots ^{254}_{98}\text{Cf}$$

The isotope $^{249}_{98}$Cf may be obtained by β^-decay of $^{249}_{97}$Bk.

This, in turn is produced by successive slow neutron irradiation of curium–244: Californium–254 may be produced by thermonuclear explosion resulting in the reaction of uranium–238 with intense neutron flux followed by a sequence of β^- decays (Cunningham, B. B. 1968. In *Encyclopedia of Chemical Elements,* ed. Clifford A. Hampel, New York: Reinhold Book Co.)

$$^{244}_{96}Cm \xrightarrow{^{1}_{0}n} ^{245}_{96}Cm \xrightarrow{^{1}_{0}n} ^{246}_{96}Cm \xrightarrow{^{1}_{0}n} \ldots \; ^{249}_{96}Cm \xrightarrow{-\beta^-} ^{249}_{97}Bk \xrightarrow{-\beta^-} ^{249}_{98}C\text{f}$$

$$^{238}_{92}\text{U} + 16\,^{1}_{0}n \longrightarrow ^{254}_{92}\text{U} \xrightarrow{\beta-} ^{254}_{93}\text{Np} \xrightarrow{\beta-} ^{254}_{94}\text{Pu} \xrightarrow{\beta-} \ldots ^{254}_{98}\text{Cf}$$

Californium is separated from other elements by fractionation and precipitation, and further purified by solvent extraction or ion exchange.

Health Hazard

Exposure to Cf radiation can cause cancer. Similar to other radioactive elements, californium can accumulate in the skeletal system, causing damage to the red cell forming mechanism.

CARBON

[7440–44–0]

Symbol C; atomic number 6; atomic weight 12.011; a Group IV A (Group 14) nonmetal element; atomic radius 0.77Å; electron configuration $ls^22s^22p^2$; primarily forms tetravalent covalent compounds with linear, triangular (planar) and tetrahedral geometry, with coordination numbers 2, 3, and 4, respectively; electronegativity 2.5; isotopic composition C–12 98.89%, C–13 1.11%; the beta emitter radioisotope C–14 has a half–life of 5,570 years.

Occurrence

Carbon is probably the most widely distributed element on earth. It is found in all living organisms; in coal, petroleum and natural gases; in numerous rocks as carbonates (limestone, dolomite and marble); in the atmosphere as carbon dioxide; and is the basic elemental constituent of all organic compounds. It forms more compounds (with the exception of hydrogen) than all other elements combined. Carbon and hydrogen together, or additionally in combination with oxygen, nitrogen, sulfur, phosphorus, and halogens form over eight million organic compounds.

Carbon also occurs in abundance in the sun, stars and the atmospheres of planets and their moons. The latter consist of carbon dioxide and methane. Its abundance in the earth's outer crust is estimated to be 0.2%.

Elemental carbon has many important applications. The diamond is a precious gem, known to mankind for ages; graphite is used as an electrode and has numerous other applications; carbon–14 isotope is used in carbon dating; and the isotope carbon–13 in tracer studies and NMR. Carbon black is used in paints, pigments and inks. Activated carbon is used as an adsorbent for purification of water and separation of gases. Coke is used for electrothermal reduction of metal oxides to their metals. These applications are discussed below in more detail.

Allotropy

Carbon exists in three allotropic forms; diamond, graphite, and fullerenes, each distinctly differing from others in physical and chemical properties. Diamond [7782–40–0] is one of the hardest substances known. The Mohs hardness is 10.0, the highest in the scale as Mohs reference standard. Its density 3.513 g/cm^3; refractive index 2.417; and melting point about 3,700°C. The carbon atoms in diamonds are arranged in cubic form having stacked layers perpendicular to the diagonals of the cube. Also, the diamond occurs in hexagonal form which is less stable than the cubic form. The hexagonal form of diamond is found in meteorites and can be synthesized.

The diamond is found in natural deposits in many parts of the world. Also, it can be synthesized from graphite or other carbonaceous materials. Graphite can be converted to diamond under high temperatures (about 1,400°C) and very high pressure (in the range 4,000–5,000 atm) in the presence of a metal catalyst such as iron or nickel. Presence of trace impurities can impart different coloration to diamonds. For example, introducing trace boron or nitrogen causes blue or yellow coloration.

Graphite [7440–44–0] is black hexagonal crystal. The hexagonal layer has each carbon atom surrounded by three other carbon atoms. The C–C bond length is 1.415Å. Each network of hexagonal layer is separated from other superposed layers by a distance of 3.35 Å, and is held by weak van der Waal force. Because of this very weak attractive force between each layer, graphite is very soft—probably one of the softest solids, with high lubricity. Its density is 2.25 g/cm^3. Graphite exhibits two manifestations; the stable hexagonal form that commonly occurs at ambient conditions, and a less stable rhombohedral form.

Fullerenes are polyhedral carbon allotropes consisting of large carbon molecules containing 60 to 120 C atoms. [60] Fullerene or fullerene–C60 is made up of arrays of 60 atoms in a roughly spherical shaped molecule. It has a geometry of truncated icosahedron consisting of 20 hexagons and 12 pentagons. The [120] fullerene is a dumbbell shaped dimer of [60]fullerene. Fullerene–C70 is slightly more stable than [60]fullerene. Many other fullerenes are known that have a different number of total carbon atoms per molecule in their five and six membered fused rings. They are strained molecules with moderate stability. The stability of this class of carbon molecules is relatively much lower than diamond or graphite. They decompose when heated at high temperatures. Their decomposition temperatures vary with the number of C atoms in the molecule and its geometric shape. The decomposition temperature of [60]fullerene, one of the most common fullerenes is 750°C.

Fullerenes are found in soot, charcoal and carbon black. They also occur in many other carbonaceous matters. They have also been detected in some meteorites and interstellar matter. In the laboratory they may be produced by passing high electric current through graphite rods and rapidly evaporating the rod in an atmosphere of helium or other inert gases. The fullerene soots produced are dissolved in an organic solvent and separated on a column. Solvent molecules are removed from the crystal by vacuum sublimation. Such preparative methods primarily yield [60]– and [70]fullerenes, and small amounts of higher clusters.

Fullerenes have potential applications in the preparation of carbon support catalyts and diamond films. They have high electrical conductivity and chemical reactivity.

Carbon also is produced and used in other forms; namely, activated carbon, carbon black, and coke, that have many commercial applications. Structurally they are amorphous forms of carbon belonging to the graphites. Activated carbon or activated charcoal has a highly porous honeycomb-like internal structure and adsorbs many gases, vapors, and colloidal solids over its very large internal surface area. Some of its major applications include purification of water and air, air analysis, waste treatment, removal of sulfur dioxide from stack gases, and decolorization of sugar.

Activated carbon is produced by destructive distillation of carbonaceous substances, such as wood, bones, and nut shells. The carbon obtained from distillation is then heated to 800–900°C with steam or carbon dioxide.

Carbon black includes several forms of artificially prepared carbon, such as furnace black, channel black, lamp black, and animal charcoal. It is a finely divided form of carbon consisting of particles of extremely fine size. It is obtained by partial combustion (in 50% required air) of vapors of heavy oil fraction of crude oil in a furnace; or by thermal cracking of natural gas. Carbon black is used in many abrasion-resistant rubber products including tire treads and belt covers. It also is used in typewriter ribbons, printing inks, carbon paper, and paint pigments. It also can be an absorber for solar energy and UV radiation.

Coke is obtained by destructive distillation or carbonization of bituminous coal, coal-tar pitch and petroleum produced during petroleum cracking. Coke from bituminous coal is used to reduce iron ore in blast furnaces; and to produce synthesis gas. Petroleum coke or that obtained from coal-tar pitch is used in electrolytic reduction of aluminum oxide to aluminum and in the preparation of several metal carbides. .

Thermochemical Properties

$\Delta H_f°$ (graphite)	0.0 kcal/mol
$\Delta H_f°$ (diamond)	0.45 kcal/mol
$\Delta H_f°$ ([60]fullerene)	10.16 kcal/mol
$\Delta H_f°$ ([70]fullerene)	9.66 kcal/mol
$\Delta G_f°$ (diamond)	0.69 kcal/mol
S° (graphite)	1.36 cal/degree mol
S° (diamond)	0.57 cal/degree mol
C_ρ (graphite)	2.03 cal/degree mol
C_ρ (diamond)	1.46 cal/degree mol

CARBON DIOXIDE

[124–38–9]

Formula: CO_2; MW 44.009; structure O=C=O, linear molecule, bond angle 180°C; net dipole moment zero.

Occurrence and Uses

Carbon dioxide is found throughout nature. Its concentration in the air is 0.036% by volume. It is the primary component of exhaled air of all animals. It also is the product of oxidation of all carbonaceous matter and an end product of complete combustion. It also is found dissolved in natural waters. It occurs in the earth's crust and in volcanic eruptions.

All plants depend on carbon dioxide and water for their survival, making their food by the process of photosynthesis. Carbon dioxide is found in abundance in the atmospheres of many other planets and their moons throughout the solar system.

Carbon dioxide is a greenhouse gas, which traps the infrared radiation reradiated back by the earth's surface, causing global warming and, therefore, changing the climate. The CO_2 concentration in the atmosphere over a 30-year period from 1960 to 1990 has increased significantly from about 320 to 356 ppm by volume, which is widely attributed to the growth of industrial and automobile CO_2 emission during this period.

Carbon dioxide has extensive commercial applications. Some important applications of this compound include carbonation of beverages; as a fire extinguishing agent; in the manufacture of carbonates; as dry ice (solid CO_2) for refrigeration; as an aerosol propellant; as a shielding gas for welding; as an inert atmosphere in preparation and handling of flammable substances; in cloud seeding; in fumigation of rice; to produce harmless smoke on stage; as an antiseptic; and as a supercritical fluid to extract organic pollutants for their analyses.

Physical Properties

Colorless, odorless and tasteless gas; 1.53 times heavier than air; density 1.80 g/L at 25°C; can be liquefied under pressure; liquefies at –56.6°C at 5.2 atm; density of liquid CO_2 at 0°C and 34 atm 0.914 g/mL; solidifies to white snow-like flakes known as dry ice, density 1.56 g/cm^3 at –79°C; dry ice sublimes to CO_2 gas at –78.5°C; critical temperature 31°C; critical pressure 72.79 atm, critical density 94 cm^3/mol; moderately soluble in water, solubility 173 mL and 88mL CO_2/100 mL water at 0°C and 20°C, respectively; solubility increases with pressure.

Thermochemical Properties

$\Delta H_f°$	–94.05 kcal/mol
$\Delta G_f°$	–94.26 kcal/mol
S°	51.1 cal/degree mol
C_ρ	8.87 cal/degree mol
ΔH_{fus}	2.156 kcal/mol

Production

Carbon dioxide is produced as a by-product in many processes. It is produced as a by-product in the manufacture of lime from calcium carbonate:

$$CaCO_3 \xrightarrow{calcination} CaO + CO_2$$

CO_2 also is derived from synthesis gas which is a mixture of CO, CO_2, H_2 and N_2 from air obtained by steam reforming. Carbon dioxide also is obtained by combustion of natural gas:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

It also is obtained as a by-product in the Haber–Bosch process for the manufacture of ammonia. The method involves passing steam and air over hot coke.

Carbon dioxide also is produced along with ethanol from fermentation of carbohydrates by yeast:

$$C_6H_{12}O_6 \xrightarrow{yeast} 2CO_2 + 2C_2H_5OH$$

In the laboratory, CO_2 may be produced by the reaction of any carbonate with a dilute mineral acid:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

Reactions

Carbon dioxide is slightly acidic in nature. Its aqueous solution is carbonic acid, H_2CO_3 , a weak unstable acid:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Reactions with alkalis yield carbonates:

$$NaOH + CO_2 \rightarrow Na_2CO_3$$

It turns lime water milky due to the formation of calcium carbonate:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

When passed through a solution of alkali or alkaline earth metal sulfide, the corresponding carbonate is produced with deposition of sulfur:

$$BaS + 3CO_2 \rightarrow 2BaCO_3 + S$$

Many metal oxides form carbonates. When passed into an aqueous solution of carbonate, the corresponding bicarbonate is produced:

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$$

When passed into an aqueous solution of chloride salt of alkali or alkaline earth metal, the product is bicarbonate:

$$CaCl_2 + CO_2 + H_2O \rightarrow CaHCO_3 + 2HCl$$

Carbon dioxide reacts with heated calcium metal, forming calcium carbide and calcium oxide:

$$3Ca + CO_2 \xrightarrow{heat} 2CaO + CaC$$

The photosynthetic conversion of carbon dioxide and water in the presence of sunlight and chlorophyll produces carbohydrates, such as glucose and other sugars, and oxygen:

$$6CO_2 + 6H_2O \xrightarrow[chlorophyll]{light} C_6H_{12}O_6 + 6O_2$$

Analysis

Carbon dioxide may be readily analyzed by various instrumental techniques, such as IR, GC, and GC/MS. Many portable infrared analyzers are available commercially for rapid, on site monitoring of CO_2. Also, it can be analyzed by GC using a TCD or an FID. It readily may be identified by mass spectrometry from its characteristic ionic mass 44. Dissolved CO_2 in water may be calculated nomographically from temperature, pH, total dissolved solids, and alkalinity. (APHA, AWWA and WEF.1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington, D.C.: American Public Health Association.)

Toxicity

Although CO_2 is nontoxic, exposure to a high concentration can cause asphyxiation due to lack of oxygen. Exposure to 5 to 10% volume in air can be fatal.

CARBON DISULFIDE

[75–15–0]
Formula: CS_2; MW 76.139
Synonym: carbon bisulfide; dithiocarbonic anhydride

Uses

Carbon disulfide is used in the manufacture of rayon, cellophane, electronic vacuum tubes, and xanthogenates. It is used to make carbon tetrachloride. It also is used as an industrial solvent; and as an analytical solvent. Because of its low response to GC-FID, it is used widely in air analysis of organic compounds.

Physical Properties

Colorless liquid; commercial grade has a pungent disagreeable odor, in its purest form the odor is sweet and pleasant; flammable; refractive index 1.6295; density 1.261 g/mL at 20°C; boils at 46.3°C; freezes at –110.8°C; critical temperature 279°C, critical pressure 77.97 atm, critical volume 173 cm^3/mol; slightly soluble in water, 0.29 g/100g at 20°C; soluble in alcohol, ether, benzene, chloroform, and oils; forms an azeotrope with water (CS_2: H_2O = 97.2%)

Thermochemical Properties

$\Delta H_f°$	21.44 kcal/mol
$\Delta G_f°$	15.60 kcal/mol
S°	36.17 cal/degree mol
C_ρ	18.10 cal/degree mol
ΔH_{vap} (at bp)	84.1 cal/g
ΔH_{fus}	1.05 kcal/mol

Preparation

Carbon disulfide is manufactured by heating sulfur vapor with charcoal, and condensing vapors of the compound formed. Alternatively, it may be obtained by heating sulfur with natural gas or petroleum fractions. Instead of sulfur, H_2S may be used. The reaction occurs at very high temperatures. The product obtained in these reactions may contain sulfur impurities. Carbon disulfide is purified by distillation.

Analysis

Elemental composition: C 15.77%, S 84.23% carbon disulfide. It may be analyzed by GC using a sulfur chemiluminescence detector or by GC/MS. A concentration of 1 ppm in the air may be measured by mass spectrometry. The primary characteristic ionic mass for identification of this compound by mass spectrometry is 76. Many GC columns are available commercially.

Hazard

Carbon disulfide is an extremely flammable liquid, the closed cup flash point being –22°F (–30°C). Its autoignition temperature is 90°C (194°F). Its vapors form explosive mixtures with air, within a wide range of 1.3 to 50.0% by volume in air. Reactions with certain substances can progress to explosive violence. They include finely divided metals, alkali metals, azides, fulminates, and nitrogen dioxide.

The compound is toxic. Repeated inhalation of vapors can produce headache, fatigue, dizziness, nervousness, psychosis, tremors, loss of appetite, and gastric problems. Ingestion of the liquid can be fatal to humans.

CARBON MONOXIDE

[630–08–0]
Formula: CO; MW 28.01

Occurrence and Uses

Carbon monoxide is found in varying concentrations in unventilated and confined spaces resulting from partial oxidation of carbonaceous matter. Burning wood, paper, kerosene, or other organic materials in inadequate air can produce this gas. It also is found in automobile exhaust and tobacco smoke emissions.

Carbon monoxide has many important industrial applications. It is used in Fischer–Tropsch process to produce liquid or gaseous hydrocarbons, synthetic fuels and many oxygenated derivatives. This process was applied before and during World War II to produce synthetic fuels. Probably the most important application of this compound involves production of oxygenated organics in the Synthol process and in oxo synthesis. Many aliphatic alcohols, alehydes and ketones are produced by catalytic hydrogenation of carbon monoxide. Oxo synthesis produces aldehydes from olefins. Carbon monoxide also is the starting material for preparing metal carbonyls. In metallurgy, it is used as a reducing agent to reduce oxides. In the Mond process it recovers nickel.

Physical Properties

Colorless, odorless and tasteless gas; density 1.229 g/L; very flammable, burns in air with a bright blue flame; liquefies at –191.5°C; solidifies at –205°C; critical temperature –140°C, critical pressure 34.53 atm, critical volume 93 cm^3/mol; soluble in chloroform, acetic acid, ethyl acetate, ethanol, and ammonium hydroxide; sparingly soluble in water (2.3 mL/100 mL water at 20°C).

Thermochemical Properties

$\Delta H_f°$	–26.41 kcal/mol
$\Delta G_f°$	–32.79 kcal/mol
S°	47.25 cal/degree mol
C_ρ	6.96 cal/degree mol
ΔH_{fus}	0.198 kcal/mol
ΔH_{vap}	1.44 kcal/mol

Production

Carbon monoxide may be prepared by several methods. Large scale production is carried out by controlled oxidation of natural gas or by the catalytic steam reforming of methane or light petroleum fractions. The products obtained are mixtures of CO, H_2, and CO_2. It also is made by gasification of coal and coke with oxygen at about 1,500°C.

Removal of CO_2 may be achieved by passing the gaseous products through an aqueous base. Alternatively, CO may be recovered by complexing with $CuAlCl_4$ in benzene or toluene. In pure form it may be prepared by passing a mixture of oxygen and carbon dioxide over incandescent graphite or coke.

Alternatively, carbon monoxide may be prepared by action of steam either on natural gas or on hot coke or coal. In the laboratory, CO may be produced by heating $CaCO_3$ with zinc dust; or by dehydration of formic acid:

$$CaCO_3 + Zn \xrightarrow{heat} CaO + CO + ZnO$$

$$HCOOH \xrightarrow{heat+catalyst} CO + H_2O$$

Reactions

Many CO reactions are industrially important; some of which are outlined briefly below:

Reaction with steam catalyzed by ZnO–CuO or Fe–Cr yields hydrogen. This reaction, known as “water gas shift,” is a source of industrial hydrogen.

$$CO + H_2O \xrightarrow{catalyst} CO_2 + H_2$$

The Fischer-Tropsch reaction involves reduction of CO with H_2 and combination with methanol and olefins in presence of various catalysts to produce an array of oxygenate products of high industrial values.

Reduction with H_2 in the presence of Fe, Ni, or Ru produces methane and other alkanes along with oxygenates.

$$CO + 3H_2 \xrightarrow{Fe/Ru} CH_4 + H_2O$$

$$CO + H_2 \xrightarrow{\sim 250°C} \underset{\text{(formaldehyde)}}{HCHO}$$

$$CO{+}2H_2 \xrightarrow{Zn/Cu} \underset{\text{(methanol)}}{CH_3OH} \xrightarrow{CO} \underset{\text{(acetic acid)}}{CH_3COOH} \xrightarrow{methanol} \underset{\text{(methyl acetate)}}{CH_3COOCH_3}$$

$$HCHO \xrightarrow{CO,H_2} \underset{\text{(glyoxal)}}{HOCH_2 \cdot CHO} \xrightarrow{H_2} \underset{\text{(ethylene glycol)}}{(CH_2OH)_2}$$

$$CO + 2H_2 \xrightarrow{Zn/Cu-225°C} CH_3OH \xrightarrow{CO,H_2} \underset{\text{(acetaldehyde)}}{CH_3CHO} + \underset{\text{(ethanol)}}{CH_3CH_2OH}$$

$$2CO + 3H_2 \xrightarrow[\text{catalyst}]{250°F} \underset{\text{(ethylene glycol)}}{(CH_2OH)_2}$$

Oxo reaction or hydroformylation reaction involves addition of a hydrogen atom and a formyl group (–CHO) to C=C double bond of an olefin making both anti–Markovnikov and Markovnikov products:

$$RCH = CH_2 \xrightarrow[\text{180°C, Co catalyst}]{CO/H_2\text{, 200 atm}} RCH_2CH_2(CHO) \text{ anti-Markovnikov}$$

$$RCH = CH_2 \xrightarrow[\text{180°C, Co catalyst}]{CO/H_2\text{, 200 atm}} RCH(CHO) \text{ Markovnikov addition}$$

Oxo reactions give both linear and branched–chain aldehydes and alchols.

Reppe reaction involves carbonylation of methanol to acetic acid and methyl acetate and subsequent carbonylation of the product methyl acetate to acetic anhydride. The reaction is carried out at 600 atm and 230°C in the presence of iodide-promoted cobalt catalyst to form acetic acid at over 90% yield. In the presence of rhodium catalyst the reaction occurs at milder conditions at 30 to 60 atm and 150–200°C. Carbon monoxide can combine with higher alcohols, however, at a much slower reaction rate.

Carbonylation of acetic acid to higher carboxylic acids can occur in presence of ruthenium/iodide catalysts. The reaction involves reduction and several carbonylation steps. The overall reaction may be written as follows:

$$CH_3COOH + CO + 2H_2 \longrightarrow CH_3CH_2COOH + H_2O$$

Carbonylation of olefins produces aldehydes that are converted to other derivatives. Reaction with ethylene yields acrolein:

$$CH_2{=}CH_2 + CO \rightarrow H_2C{=}CHCHO$$

Carbonylation of butadiene at 300 atm, catalyzed by dicobalt octacarbonyl in presence of pyridine and subsequent methylation produces methyl ester of adipic acid. The overall reaction is as follows:

$$CH_2{=}CH{-}CH{=}CH_2 + 2CO + 2CH_3OH \xrightarrow[\text{pyridine}]{\text{300 atm}} CH_3OOC{-}CH_2{-}\,{-}CH_2{-\!-}CH_2{-}CH_2{-}COOCH_3$$

Hydrolysis of the ester forms adipic acid, used to manufacture nylon–6.

Carbonylations of nitroaromatics are used to synthesize an array of products including amines, carbamates, isocyanates, ureas and azo compounds. These reactions are catalyzed by iron, ruthenium, rhodium and palladium complexes. For example, carbonylation of nitrobenzene in the presence of methanol produces a carbamate:

$$C_6H_5NO_2 + 3CO + CH_3OH \xrightarrow{\textit{catalyst}} C_6H_5NHC(O)OCH_3 + 2CO_2$$

Oxidative carbonylation reactions have been employed successfully to produce a variety of industrial products. The reaction involves carbonylation in the presence of oxygen or oxidizing agents. These reactions occur at 150–200°C and 50 to100 atm in the presence of palladium or other noble metal catalysts. Synthesis of oxalate ester to produce ethylene glycol, carbonylation of aniline to obtain alkylphenylcarbamate, and synthesis of dimethylcarbonate are some examples of such oxidative addition of carbon monoxide. The overall equations for these reactions are:

$$2RONO + 2CO \xrightarrow{\textit{catalyst}} (COOR)_2 + 2NO$$

where R is an alkyl group; RONO is obtained by the reaction:

$$2NO + 2ROH + \tfrac{1}{2}O_2 \rightarrow 2\,RONO + H_2O$$

$$C_6H_5NH_2 + CO + C_2H_5OH + \tfrac{1}{2}O_2 \xrightarrow[PdCl_2/CuCl_2]{\text{165°C, 83 atm}} \underset{\text{(ethylphenylcarbamate)}}{C_6H_5NHCOOC_2H_5 + H_2O}$$

$$2CH_3OH + C_4H_9O{-\!-}OC_4H_9 + CO \xrightarrow{\textit{Pd–Cu}} \underset{\text{(dimethylcarbonate)}}{(CH_3O)_2C{=}O + 2C_4H_9OH}$$

Carbon monoxide reacts with many finely divided metals under pressure, forming carbonyls:

$$4CO + Ni \longrightarrow \underset{\text{(nickel tetracarbonyl)}}{Ni(CO)_4}$$

$$5CO + Fe \xrightarrow{catalyst} \underset{\text{(iron pentacarbonyl)}}{Fe(CO)_5}$$

In liquid ammonia, CO reacts with alkali metals forming white solid metal carbonyls.

Carbon monoxide thermally decomposes to carbon and CO_2 when heated from 500 to 700 °C; while catalytic decomposition occurs at ambient temperatures in presence of Pd/silica gel or MnO_2/CuO catalysts.

Analysis

Elemental composition: C 42.88%, O 57.12%. Carbon monoxide may be identified and determined quantitatively at low ppm level by infrared sensors. Such CO detectors are commercially available. Also, it can be analyzed by GC using TCD or FID or by GC/MS. The characteristic ion mass for CO identification is 28 (same as N_2 or ethylene, both of which can interfere).

Hazard

Carbon monoxide is a highly flammable and poisonous gas. Its flammable limits in air are 12.5 to 74.2% by volume, and the autoignition temperature 700°C. It explodes when exposed to flame. Reactions with interhalogen compounds, such as, bromine pentafluoride or halogen oxides can cause explosion. It forms explosive products with sodium or potassium that are sensitive to heat and shock.

Carbon monoxide binds to hemoglobin, the oxygen carrier in blood, forming carboxyhemoglobin. This prevents transport of oxygen through blood into all tissues in the body. The toxic symptoms are headache, dizziness, weakness, nausea, vomiting, loss of coordination, respiratory depression, decreased pulse rate, collapse, and unconsciousness. Brief exposure to high concentrations of this gas can cause death from asphyxiation. A 5 minute exposure to 5,000 ppm can be lethal to humans.

CARBON SUBOXIDE

[504–64–3]
Formula: C_3O_2; MW 68.032; Structure O=C=C=C=O
Synonyms: tricarbon dioxide; 1,2–propadiene–1,3–dione

Uses

Carbon suboxide is used in the preparation of malonates; and as an auxiliary to improve dye affinity of fibers.

Physical Properties

Colorless gas; strong, pungent odor; gas density 2.985 g/L; liquid density 1.114 g/mL at 0°C; refractive index 1.4538 (at 0°C); vapor pressure 588 torr at 0°C; liquefies at 6.8°C; freezes at –111.3°C; burns with a blue sooty flame; reacts with water. The compound is unstable, polymerizing on storage.

Preparation

Carbon suboxide is prepared by dehydration of malonic acid with phosphorus pentoxide in vacuum at 140 to 150°C:

$$CH_2(COOH)_2 \xrightarrow[150°C,vacuum]{P_2O_5} C_3O_2 + 2H_2O$$

Alternatively, the compound may be prepared by thermal dissociation of diacetyltartaric anhydride.

Reactions

Carbon suboxide decomposes slowly in water giving malonic acid:

$$C_3O_2 + 2H_2O \rightarrow HOOCCH_2COOH$$

Reaction with ammonia gives malonamide:

$$C_3O_2 + 2NH_3 \rightarrow H_2NCOCH_2CONH_2$$

Similar reaction occurs with amines and imines; the decomposition is rapid:

$$C_3O_2 + 2NH(C_2H_5)_2 \rightarrow (C_2H_5)_2NCOCH_2CON(C_2H_5)_2$$

Photolysis produces unstable dicarbon oxide, C_2O, which reacts with olefins (Cotton, F.A., G.Wilkinson, C.A. Murillo and M. Bochmann, 1999. In *Advanced Inorganic Chemistry*, 6th ed. p 226, NY: Wiley Interscience). C_3O_2 polymerizes slowly at ambient temperature forming yellow to violet products. The products are soluble in water.

Analysis

Elemental composition: C 52.96%, O 47.04%. It may be analyzed by treatment with water. The product malonic acid formed may be measured quantitatively by direct injection of aqueous solution into a GC for FID detection. Alternatively, the aqueous solution may be evaporated and the residue may be derivatized to methyl ester and identified by mass spectrometry. Also, the gas may react with ammonia or an amine, and the amide derivative may be identified and quantitatively determined by GC–FID, GC–NPD, GC/MS or infrared techniques.

Hazard

Carbon suboxide forms explosive mixtures in air. The lower and upper explosive limits are 6 to 30% by volume in air, respectively. The gas is a strong lacrimator and an irritant to eyes, nose and respiratory tract. Exposure to high concentations is dangerous. .

CARBON TETRACHLORIDE

[56–23–5]

Formula: CCl_4; MW 153.82; tetrahedral structure; a nonpolar molecule with zero dipole moment.

Synonyms: tetrachloromethane; perchloromethane

Uses

Carbon tetrachloride is used in refrigerants; in fumigants for crops; in metal degreasing; and in the manufacture of semiconductors. It also is used as a solvent in many industrial processes. It is an excellent solvent for organic compounds that are nonpolar or have low polarity.

Physical Properties

Colorless noncombustible liquid; chloroform-like odor; refractive index 1.4601; density 1.5867g/mL at 20°C; boils at 76.8°C; freezes at –23°C; critical temperature 283.5°C, critical pressure 44.57 atm, critical volume 276 cm^3/mol; practically insoluble in water; soluble in alcohol, ether, chloroform and benzene.

Thermochemical Properties

$\Delta H_f°$	–32.37 kcal/mol
$\Delta G_f°$	–15.60 kcal/mol
S°	51.72 cal/degree mol
C_ρ	31.49 cal/degree mol
ΔH_{fus}	0.78 kcal/mol

Production

Carbon tetrachloride is made by the reaction of carbon disulfide and chlorine in the presence of a catalyst, such as iron or antimony pentachloride:

$$CS_2 + 3Cl_2 \xrightarrow{Fe} CCl_4 + S_2Cl_2$$

Sulfur chloride is removed by treatment with caustic soda solution. The product is purified by distillation.

Alternatively, CCl_4 may be prepared by heating a mixture of chlorine and methane at 250 to 400°C.

$$CH_4 + 4Cl_2 \xrightarrow{250-400^\circ C} CCl_4 + 4HCl$$

Analysis

Elemental composition: C 7.81%, Cl 92.19%. Carbon tetrachloride may be analyzed by GC or GC/MS. For GC determination, an FID or a halogen-specific detector such as ECD or HECD may be used. Trace concentrations in aqueous matrix or soil, sediments or solid wastes may be determined by ‘purge and trap’ or thermal desorption techniques followed by GC or GC/MS measurements. The characteristic masses for identification of CCl_4 by GC/MS are 117, 119 and 121.

Different sampling techniques are documented for analysis of CCl_4 in the air (Patnaik, P. 1997. *Handbook of Environmental Analysis*. Boca Raton, FL: Lewis Publishers).

Toxicity

Carbon tetrachloride is a poison and also a carcinogen. The acute toxicity of this compound in humans is of low order. However, the ingestion of the liquid can be fatal, death resulting from acute liver or kidney necrosis. (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons.) The acute poisoning effects are headache, dizziness, fatigue, stupor, nausea, vomiting, diarrhea, and liver damage. Chronic exposure can damage both liver and kidney. Carbon tetrachloride also is a suspected human carcinogen. It causes liver and thyroid cancers in experimental animals.

CARBONYL CHLORIDE

[75–44–5]
Formula: $COCl_2$; MW 98.915
Synonyms: phosgene; carbon oxychloride; chloroformyl chloride; carbonic dichloride

Uses

Carbonyl chloride is used in the manufacture of isocyanates, polycarbonate resins, polyurethane, carbamate pesticides and herbicides and dyes. It was used as a war gas.

Physical Properties

Colorless gas at ambient temperature; strong, pungent odor; density of the gas 4.045 g/L at 25°C; density of the liquid 1.392 g/mL at 4°C; liquefies to a light yellow fluid at 8.2°C; freezes at –128°C; critical temperature 182°C, critical pressure 55.96 atm, critical volume 190 cm^3/mol; slightly soluble in water with slow hydrolysis; soluble in benzene, toluene and acetic acid.

Thermochemical Properties

$\Delta H_f°$	–52.30 kcal/mol
$\Delta G_f°$	–48.90 kcal/mol
S°	67.74 cal/degree mol
C_ρ	13.78 cal/degree mol
ΔH_{fus}	1.37 kcal/mol

Preparation

Phosgene is prepared by the reaction of carbon monoxide and chlorine. The mixture of these gases is passed over activated carbon:

$$CO + Cl_2 \xrightarrow{\text{activated carbon}} COCl_2$$

Alternatively, phosgene can be made by reacting carbon monoxide with nitrosyl chloride, or by treating carbon tetrachloride with oleum.

Reaction

Phosgene reacts with water forming hydrochloric acid and carbon dioxide:

$$COCl_2 + H_2O \rightarrow CO_2 + 2HCl$$

When heated at elevated temperatures, it decomposes to carbon monoxide and chlorine. The equilibrium constant, Kc at 360°C for the reaction

$$COCl_2\ (g) \xrightarrow{360^\circ} CO\ (g) + Cl_2\ (g) \text{ is } 8.3\text{x}10^{-4}$$

In a closed container at an initial concentration of 0.5 mol/L, the above Kc value corresponds to a 4% decomposition. However, if the concentration is decreased to 0.01 mol/L, the corresponding decomposition of phosgene to carbon monoxide and chlorine at 360°C is 25%.

Reaction with ammonia yields urea:

$$COCl_2 + 4NH_3 \rightarrow NH_2CONH_2 + 2NH_4Cl$$

Reaction with alcohol can produce two different types of products. While two molar equivalent of alcohol yields dialkyl carbonate, with one molar equivalent of alcohol the product is an alkyl chloroformate:

$$COCl_2 + 2CH_3CH_2OH \rightarrow CH_3CH_2OC(O))CH_2CH_3 + 2HCl$$

(diethyl carbonate)

$$ROH + COCl_2 \rightarrow ROCOCl + HCl$$

$$C_6H_5CH_2OH + COCl_2 \rightarrow C_6H_5CH_2OCOCl + HCl$$

(benzyl alcohol) (benzyl chloroformate)

Analysis

Elemental composition: C 12.14%, O 16.17%, Cl 71.69%. Phosgene can be analyzed by GC using FID or a halogen-specific detector; or by GC/MS. Ambient air may be collected in a metal container placed in an argon bath or condensed into any other type cryogenically cooled trap. Alternatively, the air may be collected in a Tedlar bag. The sampled air may be sucked by a condensation mechanism into the GC column.

Carbonyl chloride in air at maximum allowable concentration may be measured by colorimetry. Prepare a solution containing 5% ρ–dimethylaminobenzaldehyde and 5% diphenylamine in carbon tetrachloride. Soak a paper in this solution. Allow it to dry. The color of the paper turns from yellow to deep orange in the presence of carbonyl chloride.

Toxicity

The gas is treacherously toxic, as its effects cannot be recognized immediately. The initial symptoms are mild. Death can result from severe congestion of lungs or pneumonia several hours after exposure. Toxicity is due to HCl forming from its reaction with water. The symptoms are coughing, burning of the throat, choking, chest pain, vomiting, difficulty in breathing, and cyanosis. Inhalation of this gas at 100 ppm concentration in the air for 30 minutes may be fatal to humans. (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons.)

CARBONYL FLUORIDE

[353–50–4]
Formula: COF_2; MW 66.01
Synonyms: carbon oxyfluoride; carbonyl difluoride; fluoroformyl fluoride; fluorophosgene

Uses

No commercial application of this compound is known.

Physical Properties

Colorless gas; pungent odor; hygroscopic; unstable; liquid density 1.139 g/mL (at –114°C); liquefies at –83.1°C; solidifies at –114°C; decomposes in water.

Thermochemical Properties

$\Delta H_f°$	–151.7 kcal/mol
$\Delta G_f°$	–148.0 kcal/mol
S°	61.78 cal/degree mol
C_ρ	11.19 cal/degree mol

Preparation

Carbonyl fluoride is prepared by the reaction of carbon monoxide with fluorine gas or silver fluoride:

$$CO + F_2 \rightarrow COF_2$$

Also, it may be produced by the action of carbon monoxide with bromine trifluoride, BrF_3.

Analysis

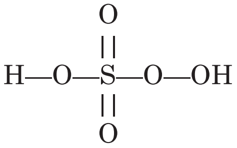
Elemental composition: C 18.19%, F 57.57%, O 24.24%. Carbonyl fluoride may be analyzed by FTIR, GC or GC/MS. For the GC analysis, it may be transported with the carrier gas helium from the reaction vessel into a cryogenically cooled injector port, then thermally desorbed and analysed by FID. The system should be free of moisture. The characteristic ions for mass spectroscopic identification are 66, 26, and 40.

Toxicity

Carbonyl fluoride is a strong irritant to the eyes, nose and respiratory tract. Contact with skin can cause irritation. Prolonged exposure to high concentrations of this gas is lethal.

CARO'S ACID

[7722–86–3]
Formula: H_2SO_5; MW 114.08;
Structure:



$$\mathrm{H{-}O{-}\underset{\underset{\displaystyle O}{||}}{\overset{\overset{\displaystyle O}{||}}{S}}{-}O{-}OH}$$

Synonyms: peroxymonosulfuric acid; persulfuric acid: sulfomonoperacid

Uses

Caro's acid is used in the preparation of dyes and bleaching agents. It also is used as a strong oxidizing reagent to convert ketones to lactones, to convert olefins to glycols and esters, and to analyse pyridine, aniline and many alkaloids.

Physical Properties

White crystalline solid; unstable, decomposes at 45°C; commercial product is a syrupy liquid containing equal parts of Caro's acid and sulfuric acid; stored at dry ice temperature; very soluble in water.

Preparation

Caro's acid may be prepared by several methods depending on what form of the reagent is desired. Most commonly, it is made by treating potassium perfulfate ($K_2S_2O_8$) with sulfuric acid. The dry form is prepared by slowly stirring 100 g $K_2S_2O_8$ into 60 mL of concentrated H_2SO_4, followed by adding 300 g potassium sulfate. A liquid Caro's acid is obtained by slowly stirring $K_2S_2O_8$ into three times the mass of H_2SO_4. The dilute form of the reagent may be obtained by either mixing $K_2S_2O_8$ to 40% H_2SO_4 or by treating $K_2S_2O_8$ with H_2SO_4 and adding ice to the mixture.

Alternatively, Caro's acid may be prepared from hydrogen peroxide by treatment with either chlorosulfonic acid or with H_2SO_4 at –40°C. A 90% H_2O_2 is used in the preparation.

Caro's acid is a strong oxidizing agent and is very unstable. All laboratory preparations must be carried out in an explosion-proof fume hood under temperature-controlled conditions and in the absence of impurities and oxidizable substances.

Hazard

Many accidents have been reported involving the preparation and the use of this compound. The compound is sensitive to heat and shock. Reactions with organic matter, finely divided metals and other readily oxidizable substances can be violent to explosive. It is a strong irritant to skin, eyes and mucous membranes.

CERIC AMMONIUM NITRATE

[16774–21–3]
Formula: $(NH_4)_2Ce(NO_3)_6$; MW 548.22
Synonyms: ammonium ceric nitrate; ammonium hexanitratocerate (IV)

Uses

Ceric ammonium nitrate is used as a volumetric oxidizing reagent in many oxidation-reduction titrations. Cerium(IV) ion is a strong oxidant similar to permanganate ion. It is the most widely-used primary standard among all Ce(IV) compounds. Other applications of this compound are in organic oxidation reactions; and as a catalyst in polymerization of olefins.

Physical Properties

Reddish-orange monoclinic crystals; very soluble in water.

Preparation

Ceric ammonium nitrate is prepared by electrolytic oxidation of cerous nitrate in nitric acid to ceric nitrate, followed by the addition of ammonium nitrate solution. It is separated from the solution by crystallization. It may be prepared alternatively by dissolving cerium(II) oxide, $CeO \cdot H_2O$ in concentrated nitric acid followed by treatment with ammonium nitrate.

Reactions

The most important reactions of this compound are the oxidations, attributed to Ce^{4+} ion in the solution. The standard reduction potential E° for the formal half-reaction: $Ce^{4+} + e^- \longleftrightarrow Ce^{3+}$ in 1 *M* H_2SO_4 is 1.44 V. The oxidizing strength is comparable to permanganate (MnO_4^-), bromate (BrO_3^-), and dichromate ($Cr_2O_7^{2-}$) anions. Analytical applications involve reactions with reductants such as sodium oxalate ($Na_2C_2O_4$) or arsenic (III) oxide (As_2O_3) in the presence of iron, with ferroin (1,10–phenanthroline iron(II) complex) as the indicator.

Analysis

Elemental compostion: Ce 25.56%, H 1.47%, N 20.44%, O 52.53%. The aqueous solution of the compound may be analyzed for Ce by AA or ICP spectrophotometry. Also, the solution may be measured for NH_4^+ ion by ammonium ion-selective electrode and the NO_3^- ion by nitrate ion-specific electrode, ion chromatography or cadmium-reduction colorimetry. For all these measurements, the solution may require sufficient dilutions. For quantitation, its solution may be standardized by titration with a reducing agent such as sodium oxalate in the presence of iron and ferroin indicator.

Hazard

The compound is a powerful oxidizing agent. Precautions should be taken to avoid accidental contacts with orgnaic or other readily oxidizable substances.

CERIUM

[7440–45–1]
Symbol: Ce; atomic number 58; atomic weight 140.115; a rare-earth metal; a lanthanide series inner-transition *f*–block element; metallic radius (alpha form) 1.8247Å(CN=12); atomic volume 20.696 cm^3/mol; electronic configuration $[Xe]4f^15d^16s^2$; common valence states +3 and +4; four stable isotopes; Ce–140 and Ce–142 are the two major ones, their percent abundances 88.48% and 11.07%, respectively. Ce–138 (0.25%) and Ce–136(0.193%) are minor isotopes; several artificial radioactive isotopes including Ce–144, a major fission product ($t_{½}$ 284.5 days), are known.

Occurrence and Uses

The element was discovered by Klaproth in 1803 and also in the same year by Berzelius and Hisinger. It is named after the asteroid Ceres. Cerium is found in several minerals often associated with thorium and lanthanum. Some important minerals are monazite, allanite, cerite, bastnasite, and samarskite. It is the most abundant element among all rare-earth metals. Its abundance in the earth's crust is estimated to be 66 mg/kg, while its concentration in sea water is approximately 0.0012 microgram/L.

The compounds of cerium have many important industrial applications, especially in the glass industry, or as catalysts (see under individual compounds). The metal itself has many uses.

Misch metal, an alloy of cerium with other lanthanides is a pyrophoric substance and is used to make gas lighters and ignition devices. Some other applications of the metal or its alloys are in solid state devices; rocket propellant compositions; as getter in vacuum tubes; and as a diluent for plutonium in nuclear fuel.

Physical Properties

Greyish lustrous metal; malleable; exhibits four allotropic modificatins: the common γ–form that occurs at ordinary temperatures and atmospheric pressure, β–form at –16°C, α–form below –172°C, and δ–form at elevated temperatures above 725°C; crystal structure—face-centered cubic type (γ–Ce); density 6.77 g/cm^3; melts at 799°C; vaporizes at 3,434°C; electrical resistivity 130 microohm.cm (at the melting point); reacts with water.

Thermochemical Properties

ΔH° (cry)	0.0
ΔH° (g)	101.1 kcal/mol
$\Delta G_f°$ (g)	92.02 kcal/mol
S° (cry)	17.21 cal/degree mol
S° (g)	45.84 cal/degree mol
C_ρ (cry)	6.43 cal/degree mol
C_ρ (g)	5.52 cal/degree mol
ΔH_{fus}	1.30 kcal/mol

Production

Cerium is obtained from its ores by chemical processing and separation. The process involves separation of cerium from other rare-earth metals present in the ore. The ore is crushed, ground, and treated with acid. The extract solution is buffered to pH 3–4 and the element is precipitated selectively as Ce^{4+} salt. Cerium also may be separated from other metals by an ion-exchange process.

Also, the metal may be obtained by high temperature reduction of cerium(III) chloride with calcium:

$$2CeCl_3 + 3Ca \xrightarrow{\text{high temperature}} 2Ce + 3CaCl_2$$

Reactions

The chemical properties of cerium, like all other elements, are governed largely by the electrons in its outermost shells. In the rare earth elements, the energies of 4*f*, 5*d*, and 6*s* orbitals are very close. Cerium, which has two 6*s*, one 5d and one 4f electrons can, therefore, exhibit the oxidation states of either +3 or +4 by the loss of either two *s* and one *d* electrons or an additional one *f* electron, respectively. Some examples of Ce^{3+} (cerous) compounds are Ce_2O_3, $Ce(OH)_3$, $Ce_2(SO_4)_3$, Ce_2S_3, $Ce(NO_3)_3$ and $Ce_2(CO_3)_3$. Similarly, it forms many ceric compounds in +4 oxidation state, such as CeO_2, $Ce(SO_4)_2$, $CeCl_4$ and CeF_4. Compounds in +2 oxidation states are also known. These include CeH_2, CeS and CeI_2.

The metal is stable in dry air at ordinary temperatures. Upon heating, it converts to ceric oxide, CeO_2. The finely divided metal may ignite spontaneously. It is oxidized in moist air at ambient temperatures. It reacts with water forming cerium(III) hydroxide.

Reactions with dilute mineral acids yield the corresponding salts:

$$Ce + 2HCl \rightarrow CeCl_2 + H_2$$

It forms cerium(II) hydride, CeH_2, when heated under hydrogen. Reaction with H_2S yields cerium sulfide, Ce_2S_3.

The standard redox potential of the reaction $Ce^{3+} + 3e^- \rightarrow Ce$ is –2.2336 V. The metal undergoes single replacement reactions, displacing less electropositive metals from their salts in solution or melt:

$$2Ce + 3HgI_2 \rightarrow 2CeI_3 + 3Hg$$

Analysis

Cerium may be analyzed in solution by AA or ICP techniques. The metal or its compounds are digested in nitric acid, diluted appropriately prior to analysis. Also, it may be measured by ICP/MS at a still lower detection level (low ppt). The metal may be analyzed nondestructively by x-ray techniques.

CERIUM(III) CHLORIDE

[7790–86–5]
Formula: $CeCl_3$; MW 246.47: forms heptahydrate, $CeCl_3 \cdot 7H_2O$, [18618–55–8]
Synonym: cerous chloride

Uses

Cerium(III) chloride is used to prepare cerium metal and other cerium salts. It also is used as a catalyst in olefin polymerization, and in incandescent gas mantles.

Physical Properties

White, very fine powder; hexagonal crystal system; heptahydrate is yellow orthogonal crystal and hygroscopic; density of anhydrous salt 3.97 g/cm³; melts at 817°C; vaporizes at 1,727°C; heptahydrate begins to lose water above 90°C and becomes anhydrous at about 230°C; soluble in water and alcohol; hexahydrate has greater solubility in these solvents.

Thermochemical Properties

$\Delta H_f°$	–251.79 kcal/mol
$\Delta G_f°$	–233.70 kcal/mol
S°	36.90 cal/degree mol
C_ρ	20.89 cal/degree mol

Production

Cerium(III) chloride is prepared by the reaction of hydrochloric acid with a cerium salt, such as cerium hydroxide or carbonate, followed by crystallization;

$$Ce(OH)_3 + 3HCl \rightarrow CeCl_3 + 3H_2O$$

$$Ce_2(CO_3)_3 + 6HCl \rightarrow 2CeCl_3 + 3CO_2 + 3H_2O$$

Reactions

Cerium chloride in aqueous phase would undergo double decomposition reactions with many soluble salts of other metals; e.g.:

$$2CeCl_3 + 3Na_2CO_3 \rightarrow Ce_2(CO_3)_3 + 6NaCl$$

$$2CeCl_3 + 3K_2C_2O_4 \rightarrow Ce_2(C_2O_4)_3 + 6KCl$$

Reactions with caustic alkalis yield cerous hydroxide:

$$2CeCl_3 + 3NaOH \rightarrow Ce(OH)_3 + 3NaCl$$

When H_2S is passed into the solution cerium sulfide is precipitated:

$$2CeCl_3 + 3H_2S \rightarrow Ce_2S_3 + 6HCl$$

Analysis

Elemental composition: Ce 56.85%, Cl 43.15%. In the aqueous phase following acid digestion, cerium may be analyzed by various instrumental techniques (see Cerium). Chloride ion in the solution may be measured by ion chromatography, chloride ion-selective electrode or titration with silver nitrate using potassium chromate indicator. The solution may require appropriate dilution for analysis of both the metal and the chloride anion.

CERIUM(III) HYDROXIDE

[15785–09–8]
Formula: $Ce(OH)_3$; MW 191.14
Synonyms: cerous hydroxide; cerium hydroxide; cerous hydrate

Uses

The pure compound is used in glazes and enamels as an opacifying agent. It also is used to make colored glass, imparting yellow color to the glass. The crude form is used in flaming arc lamps. Another application of this compound is in the preparation of several other cerium salts.

Physical Properties

White gelatinous precipitate; decomposes on heating, forming oxide; soluble in acids and ammonium carbonate solution; insoluble in alkalis.

Preparation

Cerium(III) hydroxide is obtained in industrial scale from monazide sand, (Ce, La, Th)PO_4. In the laboratory, it may be prepared by treating caustic soda solution with cerium(III) chloride, followed by crystallization.

$$CeCl_3 + 3NaOH \rightarrow Ce(OH)_3 + NaCl$$

Analysis

Elemental composition: Ce 73.30%, H 1.58%, O 25.11%. The compound may be analyzed for Ce in aqueous phase by AA or ICP spectrophotometry after it is digested with nitric acid and diluted appropriately.

CERIUM(III) NITRATE

[10108–73–3]
Formula: $Ce(NO_3)_3$; MW 326.15; also forms tri-, tetra- and hexahydrates; the hexahydrate, $Ce(NO_3)_3 \cdot 6H_2O$ is most stable.
Synonym: cerous nitrate

Uses

Cerium(III) nitrate is used for the separation of cerium from other rare-earth elements. It also is used as a catalyst in hydrolysis of phosphoric acid esters.

Physical Properties

Hexahydrate is a colorless crystal; hygroscopic; loses water on heating—three molecules of water of crystallization expelled at 150°C; decomposes at 200°C; readily dissolves in water, alcohol, and acetone.

Thermochemical Properties

$\Delta H_f°$ ($Ce(NO_3)_3$)	–293.0 kcal/mol
$\Delta H_f°$ ($Ce(NO_3)_3 \cdot 3H_2O$)	–516.0 kcal/mol
$\Delta H_f°$ ($Ce(NO_3)_3 \cdot 4H_2O$)	–588.9 kcal/mol
$\Delta H_f°$ ($Ce(NO_3)_3 \cdot 6H_2O$)	–729.1 kcal/mol

Preparation

Cerium(III) nitrate may be prepared by the action of nitric acid on a cerium(III) salt, followed by crystallization:

$$Ce_2(CO_3)_3 + 6HNO_3 \rightarrow 2Ce(NO_3)_3 + 3CO_2 + 3H_2O$$

Analysis

Elemental composition: Ce 42.96%, N 12.88%, O 44.15%. The aqueous solution of this water-soluble compound may be analyzed directly for Ce (without any acid digestion) by AA or ICP spectrophotometry, and for the nitrate ion by ion chromatography or nitrate ion-selective electrode. The solution may require sufficient dilution for analysis.

CERIUM(IV) OXIDE

[1306–38–3]
Formula: CeO_2; MW 172.11
Synonyms: ceria; ceric oxide

Uses

Cerium(IV) oxide is used in the glass industry as an abrasive for polishing glass and as an opacifier in photochromic glass. It inhibits discoloration of glass made for shielding radiation. It also is used in ceramic coatings, enamels, and refractory materials. Other applications of this compound are in semiconductors, cathodes, capacitors, and phosphors; as a diluent in nuclear fuels; as a catalyst in organic synthesis; and in oxidimetry for analyzing cerium.

Physical Properties

White powder in pure form; technical grade material is pale yellow; presence of other lanthanide elements as impurities may impart reddish color; cubic crystal; density 7.65 g/cm^3; melts at 2,400°C; insoluble in water.

Thermochemical Properties

$\Delta H_f°$	–269.21 kcal/mol
$\Delta G_f°$	–244.89 kcal/mol
S°	14.89 cal/degree mol
C_ρ	14.72 cal/degree mol

Preparation

Cerium(IV) oxide may be obtained by heating cerium oxalate, carbonate or other salts at elevated temperatures:

$$Ce_2(C_2O_4)_3 + 2O_2 \xrightarrow{heat} 2CeO_2 + 6CO_2$$

Analysis

Elemental composition: Ce 81.41%, O 18.59%. The oxide can be determined by x-ray techniques. The compound may be digested with HNO_3—HCl mixture, the acid extract diluted appropriately and analyzed by AA or ICP spectrophotometry (see Cerium).

CERIUM(IV) SULFATE

[13590–82–4]
Formula: $Ce(SO_4)_2$; MW 332.35; also forms a tetrahydrate, $Ce(SO_4)\cdot4H_2O$ [10294–42–5]
Synonym: ceric sulfate

Uses

Cerium(IV) sulfate is used in radiation dosimeters and as an oxidizing agent in volumetric analysis. The tetrahydrate is used in dyeing and printing textiles, and in waterproofing.

Physical Properties

White crystalline powder; orthogonal crystal system; the tetrahydrate is a yellow-to-orange powder which, on heating at 180°C, loses all molecules of water; density of tetrahydrate 3.91 g/cm^3; anhydrous salt decomposes at 350°C forming $CeOSO_4$; soluble in water (decomposes); soluble in dilute H_2SO_4 and other concentrated mineral acids.

Thermochemical Properties

$\Delta H_f°$ (aq)	–595.9 kcal/mol
$\Delta G_f°$ (aq)	–523.6 kcal/mol

Preparation

Cerium(IV) sulfate is prepared by heating cerium(IV) oxide, CeO_2 with concentrated H_2SO_4. Also it may be obtained by the reaction of H_2SO_4 with cerium carbonate:

$$Ce(CO_3)_2 + 2H_2SO_4 + H_2O \rightarrow Ce(SO_4)_2 \cdot 4H_2O + 2CO_2$$

Analysis

Elemental composition: Ce 42.18%, S 19.30%, O 38.53%. It is digested with nitric acid, diluted appropriately and analyzed for Ce by AA or ICP spectroscopy (see Cerium). The compound may be dissolved in small quantities of water (forms a basic salt when treated with large a volume of water). The solution is analyzed for sulfate ion by gravimetry following precipitation with barium chloride. Alternatively, the compound is dissolved in hot nitric acid and the solution analyzed for sulfate by ion-chromatography.

CESIUM

[7440-46-2]
Symbol Cs: atomic number 55; atomic weight 132.905; a Group IA (Group 1) alkali metal element; electron configuration [Xe]$6s^1$; atomic radius 2.65 Å; ionic radius (Cs^+) 1.84 Å; ionization potential 3.89 eV; valence +1; natural isotope Cs-133; 37 artificial isotopes ranging in mass numbers from 112 to 148 and half-lives 17 microseconds (Cs-113) to 2.3×10^6 years (Cs-135).

Occurrence and Uses

Cesium was discovered by Bunsen and Kirchoff in 1860. It is found in the minerals pollucite, lepidolite, and the borate rhodizite. Pollucite, $CsAlSi_2O_6$, is a hydrated silicate of aluminum and cesium. The concentration of cesium in the earth's crust is estimated to be 3 mg/kg, and in sea water 0.3µg/L.

Cesium is used as a getter in electron tubes. Other applications are in photoelectric cells; ion propulsion systems; heat transfer fluid in power generators; and atomic clocks. The radioactive Cs-37 has prospective applications in sterilization of wheat, flour, and potatoes.

Physical Properties

Golden yellow, soft and ductile metal; body-centered cubic structure; density 1.93 g/cm^3; melts at 28.44°C; vaporizes at 671°C; vapor pressure 1 torr at 280°C; electrical resistivity 36.6 microhm-cm (at 30°C); reacts with water; dissolves in liquid ammonia forming a blue solution.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	18.28 kcal/mol
$\Delta G_f°$ (gas)	11.85 kcal/mol
S° (cry)	20.36 cal/degree mol
S° (gas)	41.97 cal/degree mol
C_ρ (cry)	7.70 cal/degree mol
ΔH_{fus}	0.502 kcal/mol

Production

Cesium is obtained from its ore pollucite. The element in pure form may be prepared by several methods: (i) electrolysis of fused cesium cyanide, (ii) thermal reduction of cesium chloride with calcium at elevated temperatures, and (iii) thermal decomposition of cesium azide. It is stored under mineral oil. The element must be handled under argon atmosphere.

Reactions

Cesium is highly reactive. It is the most electropositive metal–more electropositive and reactive than other alkali metals of lower atomic numbers. The standard redox potential E° for the reduction $Cs^+ + e^- \rightarrow Cs$ is –3.026 V. It reacts explosively with water, forming cesium hydroxide, CsOH and hydrogen:

$$Cs + H_2O \rightarrow CsOH + \tfrac{1}{2}H_2$$

Combustion with oxygen (or air) first forms oxide, Cs_2O, which converts to the peroxide, Cs_2O_2, and then superoxide, CsO_2. Peroxide and superoxide are also formed by passing a stoichiometric amount of oxygen in the solution of cesium in liquid ammonia. Cesium is also known to form highly colored suboxides such as $Cs_{11}O_3$ which look metallic.

Cesium combines with most nonmetals forming one or more binary compounds. With sulfur, it forms ionic sulfides, such as Cs_2S, CsS_4 and Cs_2S_6. It reacts violently with halogens forming the corresponding halides. Reaction with nitrogen yields cesium nitride Cs_3N. Heating with carbon produces interstitial compounds of nonstoichiometric compositions. Cesium dissolves in alcohols forming cesium alkoxides with liberation of hydrogen.

$$Cs + CH_3OH \rightarrow CH_3OCs + \tfrac{1}{2}H_2$$

Complex alkoxides of the type $[CsOR]_n$ are known, structures of which have not been well defined. It reacts with amines forming amido complexes of the type CsNHR or $CsNR_2$. The structures of crystalline complexes are complicated, depending upon the solvent and other factors.

Analysis

Cesium can be analyzed by various instrumental techniques including atomic absorption and atomic emission spectrophotometry and various x-ray methods. The most sensitive wavelength for AA measurement is 852.1 nm. It imparts a reddish violet color to flame. It is identified by specific line spectra having two bright lines in the blue region and several other lines in the red, yellow, and green.

Hazard

Cesium is a pyrophoric metal. It ignites spontaneously in air or oxygen. It reacts violently with cold water evolving hydrogen. Similar violent reactions occur with anhydrous acids and halogens.

CESIUM CHLORIDE

[7647-17-8]
Formula: CsCl; MW 168.36

Uses

Cesium chloride is used in radio and television vacuum tubes. It also is used in ultracentrifuge separations; x-ray fluorescent screens; as radiogrpahic contrast medium, and to prepare cesium and other cesium salts.

Physical Properties

White cubic crystal; hygroscopic; density 3.99 g/cm³; melts at 645°C; vaporizes at 1297°C; very soluble in water, soluble in ethanol.

Thermochemical Properties

$\Delta H_f°$	–105.88 kcal/mol
$\Delta G_f°$	–99.07 kcal/mol
S°	24.19 cal/degree mol
C_ρ	12.55 cal/degree mol
ΔH_{fus}	3.80 kcal/mol

Preparation

Cesium chloride is prepared by the treatment of cesium oxide or any cesium salt with hydrochloric acid followed by evaporation and crystallization of the solution.

Analysis

Elemental composition: Cs 78.94%, Cl 21.06%. An aqueous solution may be analyzed for the element Cs by atomic absorption or emission spectroscopy and chloride by ion chromatography, chloride ion-selective electrode, or by titration with a standard solution of silver nitrate or mercuric nitrate.

CESIUM HYDROXIDE

[21351-79-1]
Formula: CsOH; MW 149.91
Synonym: cesium hydrate

Uses

Cesium hydroxide is used as electrolyte in alkaline storage batteries. Other applications of this compound involve catalytic use in polymerization of cyclic siloxane; and treatment of hazardous wastes.

Physical Properties

White to yellowish fused crystalline mass; highly deliquescent; very alkaline; density 3.68 g/cm³; melts 272°C; highly soluble in water; soluble in ethanol; aqueous solution is very alkaline.

Thermochemical Properties

$\Delta H_f°$	–99.7 kcal/mol

Preparation

Cesium hydroxide is prepared by electrolysis of cesium salts to obtain cesium metal, which then reacts with water to yield hydroxide. It also is prepared by the action of barium hydroxide with an aqueous solution of cesium sulfate.

Reactions

Cesium hydroxide is the strongest base known. Its aqueous solution undergoes neutralization reactions with acids. Precipitation reactions don't yield crystalline cesium salts because of their high solubility.

Analysis

Elemental composition: Cs 88.65%, H 0.67%, O 10.67%. CsOH can be standardized by acid-base titration using HCl or H_2SO_4 and a color indicator, or by potentiometric titration to neutral pH.

CHLORINE

[7782-50-5]
Symbol Cl; atomic number 17; atomic weight 35.452; a nonmetallic Group VIIA (Group 17) halogen group element; electron configuration $[Ne]3s^23p^5$; most common valence –1; also oxidation states from +1 to +7 are known; electronegativity 3.0; occurs as a diatomic molecule Cl_2 containing a single covalent bond in which Cl–Cl bond distance 1.99 Å; two stable isotopes Cl-35 (75.53%) and Cl-37 (24.37%); seven radioactive isotopes.

Occurrence and Uses

Chlorine does not occur in the elemental state because of its high reactivity. In nature the element occurs mainly as sodium chloride in seawater. Its abundance in seawater is 1.9% by weight. It also exists as chloride in many rocks and minerals such as carnallite ($KMgCl_3 \cdot 6H_2O$) and sylvite (KCl).

Chlorine was discovered by Scheele in 1774 and named by Davy in 1810. Chlorine has numerous industrial applications. Some of the most important uses of chlorine are (i) in the production of a large number of organic chloro derivatives used in processing or producing paper, textiles, paints, dyes, medicines, antiseptics, petrochemicals, pesticides, plastics, foodstuffs, solvents, and other consumer products, (ii) as a disinfectant and bactericide in water treatment and purification, (iii) as an oxidizing agent, (iv) as a substituent agent in a number of organic reactions, and (v) in making chlorinated lime (bleaching powder) for bleaching fabrics and other substances. Other uses are in food processing; shrink proofing wool; and removal of tin and zinc from iron.

Radioactive Cl-36 has a half-life 440,000 yr (β^- decay). It is used as a tracer for studying corrosion of steel by salt water; to measure chlorosubstitution mechanisms in organics; and to determine geological age of meteorites.

Physical Properties

Greenish-yellow gas; suffocating odor (odor threshold 3 ppm); gas density in the air 2.46 (air = 1); becomes a pale yellow liquid at –34.04°C; the color decreases with lowering temperature; becomes a pale yellow crystal at –101.5°C; critical temperature 143.8°C; critical pressure 76.89 atm; critical volume 123 cm^3/mol; moderately soluble in water; solubility in water 0.061 mol Cl_2/L at 20°C; bulk solubility in water (including all species formed) 0.091 mol/L.

Thermochemical Properties

$\Delta H_f°$(Cl_2 gas)	0.0
$\Delta H_f°$ (Cl gas)	28.99 kcal/mol
$\Delta G_f°$ (Cl gas)	25.17 kcal/mol
S° (Cl gas)	39.48 cal/degree mol
C_ρ (Cl gas)	5.21 cal/degree mol
ΔH_{vap}	4.88 kcal/mol
ΔH_{fus}	1.53 kcal/mol

Production

Chlorine is produced industrially by electrolysis of brine using either mercury cathode cells or, preferably, various commercially available membrane cells. Chlorine gas is liberated at the anode while sodium hydroxide and hydrogen are liberated at the cathode:

$$Na^+ + Cl^- + H_2O \rightarrow Na^+ + OH^- + ½Cl_2 + ½H_2$$

Also, Cl is made by electrolysis of fused sodium chloride, magnesium chloride salt, or hydrochloric acid. The electrolytic process has practically superseded the Weldon and Deacon processes employed earlier to produce chlorine. The Weldon process involves the action of HCl on manganese dioxide ores to produce chlorine and manganese chloride. The $MnCl_2$ liquor obtained is first converted into calcium manganite ($CaO \cdot 2MnO_2$) or "Weldon mud," from which MnO_2 is generated back for reuse. Deacon's process involves catalytic oxidation of hydrogen chloride, catalyzed by copper:

$$2HCl + ½O_2 \xrightarrow[\text{Cu catalyst}]{400^\circ C} Cl_2 + H_2O$$

The efficiency of Deacon's process is improved by passing the HCl over CuO at 200°C. The product $CuCl_2$ is oxidized at 300°C by treatment with oxygen:

$$2HCl + CuO \xrightarrow{200^\circ C} CuCl_2 + H_2O$$

$$2CuCl_2 + O_2 \xrightarrow{300^\circ C} 2Cl_2 + 2CuO$$

In the laboratory, chlorine may be prepared by oxidation of HCl with manganese dioxide:

$$4HCl + MnO_2 \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

Reactions

Chlorine gas is noncombustible but, like oxygen, it supports combustion. It combines with practically all elements except nitrogen and the inert gases, helium, neon, argon, crypton, and radon. A few compounds with the inert gas xenon are also known. The diatomic Cl_2 molecule can dissociate into Cl atoms upon heating or irradiation with UV.

Chlorine is moderately soluble in water forming an equilibrium between dissolved chlorine and hypochlorous acid in the aqueous solution:

$$Cl_2\ (g) \rightarrow Cl_2\ (aq) \qquad K_1 = 0.062$$

$$Cl_2\ (aq) + H_2O \rightarrow H^+\ (aq) + Cl^-\ (aq) + HOCl\ (aq) \qquad K_2 = 4.2 \times 10^{-4}$$

The concentration of hypochlorous acid in a saturated solution of chlorine in water at 25°C is 0.030 mol/L while dissolved chlorine, Cl_2 (aq) is 0.061 mol/L (Cotton, F. A., G. Wilkinson, C. A. Murillo and M. Bochmann. 1999. *Advanced Inorganic Chemisry*, 6th ed. New York: John Wiley & Sons).

Chlorine reactions may be classified broadly under two types: (i) oxidation-reduction and (ii) substitution reactions. The standard electrode potential for $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$ in aqueous solution is –1.36 V. Some examples of both types are highlighted briefly below:

Chlorine combines with hydrogen forming hydrogen chloride, HCl. The reaction occurs rapidly when exposed to light, involving a photochemical chain initiation step.

$$Cl_2 + H_2 \xrightarrow{hv} 2HCl$$

Reactions with most metals yield metal chlorides. Alkali metals are obviously most reactive. With metals that exhibit varying oxidation states, the nature of the product depends on the amount of chlorine. For example, iron reacts with a limited amount of chlorine to produce iron(II) chloride, while in excess chlorine the product is iron(III) chloride:

$$Fe + Cl_2 \rightarrow FeCl_2$$

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

Among halogens, chlorine can oxidize bromide and iodide ions in solution under acidic conditions, but not fluoride. For example, it can liberate iodine in acid pH, a reaction widely employed in the iodometric titration to measure residual chlorine in water:

$$Cl_2\ (aq) + 2I^-\ (aq) \rightarrow I_2\ (g) + 2Cl^-\ (aq)$$

When chlorine is dissolved in a base, the hypochlorous acid, HOCl, is neutralized, forming hypochlorite ion, OCl^-:

$$Cl_2 + 2OH^- \rightarrow OCl^- + Cl^- + H_2O$$

However, in hot basic solution it forms chlorate, ClO_3^- and chloride, Cl^-:

$$3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 2H_2O$$

Reaction with lime produces a calcium salt, known as bleaching powder:

$$Cl_2\ (g) + CaO\ (s) \rightarrow CaCl(OCl)\ (s)$$

Also, bleaching powder is made by passing Cl_2 gas over slaked lime:

$$Ca(OH)_2 + Cl_2 \rightarrow CaCl(OCl) + H_2O$$

Chlorine readily combines with many nonmetals. Reaction with sulfur yields sulfur dichloride, SCl_2; and with phosphorus the products are phosphorus trichloride, PCl_3 and phosphorus pentachloride, PCl_5.

Chlorine forms carbonyl chloride, COCl with carbon monoxide; sulfuryl chloride SO_2Cl with sulfur dioxide; and chloramines (monochloramine, NH_2Cl, and dichloramine, $NHCl_2$) with ammonia. Chloramines are often found at trace concentrations in sewage wastewater following chlorine treatment.

Chlorine oxidizes hydrogen sulfide to sulfur:

$$Cl_2 + H_2S \rightarrow S + 2HCl$$

Many interhalogen compounds of chlorine with fluorine, bromine and iodine are known. These include ClF, ClF_3, BrCl, ICl, and ICl_3.

$$Cl_2 + F_2 \xrightarrow{200^\circ C} 2ClF$$

$$Cl_2 + 3F_2 \xrightarrow{280^\circ C} 2ClF_3$$

Several classes of organic compounds can react with chlorine. While chlorine adds to an olefinic double bond (=C=C=) yielding addition products, reactions with aromatics and saturated hydrocarbons produce substitution products:

$$\underset{\text{(ethylene)}}{CH_2{=}CH_2} + Cl_2 \xrightarrow{\text{room temperature}} \underset{\text{(ethylene dichloride)}}{ClCH_2CH_2Cl}$$

The above reaction is rapid.

With alkanes, substitution occurs producing alkyl chlorides:

$$RH + Cl_2 \xrightarrow[\text{room temperature, } CCl_4]{sunlight} RCl + HCl$$

The reaction with an alkane, for example, ethane, occurs at room temperature in the presence of UV light. However, substitution can occur in the dark when the gaseous mixture of chlorine and ethane is at 100°C.

$$\underset{\text{(benzene)}}{C_6H_6} + Cl_2 \xrightarrow[\text{room temperature}]{FeCl_3} \underset{\text{(chlorobenzene, 90\%)}}{C_6H_5Cl} + HCl$$

Benzene undergoes a substitution reaction yielding 90% chlorobenzene.

Analysis

Chlorine gas may be identified readily by its distinctive color and odor. Its odor is perceptible at 3 ppm concentration in air. Chlorine may be measured in water at low ppm by various titrimetry or colorimetric techniques (APHA, AWWA and WEF. 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington DC: American Public Health Association). In iodometric titrations aqueous samples are acidified with acetic acid followed by addition of potassium iodide. Dissolved chlorine liberates iodine which is titrated with a standard solution of sodium thiosulfate using starch indicator. At the endpoint of titration, the blue color of the starch solution disappears. Alternatively, a standardized solution of a reducing agent, such as thiosulfate or phenylarsine oxide, is added in excess to chlorinated water and the unreacted reductant is then back titrated against a standard solution of iodine or potassium iodate. In amperometric titration, which has a lower detection limit, the free chlorine is titrated against phenyl arsine oxide at a pH between 6.5 and 7.5.

Free and combined chlorine or the total chlorine in water may be measured by titration with ferrous ammonium sulfate using N,N–diethylphenylenediamine (DPD) indicator. Chlorine in aqueous solutions may be measured rapidly using several colorimetric methods that involve addition of various color-forming reagents, and measuring the color intensity using a spectrophotometer or filter photometer. Such reagents include DPD; 3,5-dimethoxy-4-hydroxybenzaldazine (syringaldazine); or 4,4',4"-methylidyne tris(N,N-dimethylaniline) (also known as leucocrystal violet). Several types of chlorine meters are available commercially for rapid *in-situ* colorimetric measurements of chlorine in water.

Hazard

Chlorine is a pungent suffocating gas, exposure to which can cause irritation of the eyes, nose and throat; burning of mouth; coughing; choking; nausea, vomiting; dizziness and respiratory distress. Exposure to 15–20 ppm of chlorine in air can cause irritation and coughing. A 30 minute exposure to

500–800 ppm can be fatal to humans (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons).

Chlorine-hydrogen mixture can explode in the presence of sunlight, heat or a spark. Also, it can explode when mixed with acetylene or diborane at ordinary temperatures, and with ethylene, fluorine, and many hydrocarbons in the presence of heat, spark or catalysts.

CHLORINE DIOXIDE

[10049-04-4]
Formula: ClO_2; MW 67.45
Synonyms: chlorine peroxide; chloroperoxyl; Alcide

Uses

Chlorine dioxide is used for bleaching textiles, paper-pulp, cellulose, leather, beeswax, oils, and fats. Other applications are in water treatment processes to kill bacteria, oxidize impurities, and control the taste and odor of water. It also is used to prepare many chlorite salts. Dilute solutions are used as antiseptics.

Physical Properties

Yellow to red-yellow gas at room temperature; pungent chlorine-like odor; density 9.99 g/L at 11°C; liquefies to a reddish brown liquid at 11°C; liquid density 1.64 g/mL at 0°C; freezes at –59.5° C to red crystals (explodes); soluble in water, decomposes in hot water; soluble in alkalis and H_2SO_4.

Thermochemical Properties

$\Delta H_f°$(g)	24.5 kcal/mol
$\Delta H_f°$(aq)	17.9 kcal/mol
$\Delta G_f°$ (g)	28.8 kcal/mol
S° (g)	61.4 cal/degree mol
S° (aq)	39.4 cal/degree mol
C_ρ (g)	10.0 cal/degree mol

Preparation

Chlorine dioxide is prepared by passing nitrogen dioxide through sodium chlorate packed in a column:

$$NaClO_3 + NO_2 \rightarrow NaNO_3 + ClO_2$$

Also, it may be prepared by the reaction of chlorine with sodium chlorite:

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl$$

Alternatively, it may be obtained by the treatment of sodium chlorate or potassium chlorate with sulfur dioxide and sulfuric acid:

$$2NaClO_3 + SO_2 + H_2SO_4 \rightarrow 2ClO_2 + 2\ NaHSO_4$$

Reactions

In chlorine dioxide, chlorine is in oxidation state +4, which makes the compound highly unstable. The pure compound or its mixture in air at 10% or greater concentrations detonates when exposed to light, or subjected to heat or a spark. The compound also decomposes in the dark in the presence of chlorides. In water, it hydrolyzes slightly to chlorous acid, $HClO_2$ and chloric acid, $HClO_3$. However, in hot water it decomposes, forming chloric acid, chlorine and oxygen:

$$4ClO_2 + H_2O \rightarrow 2HClO_3 + Cl_2 + O_2$$

Reaction with sodium hydroxide in the presence of carbonaceous matter and lime produces sodium chlorite.

Being a strong oxidizing agent, its reactions with reducing agents or oxidizable substances can be violent to explosive. Under controlled conditions, it can be combined with many metals to obtain their chlorite salts.

Hazard

Chlorine dioxide explodes violently when exposed to sunlight, heat, dust or sparks. Also, it detonates at concentrations above 10% in air in the presence of light, heat or catalyst. Reactions with organic substances, metal hydrides, sulfur and phosphorus are violent. The gas is highly irritating to eyes, nose, and throat. Inhalation can produce coughing, respiratory distress, and lung congestion.

CHLORINE MONOXIDE

[7791-21-1]
Formula: Cl_2O; MW 86.905
Synonyms: dichlorine monoxide; dichloroxide; hypochlorous anhydride; dichloromonoxide

Uses

Chlorine monoxide is used as a selective chlorinating agent.

Physical Properties

Yellowish-brown gas; disagreeable suffocating odor; unstable at room temperature; gas density 3.89 g/L at 0°C; condenses to a reddish brown liquid at 2.2°C; freezes at –20°C; highly soluble in water; also soluble in alkalis, sulfuric acid, and carbon tetrachloride.

Thermochemical Properties

$\Delta H_f°$ (g)	19.2 kcal/mol
$\Delta G_f°$ (g)	23.4 kcal/mol
S° (g)	63.6 cal/degree mol
C_ρ	10.85 cal/degree mol

Preparation

Chlorine monoxide is prepared by passing chlorine gas over yellow mercuric oxide. It is stored below –80°C as a liquid or solid.

Reactions

The oxidation state of chlorine is +1. The compound is highly unstable, decomposing to chlorine and oxygen when exposed to light, heat, spark, or under catalytic conditions. It reacts with hot water forming hypochlorous acid:

$$Cl_2O + H_2O \rightarrow 2HOCl$$

It oxidizes a number of compounds, undergoing violent decomposition. It reacts with metals under controlled conditions, forming their hypochlorites.

Hazard

Although a nonflammable gas, it reacts explosively with many substances, including organics, metals, metal sulfides, sulfur, phosphorus, nitric oxide, ammonia, carbon disulfide, metal hydrides, and charcoal. It is a severe irritant to the eyes, nose, skin, and respiratory tract. Inhalation of the gas at 100 ppm can be fatal to humans.

CHLORINE TRIFLUORIDE

[7790-91-2]
Formula: ClF_3; MW 92.45
Synonym: chlorotrifluoride

Uses

Chlorine trifluoride is used in rocket propellant; incendiaries; and in processing of nuclear reactor fuel. It also is used as a fluorinating agent and as an inhibitor of fluorocarbon polymer pyrolysis.

Physical Properties

Colorless gas; sweetish but suffocating odor; density of the liquid 1.77 g/mL at 13°C; condenses to a greenish yellow liquid at 11.75°C; freezes to a white solid at –76.3°C; reacts violently with water.

Thermochemical Properties

$\Delta H_f°$ (l)	–45.3 kcal/mol

Preparation

Chlorine trifluoride is obtained by heating chlorine or chlorine monofluoride with fluorine:

$$Cl_2 + 3F_2 \xrightarrow{250^\circ C} 2ClF_3$$

$$ClF + F_2 \xrightarrow{250^\circ C} ClF_3$$

The gas is purified by distillation in a special steel apparatus.

Hazard

Although nonflammable, ClF_3 gas is dangerously reactive. It reacts explosively with water and violently with most common substances. Organic materials burst into flame in contact with the liquid. The gas is a severe irritant to the eyes, nose, throat and skin. Inhalation can cause lung damage. The liquid is dangerously corrosive to skin.

CHROMIUM

[7440-47-3]
Symbol: Cr; atomic number 24; atomic weight 51.996; a Group VI-B (Group 6) transition metal; atomic radius 1.27Å; electron configuration $[Ar]3d^54s^1$; common valences +2, +3 and +6; also oxidation states +4, +5 and 0 are known; isotopes and their abundances: Cr–50 (4.31%), Cr–52 (83.76%), Cr–53 (9.55%), Cr–54 (2.386%).

Occurrences and Uses

Chromium occurs in the minerals chromite, $FeO\bullet Cr_2O_3$ and crocoite, $PbCrO_4$. The element is never found free in nature. Its abundance in earth's crust is estimated in the range 0.01% and its concentration in sea water is 0.3 μg/L. The element was discovered by Vaquelin in 1797.

The most important application of chromium is in the production of steel. High-carbon and other grades of ferro-chomium alloys are added to steel to improve mechanical properties, increase hardening, and enhance corrosion resistance. Chromium also is added to cobalt and nickel-base alloys for the same purpose.

Refractory bricks composed of oxides of magnesium, chromium, aluminum and iron and trace amounts of silica and calcium oxide are used in roofs of open hearths, sidewalls of electric furnaces and vacuum apparatus and copper converters. Such refractories are made in an arc furnace by fusing mixtures of magnesite and chrome ore.

Chromium coatings are applied on the surface of other metals for decorative purposes, to enhance resistance, and to lower the coefficient of friction. Radioactive chromium–51 is used as a tracer in the diagnosis of blood volume.

Physical Properties

Hard blue-white metal; body-centered cubic crystal; density 7.19 g/cm^3; melts at 1,875°C; vaporizes at 2,199°C; electrical resistivity at 20°C, 12.9 microhm–cm; magnetic susceptibility at 20°C, 3.6×10^{-6} emu; standard electrode potential 0.71 V (oxidation state 0 to +3).

Reactions

Chromium is oxidized readily in air forming a thin, adherent, transparent coating of Cr_2O_3.

Chromium forms both the chromous (Cr^{2+}) and chromic (Cr^{3+}) compounds that are highly colored.

Chromium metal reacts readily with dilute acids forming a blue Cr^{2+} (aq) solution with the evolution of hydrogen:

$$Cr + 2HCl \rightarrow CrCl_2 + H_2$$

Chromium in metallic form and as Cr^{2+} ion are reducing agents. The Cr^{2+} reduces oxygen within minutes, forming violet Cr^{3+} ion:

$$4Cr^{2+}(aq) + O_2(g) + 4H^+ (aq) \rightarrow 4Cr^{3+} + 2H_2O\ (l)$$

The standard redox potential for the overall reaction is 1.64V.

Cr^{3+} ion forms many stable complex ions. In the aqueous medium, it forms the violet $Cr(H_2O)_6{}^{3+}$ ion which is slightly basic. Chromium(III) ion is amphoteric, exhibiting both base and acid behavior.

Chromium reaction in an aqueous solution with a base produces a pale blue-violet precipitate having composition: $Cr(H_2O)_3(OH)_3$.

$$Cr(H_2O)_6{}^{3+}\ (aq) + 3OH^-\ (aq) \rightarrow Cr(H_2O)_3(OH)_3\ (s) + H_2O$$

The above precipitate redissolves in excess base:

$$Cr(H_2O)_3(OH)_3\ (s) + H^+\ (aq) \rightarrow Cr(H_2O)_4(OH)_2{}^+\ (aq) + H_2O$$

Chromium forms chromium(VI) oxide in which the metal is in +6 oxidation state. In acid medium it yields yellow chromate ion, $CrO_4{}^{2-}$, and the red-orange dichromate ion, $Cr_2O_7{}^{2-}$.

Chromium is oxidized in nitric, phosphoric or perchloric acid forming a thin oxide layer on its surface, thus making the metal even more unreactive to dilute acids.

Elemental chromium reacts with anhydrous halogens, hydrogen fluoride, and hydrogen chloride forming the corresponding chromium halides. At elevated temperatures in the range 600 to 700°C, chromium reacts with hydrogen sulfide or sulfur vapor, forming chromium sulfides.

Chromium metal reacts at 600 to 700°C with sulfur dioxide and caustic alkalis. It combines with phosphorus at 800°C. Reaction with ammonia at

850°C produces chromium nitride, CrN. Reaction with nitric oxide forms chromium nitride and chromium oxide.

$$5Cr + 3NO \xrightarrow[\text{temperature}]{\text{elevated}} 3CrN + Cr_2O_3$$

Production

Chromium metal is produced by thermal reduction of chromium(III) oxide, Cr_2O_3 by aluminum, silicon or carbon. The starting material in all these thermal reduction processes are Cr_2O_3 which is obtained from the natural ore chromite after the removal of iron oxide and other impurities. In the aluminum reduction process, the oxide is mixed with Al powder and ignited in a refractory-lined vessel. The heat of reaction is sufficient to sustain the reaction at the required high temperature. Chromium obtained is about 98% pure, containing traces of carbon, sulfur and nitrogen.

$$Cr_2O_3 + 2Al \xrightarrow{ignite} 2Cr + Al_2O_3$$

The carbon reduction process is carried out at 1,300 to 1,400°C at low pressure in a refractory reactor:

$$Cr_2O_3 + 3C \xrightarrow{1400^\circ C} 2Cr + 3CO$$

The silicon reduction process is not thermally self-sustaining and, therefore, is done in an electric arc furnace:

$$2Cr_2O_3 + 3Si \rightarrow 4Cr + 3\,SiO_2$$

Chromium may be produced from high-carbon ferrochrome by electrolytic process. Alternatively, the metal may be obtained by electrolysis of chromic acid, H_2CrO_4.

High-carbon ferrochromium alloys are made by the reduction of chromite ore with carbon in an arc furnace. On the other hand, low-carbon ferrochromium is obtained by silicon reduction of the ore. The carbon content of ferrochromium can be reduced further by heating high-carbon alloys with ground quartzite or by oxidation in vacuum and removal of carbon monoxide formed. Ferrochromium alloys are used in the manufacture of stainless steel.

Analysis

Chromium metal may be analyzed by various instrumental techniques including flame and furnace AA spectrophotometry (at 357.9 nm); ICP emission spectrometry (at 267.72 or 206.15 nm), x-ray fluorescence and x-ray diffraction techniques, neutron activation analysis, and colorimetry.

Chromium metal may be detected in high nanogram to low microgram ranges by these techniques. While AA, ICP, and colorimetric methods require chromium to be brought into aqueous phase, the metal may be analyzed nondestructively in the solid phase by x-ray techniques. ICP–MS technique may be applied to measure the metal at a much lower detection level.

Toxicity

While chromium metal or trivalent chromium is not very toxic, hexavalent chromium (Cr^{6+}) is carcinogenic and moderately toxic. Cr^{6+} is corrosive to skin and causes denaturation and precipitation of tissue proteins. Inhalation of Cr^{6+} dust or mist can cause perforation of the nasal septum, lung irritation, and congestion of the respiratory passsages. Chronic exposure may produce cancer of the respiratory tract.

CHROMIUM(II) CHLORIDE

[10049-05-5]
Formula: $CrCl_2$; MW 122.90; also forms a tetrahydrate, tetraaquochomium dichloride $Cr(H_2O)_4Cl_2$ [13931-94-7]
Synonym: chromous chloride

Uses

Chromium(II) chloride is used as a reducing agent; as a catalyst in organic reactions; in chromium plating of metals; and as an analytical reagent for the dehalogenation of vic-dihalides. As a reducing agent, it is used to reduce alpha-haloketones to parent ketones, epoxides to olefins, chloroimides to imines, and aromatic aldehydes to corresponding alcohols.

Physical Properties

White lustrous needles or fibrous mass; hygroscopic; density 2.88 g/cm^3; melts at 814°C; vaporizes at 1,300°C; highly soluble in water, forming blue solution; insoluble in ether. The tetrahydrate occurs in blue hygroscopic crystalline form, that changes to green modification above 38°C; decomposes to trihydrate at 51°C; soluble in water.

Thermochemical Properties

$\Delta H_f°$	–94.50 kcal/mol
$\Delta G_f°$	–85.09 kcal/mol
S°	27.56 cal/degree mol
C_ρ	17.02 cal/degree mol
ΔH_{fus}	7.70 kcal/mol
ΔH_{vap}	47.08 kcal/mol

Preparation

Chromium(II) chloride may be prepared by the reaction of chromium with anhydrous hydrogen chloride at 600 to 700°C:

$$Cr + 2HCl \xrightarrow{600-700^\circ C} CrCl_2 + H_2$$

Also, the compound may be prepared by the reduction of chromium(III) chloride with hydrogen at 500 to 600°C:

$$2CrCl_3 + H_2 \xrightarrow{500-600^\circ C} 2CrCl_2 + 2HCl$$

An aqueous solution of chromium(II) chloride for organic reduction may be prepared as follows:

Amalgamate zinc by shaking 400 g zinc dust with a solution containing 32g $HgCl_2$, 20 mL conc. HCl and 400 mL water. Decant the aqueous phase. To the amalgamated zinc add 800 mL water, 80 mL conc. HCl, and 200 g $CrCl_3 \cdot 6H_2O$. Bubble CO_2 through the solution to agitate it and prevent any possible reoxidation of chromium by air. The solution that turns light blue may be used in organic reduction.

Analysis

Elemental composition: Cr 42.31%, Cl 57.69%. The metal may be analyzed by AA, ICP, or other instrumental techniques. Chloride may be measured by ion chromatography or by using a chloride ion selective electrode. Because of the blue color of its aqueous solution, end point detection in titrimetric methods may be difficult.

CHROMIUM(III) CHLORIDE

[10025-73-7]

Formula: $CrCl_3$; MW 158.35; also forms several hexahydrate isomers, the most common of which is dark green colored *trans*-isomer of dichlorotetraaquochromium chloride dihydrate, *trans*-$[CrCl_2(H_2O)_4Cl] \cdot 2H_2O$ [10064-12-5].

Synonyms: chromic chloride; chromium trichloride; chromium sesquichloride.

Uses

Chromium(III) chloride is used for chromium plating; as textile mordant; in tanning; as a waterproofing agent; and as catalyst for polymerization of olefins.

Physical Properties

Reddish violet crystals; hexagonal plates; density 2.87g/cm^3; melts at 1,152°C; decomposes at 1,300°C; slightly soluble in water. The color of hexahydrates range from light-green to violet; all are hygroscopic; density 1.76 g/cm^3; soluble in water and ethanol; insoluble in ether; dilute aqueous solutions are violet in color.

Thermochemical Properties

$\Delta H_f°$	–133.01 kcal/mol
$\Delta G_f°$	–116.18 kcal/mol

S°	29.40 cal/degree mol
Cρ	21.94 cal/degree mol

Preparation

Chromium(III) chloride hexahydrate may be prepared by treating chromium hydroxide with hydrochloric acid:

$$Cr(OH)_3 + 3HCl + 3H_2O \rightarrow CrCl_3 \cdot 6H_2O$$

The anhydrous chromium(III) chloride may be obtained by heating the hydrated salt $CrCl_3 \cdot 6H_2O$ with $SOCl_2$ and subliming the product in a stream of chlorine at 600°C. Alternatively, the red-violet anhydrous chloride can be obtained by passing chlorine gas over a mixture of chromic oxide and carbon:

$$Cr_2O_3 + 3C + 3Cl_2 \rightarrow 2CrCl_3 + 3CO$$

Reactions

Chromium(III) chloride at elevated termperatures decomposes to chromium(II) chloride and chlorine:

$$2CrCl_3 \xrightarrow{\sim 600^\circ C} 2CrCl_2 + Cl_2$$

Heating with excess chlorine produces vapors of chromium(IV) chloride, $CrCl_4$. The tetrahedral tetrachloride is unstable, and occurs only in vapor phase.

When heated with hydrogen, it is reduced to chromium(II) chloride with the formation of hydrogen chloride:

$$2CrCl_3 + H_2 \xrightarrow{500^\circ C} 2CrCl_2 + 2HCl$$

Chromium(III) chloride has very low solubility in pure water. However, it readily dissolves in the presence of Cr^{2+} ion. Reducing agents such as $SnCl_2$ can "solubilize" $CrCl_3$ in water. It forms adducts with many donor ligands. For example, with tetrahydrofuran (THF) in the presence of zinc, it forms the violet crystals of the complex $CrCl_3 \cdot 3THF$.

Analysis

Elemental composition: Cr 32.84%, Cl 67.16%. Chromium(III) chloride may be solubilized in water by a reducing agent and the aqueous solution may be analyzed for chromium by AA, ICP, or other instrumental techniques. Alternatively, the compound may be digested with nitric acid, brought into aqueous phase, diluted appropriately, and analyzed for the metal as above. The aqueous solution (when a nonchloride reducing agent is used for dissolution of the anhydrous compound in water) may be analyzed for chloride ion by ion chromatography or chloride-selective electrode. The water-soluble hexahydrate may be measured in its aqueous solution as described above.

CHROMIUM HEXACARBONYL

[13007-92-6]
Formula: $Cr(CO)_6$; MW 220.058; the CO group is bound to Cr atom through C atom; Cr–C bond distance 1.909Å.
Synonym: chromium carbonyl

Uses

Chromium hexacarbonyl is used as an additive to gasoline to increase the octane number; as a catalyst in isomerization and polymerization reactions; and in the preparation of chromium mirror or plate.

Physical Properties

White orthogonal crystal; density 1.77 g/cm^3; sublimes at ordinary temperatures; vapor pressure 1 torr at 48°C; decomposes at 130°C; insoluble in water and alcohols; soluble in ether, chloroform and methylene chloride.

Preparation

Chromium hexacarbonyl is prepared by the reaction of anhydrous chromium(III) chloride with carbon monoxide in the presence of a Grignard reagent. A 60% product yield may be obtained at the carbon monoxide pressures of 35 to 70 atm. Other chromium salts may be used with carbon monoxide and Grignard reagent in the preparation. The compound may also be obtained by the reaction of a chromium salt with carbon monoxide in the presence of magnesium in ether or sodium in diglyme.

Reaction

Chromium hexacarbonyl decomposes on strong heating (explodes around 210°C). The product is chromous oxide, CrO. In inert atmosphere the products are chromium and carbon monoxide. It also is decomposed by chlorine and fuming nitric acid. Photochemical decomposition occurs when its solutions are exposed to light.

Some important reactions of chromium hexacarbonyl involve partial or total replacements of CO ligands by organic moieties. For example, with pyridine (py) and other organic bases, in the presence of UV light or heat, it forms various pyridine-carbonyl complexes, such as $(py)Cr(CO)_5$, $(py)_2Cr(CO)_4$, $(py)_3Cr(CO)_3$, etc. With aromatics (ar), it forms complexes of the type, $(ar)Cr(CO)_3$. Reaction with potassium iodide in diglyme produces a potassium diglyme salt of chromium tetracarbonyl iodide anion. The probable structure of this salt is $[K(diglyme)_3][Cr(CO)_4I]$.

Analysis

Elemental composition: Cr 23.63%, C 32.75%, O 43.62%. A small amount of solid compound may be digested cautiously with nitric acid and the aqueous acid extract may be analyzed for chromium by AA, ICP, or a related technique. The carbonyl ligand may be determined by thermal decomposition of the compound in an inert atmosphere at temperatures below 180°C followed by the measurement of carbon monoxide by IR, GC–TCD, or GC/MS. Alternatively, the compound may be dissolved in chloroform and analyzed by the above techniques. The characteristic mass ions for GC/MS determination should be 28 for CO and 220 for the molecular ion.

Hazard

Chromium hexacarbonyl is highly toxic by all routes of exposure. The symptoms include headache, dizziness, nausea and vomiting. The LD_{50}(oral) in mice is 150 mg/kg (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. NewYork: John Wiley & Sons). It explodes upon heating at 210°C.

CHROMIUM(III) HYDROXIDE TRIHYDRATE

[1308-14-1]
Formula: $Cr(OH)_3 \cdot 3H_2O$; MW 157.06; occurs only as hydrates
Synonyms: chromic hydroxide; chromic oxide hydrous; chromic oxide gel; chromium hydrate; chromic hydrate.

Uses

Chromium(III) hydroxide is used as green pigment; as mordant; as a tanning agent; and as a catalyst.

Physical Properties

Bluish-green powder or green gelatinous precipitate; decomposes to chromium(III) oxide on heating; insoluble in water; soluble in dilute mineral acids when freshly prepared, becoming insoluble on aging; soluble in strong alkalis.

Preparation

Chromium(III) hydroxide may be prepared by precipitation from mixing ammonium hydroxide solution with a soluble chromium(III) salt, such as chromium(III) chloride or nitrate:

$$CrCl_3 + 3NH_4OH \rightarrow Cr(OH)_3 + 3NH_4Cl$$

Analysis

The aqueous solution may be analyzed for chromium by AA or ICP techniques. Chromium(III) may be measured by ion chromatography. Additionally, the compound may be decomposed thermally to chromium(III) oxide, Cr_2O_3, which can be identified by x-ray techniques. Water content of the hydroxide may be measured by gravimetry.

CHROMIUM(III) FLUORIDE

[7788-97-8]
Formula: CrF_3; MW 108.99; also forms a trihydrate, triaquochromium trifluoride, $CrF_3 \cdot 3H_2O$ [16671-27-5]; tetrahydrate $CrF_3 \cdot 4H_2O$ and nonahydrate $CrF_3 \cdot 9H_2O$ are also known.
Synonyms: chromic fluoride; chromium trifluoride

Uses

Some important uses are in printing and dyeing woolens; mothproofing of woolen materials; metal polishing; coloring marbles; and as a catalyst in halogenation reactions.

Physical Properties

Dark green needles (anhydrous salt) or green hexagonal crystals (trihydrate); density 3.8 g/cm^3 (anhydrous fluoride), 2.2 g/cm^3 (trihydrate); anhydrous salt melts at 1,100°C and sublimes above this temperature; practically insoluble in water and ethanol (anhydrous salt); trihydrate sparingly soluble in water; soluble in HCl forming a violet solution.

Thermochemical Properties

$\Delta H_f°$	–277.0 kcal/mol
$\Delta G_f°$	–260.0 kcal/mol
S°	22.44 cal/degree mol
C_ρ	18.81 cal/degree mol

Preparation

Chromium(III) fluoride may be prepared by heating chromium trichloride under a stream of hydrogen fluoride:

$$CrCl_3 + 3HF \xrightarrow{heat} CrF_3 + 3HCl$$

The compound may be prepared by the reaction of chromium hydroxide with hydrofluoric acid:

$$Cr(OH)_3 + 3HF \xrightarrow{heat} CrF_3 + 3H_2O$$

Analysis

Elemental composition: Cr 47.71%, F 52.29%. A nitric or hydrochloric acid solution of the compound may be analyzed for chromium by various instrumental techniques (see Chromium). The solution may be diluted appropriately and measured for fluoride ion by using a fluoride-selective electrode or by ion chromatography.

CHROMIUM(III) OXIDE

[1308-38-9]
Formula: Cr_2O_3; MW 151.99
Synonyms: chromic oxide; chromia; chromium sesquioxide; green cinnabar; chrome green; chrome oxide green; oil green; leaf green; ultramarine green; CI 77288

Uses

Chromium(III) oxide is used as pigment for coloring green on glass and fabrics. Other important applications are in metallurgy; as a component of refractory bricks, abrasives and ceramics; and as a catalyst in hydrogenation, hydrogenolysis and many other organic conversion reactions. It also is used to prepare other chromium salts.

Physical Properties

Green hexagonal crystal system; corundum type structure; density 5.22 g/cm³; melts at 2,330°C; vaporizes above 3,000°C; insoluble in water and alcohol.

Thermochemical Properties

$\Delta H_f°$	–272.4 kcal/mol
$\Delta G_f°$	–252.9 kcal/mol
S°	19.41 cal/degree mol
C_ρ	28.37 cal/degree mol
ΔH_{fus}	31.07 kcal/mol

Preparation

Chromium(III) oxide may be prepared by several methods which include (i) burning the metal in oxygen, (ii) by heating chromium(III) hydroxide, (iii) by heating chromium(VI) oxide, CrO_3,(iv) thermal decomposition of dry ammonium dichromate, $(NH_4)_2Cr_2O_7$, and (v) by heating a mixture of sodium chromate, Na_2CrO_4 or sodium dichromate, $Na_2Cr_2O_7$ with sulfur followed by treatment with water to remove the soluble sodium sulfate formed in the reaction.

Reactions

Chromium(III) oxide is amphoteric. Although insoluble in water, it dissolves in acid to produce hydrated chromium ion, $[Cr(H_2O)_6]^{3+}$. It dissolves in concentrated alkali to yield chromite ion. When heated with finely divided aluminum or carbon it is reduced to chromium metal:

$$Cr_2O_3 + 3Al \xrightarrow{heat} 2Cr + Al_2O_3$$

Heating with chlorine and carbon yields chromium(III) chloride:

$$Cr_2O_3 + 3Cl_2 + 3C \xrightarrow{heat} 2CrCl_3 + 3CO$$

Analysis

Elemental composition; Cr 68.43%, O 31.57%. The compound may be identified nondestructively by various x-ray techniques. It may be digested with concentrated nitric acid, the acid extract diluted appropriately and analyzed for chromium by flame or furnace AA or ICP spectrophotometry.

CHROMIUM(VI) OXIDE

[1333-82-0]
Formula: CrO_3; MW 99.994
Synonyms: chromium trioxide; chromic anhydride; "chromic acid"

Uses

Chromium(VI) oxide is used for chromium plating; copper stripping; as an oxidizing agent for conversion of secondary alcohols into ketones (Jones oxidation); as a corrosion inhibitor; in purification of oil; and in 'chromic mixtures' for cleaning laboratory glassware.

Physical Properties

Dark-red crystals, flakes or granular powder; bipyramidal prismatic system; density 2.70 g/cm^3; melts at 197°C; decomposes on further heating; highly soluble in water, 61.7 g and 67 g/100 mL at 0°C and 100°C, respectively; soluble in sulfuric and nitric acids.

Thermochemical Properties

$\Delta H_f°$(cry)	–140.9 kcal/mol
$\Delta H_f°$(g)	–92.2 kcal/mol
ΔH_{fus}	3.77 kcal/mol

Preparation

Chromium(VI) oxide is prepared by heating sodium dichromate dihydrate with a slight excess of sulfuric acid in a steel tank or cast iron container:

$$Na_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2CrO_3 + 2NaHSO_4 + H_2O$$

The temperature of the mixture is kept above the melting point of chromium(VI) oxide to evaporate water and separate the top layer of sodium bisulfate from the molten chromium(VI) oxide at the bottom. Temperature control and duration of heating is very crucial in the process. Temperatures over 197°C (melting point), or allowing the molten mass to stand for a longer time, may result in decomposition of the product.

Reactions

Chromium(VI) oxide decomposes to chromium(III) oxide liberating oxygen when heated at 250°C:

$$4Cr_2O_3 \xrightarrow{250^\circ C} 2CrO_3 + 3O_2$$

The red oxide is the acid anhydride of two acids, namely, chromic acid, H_2CrO_4 or $CrO_2(OH)_2$ and the dichromic acid $H_2Cr_2O_7$. Both the chromic and dichromic acids exist only in the aqueous solution and have not been isolated from the solution. Dissolution of CrO_3 in water produces H^+ ion along with dichromate ion, $Cr_2O_7^{2-}$ as follows:

$$2CrO_3 + H_2O \rightarrow 2H^+ + \underset{\text{(red-orange dichromic acid)}}{Cr_2O_7^{2-}}$$

The aqueous solution of CrO_3 is, therefore, strongly acidic because of this proton release. The $Cr_2O_7^{2-}$ ion in the aqueous solution is susceptable to further decomposition, forming chromate ion:

$$Cr_2O_7^{2-} \rightarrow CrO_4^{2-} + CrO_3$$

In the above reaction the equilibrium, however, lies far to the left. Therefore the chromium(VI) oxide solution also contains trace amounts of chromate ion, CrO_4^{2-}.

Addition of stoichiometric amounts of caustic soda or caustic potash yields orange dichromate salt which can be crystallized from the solution.

$$Cr_2O_7^{2-} + 2Na^+ \rightarrow Na_2Cr_2O_7$$

If excess base is added to this solution, it turns yellow, and yellow chromate salt may crystallize out. Thus, as mentioned above, in an aqueous solution of CrO_3, there is an equilibrium between two Cr^{6+} species, namely, the chromate and dichromate ions:

$$\underset{\text{yellow}}{2CrO_4^{2-}} + 2H^+ \rightarrow \underset{\text{orange}}{Cr_2O_7^{2-}} + H_2O \qquad K_c = 4.2\text{x}10^{14}$$

The addition of base (OH^-) shifts the equilibrium to the left while acidification of the solution shifts the equilibrium to the right in favor of $Cr_2O_7^{2-}$. In other color/pH relations, red CrO_3 is acidic, green Cr_2O_3 is amphoteric and the black CrO is basic in nature.

In acid medium chromic acid oxidizes secondary alcohols to ketones:

$$R_2CHOH + 2H_2CrO_4 + 6H^+ \xrightarrow{acetone} 3R_2C{=}O + 2Cr^{3+} + 8H_2O$$

The reaction usually is carried out in acetone or acetic acid. Chromium is reduced from +6 to +3 oxidation state.

Reaction with hydrochloric acid yields chromyl chloride:

$$CrO_3 + 2HCl \rightarrow CrO_2Cl_2 + H_2O$$

A similar reaction occurs with HF to yield chromyl fluoride CrO_2F_2. However, fluorination with F_2 yields the oxohalide, $CrOF_4$.

Analysis

Elemental composition: Cr 52.00%, O 48.00%. The compound may be identified from its dark red color. Other color phases are noted above. Chromium may be measured in the aqueous phase by AA, ICP or x-ray techniques, or in the solid phase by x-ray methods. Hexavalent chromium (Cr^{6+}) may be analyzed by ion chromatography. For this, the aqueous sample is adjusted to pH 9 to 9.5 with a concentrated buffer (ammonium sulfate and ammonium hydroxide mixture) and mixed into the eluent stream of the buffer. Cr^{6+} is separated from Cr^{3+} on a column, and derivatized with an azide dye as a colored product measured at 530 nm, which is identified from its retention time. (APHA, AWWA, and WEF. 1999. *Standard Methods for The Examination of Water and Wastewater*, 20th ed., Washington, DC: American Public Health Association.)

CHROMIUM(III) SULFATE

[10101-53-8]
Formula: $Cr_2(SO_4)_3$; MW 392.16; several hydrates are known; these include the pentadecahydrate $Cr_2(SO_4)_3 \cdot 15H_2O$ and the octadecahydrate $Cr_2(SO_4)_3 \cdot 18H_2O$
Synonym: chromic sulfate

Uses

Chromium(III) sulfate is used as the electrolyte for obtaining pure chromium metal. It is used for chrome plating of other metals for protective and decorative purposes. Other important applications of this compound are as a mordant in the textile industry; in tanning leather; to dissolve gelatin; to impart green color to paints, varnishes, inks, and ceramic glazes; and as a catalyst.

Physical Properties

Reddish-brown hexagonal crystal; the pentadecahydrate is a dark green amorphous substance while the octadecahydrate is a violet cubic crystal; the densities are 3.10 g/cm^3 (the anhydrous salt), 1.87 g/cm^3 (pentadecahydrate), 1.709/cm^3 (octadecahydrate); the anhydrous sulfate is insoluble in water and acids; the hydrate salts are soluble in water; the pentadecahydrate is insoluble in alcohol, but the octadecahydrate dissolves in alcohol.

Preparation

Chromium(III) sulfate is prepared by treating chromium(III) hydroxide with sulfuric acid followed by crystallization:

$$2Cr(OH)_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 6H_2O$$

Analysis

Elemental composition: Cr 26.72%; S 24.52%, O 48.95%. Chromium may be analyzed in the acid extract of the salt by various instrumentation techniques (see Chromium).

CHROMYL CHLORIDE

[14977-61-8]
Formula: CrO_2Cl_2; MW 154.90; tetrahedral structure, Cr=O bond distance 1.581 Å and Cr–Cl bond distance 2.126Å.
Synonyms: chromium dioxychloride; dichlorodioxochromium; chlorochromic anhydride.

Uses

Chromyl chloride is used in many organic synthetic reactions including oxidation and chlorination. It also is used as a catalyst in olefin polymerization; in the preparation of chromium complexes; and as a solvent for chromic anhydride.

Physical Properties

Dark red, fuming liquid; reddish yellow vapors; musty buring odor; density 1.91 g/mL; freezes at –96.5°C; boils at 117°C; reacts with water; soluble in chloroform, carbon tetrachloride, benzene, carbon disulfide and nitrobenzene.

Preparation

Chromyl chloride is prepared by reacting chromium(III) chloride with hydrochloric acid:

$$CrO_3 + 2HCl \rightarrow CrO_2Cl_2 + H_2O$$

Also, it may be prepared by warming potassium dichromate with potassium chloride in concentrated sulfuric acid:

$$K_2Cr_2O_7 + 4KCl + 3H_2SO_4 \rightarrow 2Cr_2O_2Cl_2 + 3K_2SO_4 + 3H_2O$$

Reactions

Chromyl chloride reacts with water, hydrolyzing to CrO_4^{2-} and HCl. The compound is sensitive to light but stable in the dark.

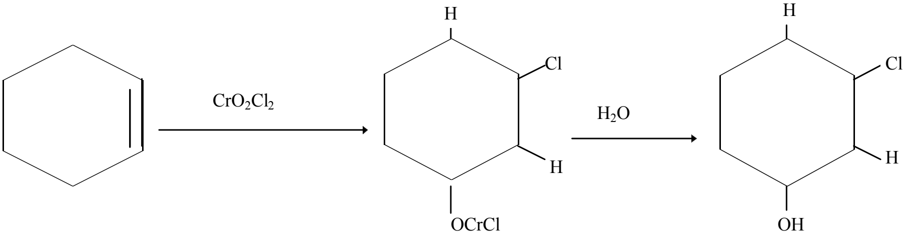
Chromyl chloride is a powerful oxidizing agent employed in organic synthesis. It oxidizes toluene to benzaldehyde. The reaction is catalyzed by trace olefin.

$$C_6H_5CH_3 \xrightarrow{CrO_2Cl_2} C_6H_5CHO$$

It reacts with olefins forming their chromyl chloride derivatives which on hydrolysis yield chloroalcohols (chlorohydrins) that are mostly the ß-chloroprimary alcohols:

$$RCH{=}CH_2 \xrightarrow[hydrolysis]{CrO_2Cl_2} RCHClCH_2OH$$
(35–50% yield)

Reaction with cyclohexene yields a trans– ß–chlorohydrin:



Chromyl chloride also oxidizes saturated hydrocarbons. For example, it oxidizes isobutane to tert-butyl chloride:

$$(CH_3)_2CHCH_3 \xrightarrow{CrO_2Cl_2} (CH_3)_3CCl$$

and cyclohexane to chlorocyclohexane:

$$C_6H_{12} \xrightarrow{CrO_2Cl_2} C_6H_{11}Cl$$

Analysis

Elemental composition: Cr 33.57%, Cl 45.77%, O 20.66%. A trace amount may be dissolved in a suitable organic solvent and identified and measured quantitatively by GC–FID, GC–ECD, or by mass spectroscopy. For GC–ECD determination, use a nonchlorinated solvent. Chromium may be determined by AA or ICP techniques following thorough digestion in nitric acid.

Hazard

Chromyl chloride reacts violently with alcohol, ammonia, and turpentine, igniting these liquids. Reactions with other oxidiazable substances can be violent. The liquid is corrosive and possibly a poison. Skin contact can cause blisters. Exposure to its vapors causes severe irritation of the eyes, nose, and respiratory tract. Prolonged or excessive inhalation can cause death.

COBALT

[7440-48-4]
Symbol: Co; atomic number 27; atomic weight 58.933; a transtion metal, Group VIII (Group 9) element; electron configuration $[Ar]3d^74s^2$; valence +2 and +3; also valences 0, +1, +4, and +5 are known; natural isotopes Co-59 (99.8%) and Co-57 (0.2%); radioactive isotope Co-60.

Occurrence and Uses

Cobalt has been in use as a coloring agent for glass since ancient times. The metal was isolated by Brandt in 1735 and confirmed as an element by Bergman in 1780. Cobalt is widely distributed in nature, but in small concentrations. Its concentration in the earth's crust is estimated to be about 0.0025% and in the sea water is about 0.02 µg/L. Cobalt minerals with their chemical formula and CAS Registry numbers are tabulated below:

Mineral	CAS Registry	Chemical Formula	%
cobaltite	[1303-15-7]	$CoAsS_3$	35.5
carrolite	[12285-42-6]	$CuCo_2S_4$	38.7
cattierite	[12017-06-0]	$CoS_2(Co,Ni)S_2$	-----
linnaeite	[1308-08-3]	Co_3S_4	48.7
siegenite	[12174-56-0]	$(Co,Ni)_3S_4$	26.0
erythrite	[149-32-6]	$3CoO \cdot As_2O_5 \cdot 8H_2O$	29.5
heterogenite	[12323-83-0]	$CuO \cdot 2Co_2O_3 \cdot 6H_2O$*	57.0
asbolite	[12413-71-7]	$CoO \cdot 2MnO_2 \cdot 4H_2O$	-----
safflorite	[12044-43-8]	$CoAs_2$ (orthogonal)	28.2
smaltite	[12044-42-1]	$CoAs_2$ (cubic), $(Co, Ni)As_3$	28.2
skutterudite	[12196-91-7]	$CoAs_3(Co,Ni)As_3$	20.8

* The ore contains varrying waters of crystalization.

Most cobalt found on earth is diffused into the rocks. It also is found in coal and soils, and at trace concentations in animals and plants. It is an essential element for plants and animals (as vitamin B12). Its absence in animals can cause retarded growth, anemia and loss of apetite. The element has been detected in meteorites and in the atmospheres of the sun and other stars.

The most imporant use of cobalt is in the manufacture of various wear-resistant and superalloys. Its alloys have shown high resistance to corrosion and oxidation at high temperatures. They are used in machine components. Also, certain alloys are used in desulfurization and liquefaction of coal and hydrocracking of crude oil shale. Cobalt catalysts are used in many industrial processes. Several cobalt salts have wide commercial applications (see individual salts). Cobalt oxide is used in glass to impart pink or blue color. Radioactive cobalt–60 is used in radiography and sterilization of food.

Physical Properties

Silvery-white metal; occurs in two allotropic modifications over a wide range of temperatures–the crystalline closed-packed-hexagonal form is known as alpha form and a face-centered cubic form is the beta (or gamma) form. The alpha form predominates at temperatures up to 417°C and transforms to beta allotrope above this temperature; density 8.86 g/cm^3; cast hardness (Brinnel) 124; melts at 1,493°C; vaporizes at 2,927°C; Curie temperature 1,121°C; electrical resistivity 5.6 microhm-cm at 0°C; Young's modulus 211 Gpa (3.06x10^{7}psi); Poisson's ratio 0.32; soluble in dilute acids.

Thermochemical Properties

$\Delta H_f°$(cry)	0.0
S° (cry)	7.14 cal/degree mol
C_ρ (cry)	5.93 cal/degree mol
$\Delta H_f°$(g)	101.51 kcal/mol
$\Delta G_f°$ (g)	90.89 kcal/mol
S° (g)	42.90 cal/degree mol
ΔH_{fus}	65.73 kcal/mol
Coeff. linear expansion, 40°C	1.336x10^{-5}/°C

Production

Cobalt is obtained from its ores, which are mostly sulfide, arsenic sulfide or oxide in nature. The finely ground ore is subjected to multistep processing, depending on the chemical nature of the ore.

When the sulfide ore carrollite, $CuS\cdot Co_2S_3$, is the starting material, first sulfides are separated by flotation with frothers. Various flotation processes are applied. The products are then treated with dilute sulfuric acid producing a solution known as copper-cobalt concentrate. This solution is then electrolyzed to remove copper. After the removal of copper, the solution is treated with calcium hydroxide to precipitate cobalt as hydroxide. Cobalt hydroxide is filtered out and separated from other impurities. Pure cobalt hydroxide then is dissolved in sulfuric acid and the solution is again electrolyzed. Electrolysis deposits metallic cobalt on the cathode.

Production of cobalt in general is based on various physical and chemical processes that include magnetic separation (for arsenic sufide ores), sulfatizing roasting (for sulfide ores), ammoniacal leaching, catalytic reduction, and electrolysis.

Finely divided cobalt particles can be prepared by reduction of cobalt(II) chloride by lithium naphthalenide in glyme.

Reactions

Finely divided cobalt is pyrophoric. But the lump metal is stable in air at ordinary temperatures. It is oxidized on heating at 300°C to cobalt oxide.

Reactions with dilute mineral acids yield the corresponding Co^{2+} salts. With hydrochloric acid the reaction is slow. The metal liberates hydrogen from dilute mineral acids:

$$Co + 2HNO_3 \rightarrow Co(NO_3)_2 + H_2$$

Cobalt combines with halogens at ordinary temperatures to form their corresponding halides. It reacts with ammonia gas at 470°C to form cobalt nitride, which decomposes at 600°C.

$$4Co + 2NH_3 \xrightarrow{470^\circ C} Co_4N_2 + 3H_2$$

Also it combines with other nonmetals on heating to yield the corresponding binary compounds. With sulfur and phosphorus, cobalt forms sulfides CoS and Co_2S_3 and phosphide Co_2P, respectively. Also, two other cobalt sulfides of stoichiometric compositions, CoS_2 and Co_3S_4 are known. With antimony and arsenic, several antimonides and arsenides are formed. Three antimonides with formulas CoSb, $CoSb_2$, and $CoSb_3$ have been reported. Three cobalt arsenides, CoAs, $CoAs_2$, and $CoAs_3$ are also known. Cobalt also combines with carbon at elevated temperatures to form carbides of various compositions, namely Co_3C, Co_2C and CoC_2 obtained by dissolution of cobalt in the solid solution. The carbide Co_3C is the primary product when the metal is heated above 1,300°C with carbon in steel containers. When heated with carbon monoxide above 225°C, the carbide Co_2C is readily obtained with deposition of elemental carbon. However, when the metal is in a finely divided state and heated with carbon monoxide at 200°C under pressure (100atm), the product is dicobalt octacarbonyl, $Co_2(CO)_8$.

When hydrogen sulfide is passed through an ammoniacal or alkaline cobalt solution, a black precipitate of cobalt(II) sulfide, CoS forms.

Cobalt in its trivalent state forms many stable complexes in solution. In these complexes, the coordination number of Co^{3+} is six. The Co^{2+} ion also forms complexes where the coordination number is four. Several complexes of both the trivalent and divalent ions with ammonia, amines, ethylene diamine, cyanide, halogens and sulfur ligands are known (see also Cobalt Complexes).

Analysis

The element may be analyzed in aqueous acidified phase by flame and furnace atomic absorption, ICP emission and ICP-MS spectroscopic methods. Also, at trace concentrations the element may be measured by x-ray fluorescence and neutron activation analysis. Wavelength for AA measurement is 240.7 nm and for ICP analysis is 228.62 nm.

Hazard

In finely powdered form, cobalt ignites spontaneously in air. Reactions with acetylene and bromine pentafluoride proceed to incandescence and can become violent. The metal is moderately toxic by ingestion. Inhalation of dusts can damage lungs. Skin contact with powdered material can cause dermatitis.

COBALT(II) ACETATE

[71-48-7]
Formula: $Co(C_2H_3O_2)_2 \cdot 4H_2O$; MW 177.02; the commercial product is manufactured and sold in the tetrahydrate form of the compound,

$Co(C_2H_3O_2)_2 \cdot 4H_2O$ [6147-53-1], MW 249.08
Synonym: cobaltous acetate

Uses

Cobalt(II) acetate is used for bleaching and drying varnishes and laquers. Other applications are: as a foam stabilizer for beverages; in sympathetic inks; as a mineral supplement in animal feed; and as a catalyst for oxidation. It also is used in aluminum anodizing solutions.

Physical Properties (Tetrahydrate)

Red-to-violet monoclinic crystals (anhydrous acetate is light pink in color); density 1.705 g/cm^3; becomes anhydrous when heated at 140°C; soluble in water, alcohols and acids.

Preparation

Cobalt(II) acetate is prepared by dissolving cobalt(II) carbonate or hydroxide in dilute acetic acid, followed by crystallization. Also, it may be prepared by oxidation of dicobalt octacarbonyl in the presence of acetic acid.

Analysis

Elemental composition (tetrahydrate salt): Co 23.66%, C 19.29%, H 5.67%, O 51.39%. The aqueous solution may be analyzed for cobalt by various instrumental techniques (see Cobalt). The water of crystallization may be measured by gravimetry under controlled heating at 140°C.

COBALT(II) CARBONATE

[513-79-1]
Formula: $CoCO_3$; MW 118.94; also forms a hexahydrate, $CoCO_3 \cdot 6H_2O$
Synonym: cobaltous carbonate

Uses

The compound occurs in nature as the mineral cobalt spar or sphaerocobaltite. It is used in ceramics; in cobalt pigments; as a catalyst; as a temperature indicator; and in the preparation of other cobalt(II) salts. It also is added to soil to provide nutritional supplement in forage for cattle.

Physical Properties

Pink rhombohedral crystals; refractive index 1.855; density 4.13 g/cm^3; decomposes on heating; insoluble in water and ethanol; soluble in acids.

Preparation

Cobalt(II) carbonate is prepared by heating cobaltous sulfate, cobaltous chloride or any Co^{2+} salt with sodium bicarbonate in solution:

$$CoSO_4 + NaHCO_3 \xrightarrow{heat} CoCO_3 + NaHSO_4$$

Reactions

Cobalt(II) carbonate dissolves in concentrated HCl or HNO_3 when heated, evolving CO_2:

$$CoCO_3 + HCl \xrightarrow{heat} CoCl_2 + CO_2 + H_2O$$

It is oxidized by air or weak oxidizing agents, forming cobalt(III) carbonate, $Co_2(CO_3)_3$. It decomposes on heating, forming the oxides of cobalt with the evolution of CO_2.

Analysis

Elemental composition: Co 49.55% C 10.10%, O 40.35%. Analysis of cobalt may be performed by digesting a measured amount of the compound in hot nitric acid followed by appropriate dilution and measurement by AA, ICP or other instrumental technique (see Cobalt). Also, treatment with hot acid liberates CO_2 (with effervescence) which turns lime water milky. The CO_2 may be analyzed by several tests (see Carbon Dioxide).

Toxicity

The compound is moderately toxic by ingestion. (Lewis (Sr.), R. J. 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed. New York: Van Nostrand Reinhold.)

LD_{50} oral (rat): 640 mg/kg

COBALT CARBONATE, BASIC

[12602-23-2]
Formula: $Co_5(OH)_6(CO_3)_2$ or $2CoCO_3 \cdot 3Co(OH)_2 \cdot H_2O$; MW 516.73
Synonyms: cobalt carbonate hydroxide; cobaltous carbonate basic; basic cobalt carbonate

Uses

The cobalt carbonate basic salt is the commercially-used cobalt carbonate. It is used primarily for manufacturing cobalt pigments. It also is used to prepare cobalt(II) oxide and other cobalt salts.

Physical Properties

Red violet crystal; insoluble in water; decomposes in hot water; soluble in dilute acids and ammonia.

Preparation

The basic carbonate is prepared by adding a solution of sodium carbonate to a cobalt(II) acetate or other Co^{2+} salt solution. The precipitate is filtered and dried.

Analysis

Elemental composition: Co 57.02% , C 4.65% , H 1.17% , O 37.16%. The compound is dissolved in dilute nitric acid and analyzed for cobalt (see Cobalt).

COBALT(II) CHLORIDE

[7646-79-9]
Formula: $CoCl_2$; MW 129.84; also forms dihydrate $CoCl_2 \cdot 2H_2O$ [16544-92-6] and hexahydrate $CoCl_2 \cdot 6H_2O$ [7791-13-1]
Synonym: cobaltous chloride

Uses

Cobalt(II) chloride has several applications. It is used in hygrometers; as a humidity indicator; as a temperature indicator in grinding; as a foam stabilizer in beer; in invisible ink; for painting on glass; in electroplating; and a catalyst in Grignard reactions, promoting coupling with an organic halide. It also is used to prepare several other cobalt salts; and in the manufacture of synthetic vitamin B12.

Preparation

Cobalt(II) chloride is prepared by the action of cobalt metal or its oxide, hydroxide, or carbonate with hydrochloric acid:

$$Co(OH)_2 + 2HCl \rightarrow CoCl_2 + 2H_2O$$

The solution on concentration and cooling forms crystals of hexahydrate which on heating with $SOCl_2$ dehydrates to anhydrous cobalt(II) chloride. Alternatively, the hexahydrate may be converted to anhydrous $CoCl_2$ by dehydration in a stream of hydrogen chloride and dried in vacuum at 100–150°C. The anhydrous compound also may be obtained by passing chlorine over cobalt powder.

Physical Properties

Blue leaflets; turns pink in moist air; hygroscopic; the dihydrate is violet blue crystal; the hexahydrate is pink monoclinic crystal; density 3.36, 2.48 and 1.92 g/cm^3 for anhydrous salt, dihydrate and hexahydrate, respectively; anhydrous salt melts at 740°C and vaporizes at 1,049°C; vapor pressure 60 torr at 801°C; the hexahydrate decomposes at 87°C; the anhydrous salt and the hydrates are all soluble in water, ethanol, acetone, and ether; the solubility of hydrates in water is greater than the anhydrous salt.

Thermochemical Properties

$\Delta H_f°$	–74.69 kcal/mol
$\Delta G_f°$	–64.48 kcal/mol
S°	26.10 cal/degree mol
C_ρ	18.76 cal/degree mol

ΔH_{fus} 10.76 kcal/mol

Reactions

Cobalt(II) chloride undergoes many double decomposition reactions in aqueous solution to produce precipitates of insoluble cobalt salts. For example, heating its solution with sodium carbonate yields cobalt(II) carbonate:

$$CoCl_2 + Na_2CO_3 \xrightarrow{heat} CoCO_3 + 2NaCl$$

Reaction with alkali hydroxide produces cobalt(II) hydroxide:

$$CoCl_2 + 2NaOH \rightarrow Co(OH)_2 + 2NaCl$$

Reaction with ammonium hydrogen phosphate yields cobalt(II) phosphate:

$$3CoCl_2 + 2(NH_4)_2HPO_4 \rightarrow Co_3(PO_4)_2 + 4NH_4Cl + 2HCl$$

While cobalt(II) fluoride is the product of the reaction of anhydrous cobalt(II) chloride with hydrofluoric acid, cobalt(III) fluoride is obtained from fluorination of an aqueous solution of cobalt(II) chloride.

Addition of potassium nitrite, KNO_2 to a solution of cobalt(II) chloride yields yellow crystalline potassium hexanitrocobaltate(III), $K_3Co(NO_2)_6$.

Analysis

Elemental composition: Co 45.39%, Cl 54.61%. Aqueous solution of the salt or acid extract may be analyzed for cobalt by AA, ICP, or other instrumental techniques following appropriate dilution. Chloride anion in the aqueous solution may be measured by titration with silver nitrate using potassium chromate indicator, or by ion chromatography, or chloride ion-selective electrode.

Toxicity

The compound is toxic at high doses. Symptoms include chest pain, cutaneous flushing, nausea, vomiting, nerve deafness, and congestive heart failure. The systemic effects in humans from ingestion include anorexia, increased thyroid size, and weight loss (Lewis (Sr.), R. J. 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed. New York: Van Nostrand Reinhold). Ingestion of a large amount (30–50 g) could be fatal to children.

COBALT COMPLEXES

Cobalt forms many complexes in both the divalent and trivalent states. While the d^7Co^{2+} ion exhibits a coordination number of four or six in the trivalent state, the d^6Co^{3+} ion mostly exhibits coordination number six. Also, trivalent cobalt forms more stable complexes than Co^{2+} ion, and there are many more of them. The most common donor atom in cobalt complexes is nitrogen, having ammonia and amines as ligands forming numerous complexes. Many cobalt cyanide complexes are known in which CN^- coordinates to the cobalt ion through the carbon atom. In aquo complexes, water molecules coordinate through the oxygen atom. Sulfur ligands and halide ions also form numerous complexes with both Co^{2+} and Co^{3+} ions.

Cobalt complexes have limited but some notable applications. Pentacyanocobalt(II) ion can activate molecular hydrogen homogeneously in solution and therefore can act as a hydrogenation catalyst for conjugated alkenes. Cobalt ammine chelates exhibit catalytic behavior in hydrolysis of carboxylate esters, phosphate esters, amides, and nitriles. Single crystals of cyanide complex are used in laser studies. Many aquo-halo mixed complexes are used in making invisible or sympathetic inks and color indicators for desiccants. Certain chelators, such as cobalt ethylenediamine complexes, have unusual oxygen-carrying properties. These polyfunctional donor molecules have the ability to readily absorb and release oxygen. They are used as a convenient source of purified oxygen.

Cobalt(II) forms more tetrahedral complexes than any other transition metal ion. Also, because of small energy differences between the tetrahedral and octahedral complexes, often the same ligand forms both types of Co(II) complexes in equilibrium in solutions.

Some examples of Co^{2+} complexes having varying coordination number and geometry, are presented below:

Coordination Number	Shape	Ligand	Structure/Formula	Name of complex ion/neutral complex
4	tetrahedral	H_2O	$[Co(H_2O)_4]^{2+}$	tetraaquocobalt(II)
4	tetrahedral	$^-(Cl^-, Br^-, I^-)$	$[Co\ X_4]^{2-}$	tetrahalocobalt(II)
4	tetrahedral	SCN^-	$[Co(SCN)_4]^2$	tetrathiocyanato cobalt(II)
4	tetrahedral	Cl^-, H_2O	$[Co(H_2O)_2Cl_2]$	diaquodichlorocobalt(II)
4	tetrahedral	N_3^-	$[Co(N_3)_4]^{2-}$	tetraazido cobalt(II)
5	tetrahedral	N-methyl salicylaldimine	a dimer	bis(N-methyl salicylaldiminato)cobalt (II)
6	tetrahedral	acetylacetonate	a tetramer $Co(acac)_2$	bis(acetylacetonato)cobalt (II)
4	planar	dimethylglyoxime	$Co(dmg)_2$	bis(dimethylglyoximato) cobalt (II)
4	planar	dithioacetylacetonate	$Co(dtacac)_2$	bis(dithioacetyl acetonato)cobalt(II)
4	planar	salicylaldehyde ethylenediamine	$Co(Salen)_2$	bis(salicyaldehyde ethylenediamine) cobalt(II)
4	planar	porphyrin	$Co(porph)_2$	bis(porphyrine)cobalt(II)
4 or 6	planar/distorted octahedral	ethylenediamine accompanies with an anion	$[Co(en)_2]$ $(AgI_2)_2$	bis(ethylendiamino) cobalt(II) disilver diiodide
6	octahedral	dimethyl sulfoxide	$[Co(DMSO)_6]^{2+}$ (the ligand bound through O atom)	hexakis(dimethyl sulfoxide)cobalt(II)
6	octahedral	CN^-, H_2O	$[Co(CN)_5(H_2O)]^{3-}$	pentacyanoaquocobalt(II)
6	octahedral	SCN^-	$[Co(SCN)_6]^{2+}$	hexathiocyanatocobalt(II)
5	triagonal bipyramidal	trialkyl/aryl phosphines, halide ions, CN^-	$CoBr_2(PMe_3)_3$ $Co(CN)_2(PMe_2Ph)_3$	dibromotris(trimethyl phosphine)cobalt(II) dicyanotris(dimethylphenyl phosphine)cobalt(II)

COBALT(III) COMPLEXES

Numerous d^6 cobalt(III) complexes are known and have been studied extensively. Most of these complexes are octahedral in shape. Tetrahedral, planar and square antiprismatic complexes of cobalt(III) are also known, but there are very few. The most common ligands are ammonia, ethylenediamine and water. Halide ions, nitro (NO_2) groups, hydroxide (OH^-), cyanide (CN^-), and isothiocyanate (NCS^-) ions also form Co(III) complexes readily. Numerous complexes have been synthesized with several other ions and neutral molecular ligands, including carbonate, oxalate, trifluoroacetate and neutral ligands, such as pyridine, acetylacetone, ethylenediaminetetraacetic acid (EDTA), dimethylformamide, tetrahydrofuran, and trialkyl or arylphosphines. Also, several polynuclear bridging complexes of amido (NH_2^-), imido (NH^-), hydroxo (OH^-), and peroxo (O_2^{2-}) functional groups are known. Some typical Co(III) complexes are tabulated below:

Name	Formula
cobalt(III)hexammine chloride	$[Co(NH_3)_6]Cl_3$
chloropentamminecobalt(III) chloride	$[Co(NH_3)_5Cl]Cl_2$
aquopentamminecobalt(III)	$[Co(NH_3)_5H_2O]Cl_3$
potassium hexacyanocobaltate(III)	$K_3[Co(CN)_6]$
ammonium tetranitrodiamiminecobaltate(III)	$NH_4[Co(NH_3)_2(NO_2)_4$
potassium hexanitrocobaltate(III)	$K_3[Co(NO_2)_6]$
cyanocobalamine (Vitamin B-12)	$C_{63}H_{88}CoN_{14}O_{14}P$
barium hexacyanocobaltate(III) heptahydrate	$Ba_3[Co(CN)_6]_2 \cdot 7H_2O$

The ammine complexes of Co^{3+} are prepared by adding excess ammonia to a solution of cobalt salt followed by air oxidation and boiling. The brown solution turns pink on boiling. The cyanide complexes are made by adding excess potassium cyanide to a solution of cobalt salt. Acidification of the solution with a small amount of acetic or hydrochloric acid followed by boiling yields $K_3Co(CN)_6$. The aquo-halo mixed complexes are formed by stepwise substitution of H_2O molecule with halide ion in the coordination sphere. In general, a mixed complex may be prepared by substitution with a specific anion.

Alternatively, oxidation of a mixed solution of cobalt(II) halide-ammonium halide or cobalt(II) nitrate-ammonium nitrate in the presence of excess ammonia can form the amine complexes. Such oxidation may be carried out by passing air through the solution for several hours. The yield is high in the presence of activated charcoal.

COBALT(II) CYANIDE

[542-84-7]
Formula: $Co(CN)_2$; MW 110.99; also forms a dihydrate, $Co(CN)_2 \cdot 2H_2O$ [20427-11-6], MW 147.00 and a trihydrate $Co(CN)_2 \cdot 3H_2O$ [26292-31-9]
Synonym: cobaltous cyanide

Uses

The compound has limited commercial applications. It is used as a catalyst and in the preparation of cyanide complexes.

Physical Properties

The anhydrous form is a deep-blue powder; hygroscopic; density 1.872 g/cm^3; melts at 280°C; insoluble in water. The dihydrate is pink to reddish brown powder or needles; insoluble in water and acids; soluble in sodium or potassium cyanide solutions, ammonium hydroxide, and hydrochloric acid.

Preparation

The trihydrate salt is obtained as a reddish brown precipitate by adding potasium cyanide to a cobalt salt solution:

$$CoCl_2 + KCN + 3H_2O \rightarrow Co(CN)_2 \cdot 3H_2O + 2KCl$$

This on dehydration yields anhydrous $Co(CN)_2$. The $Co(CN)_2 \cdot 3H_2O$ precipitate formed above redissolves when excess KCN is added, forming a red solution of potassium cobalt(II) cyanide, $K_4Co(CN)_6$. Stoichiomtric amount of KCN should, therefore, be used in the preparation of cobalt(II) cyanide.

Analysis

Elemental composition: Co 53.11%, C 21.64%, N 25.25%. Cobalt(II) cyanide is digested with nitric acid, brought into aqueous phase and analyzed for Co by various instrumental techniques. For estimating cyanide anion, a weighed amount of solid is treated with dilute sulfuric acid and distilled. The distillate (HCN) is collected over NaOH solution and the alkaline distillate is measured for cyanide by titration with a standard solution of $AgNO_3$ using dimethylaminobenzalrhodanine indicator. The distillate may be analyzed alternatively by colorimetry following treatment with chloramine–T and pyridine-barbituric acid; or by cyanide ion-selective electrode (APHA, AWWA and WEF. 1999. *Standard Methods for the Examination of Water and Wastewater*. 20th ed. Washington, DC: American Public Health Association).

Toxicity

The compound is highly toxic by ingestion and possibly through other routes of exposure.

COBALT(II) FLUORIDE

[10026-17-2]
Formula: CoF_2; MW 96.93; also forms di–, tri– and tetrahydrates.
Synonyms: cobaltous fluoride; cobalt difluoride

Uses

Cobalt(II) fluoride is used as a catalyst for organic reactions.

Physical Properties

Red tetragonal crystal; density 4.46 g/cm^3; melts at 1,127°C; vaporizes around 1,400°C; sparingly soluble in water; soluble in warm mineral acids; decomposes in boiling water. Tetrahydrate is red orthogonal crystal; density 2.22 g/cm^3; decomposes on heating; soluble in water; di– and trihydrates are soluble in water.

Thermochemical Properties

$\Delta H_f°$	–165.4 kcal/mol
$\Delta G_f°$	–154.7 kcal/mol
S°	19.6 cal/degree mol
C_ρ	16.4 cal/degree mol
ΔH_{fus}	14.1 kcal/mol

Preparation

Cobalt(II) fluoride is prepared by heating anhydrous cobalt(II) chloride or oxide in a stream of hydrogen fluoride:

$$CoCl_2 + 2HF \rightarrow CoF_2 + 2HCl$$

$$CoO + 2HF \rightarrow CoF_2 + 2H_2O$$

Also, cobalt(II) fluoride can be prepared as a tetrahydrate, $CoF_2 \cdot 4H_2O$ by dissolving cobalt(II) hydroxide in hydrofluoric acid. The tetrahydrate is then dehydrated to anhydrous fluoride. Elemental fluorine combines with cobalt at 450°C forming mixtures of cobalt(II)‾and cobalt(III) fluorides.

Analysis

Elemental composition: Co 60.80%, F 39.20%. Cobalt(II) fluoride is dissolved in hot nitric acid, the solution is appropriately diluted with water and analyzed for cobalt by AA or ICP spectrophotometry (see Cobalt). A small amount of salt dissolved in cold water (hot water may partially decompose forming oxyfluoride, $CoF_2 \cdot CoO \cdot H_2O$) may be analyzed for fluoride ion by fluoride ion-selective electrode or ion chromatography.

Toxicity

The compound is toxic by ingestion.

LD_{50} oral (rat): 150 mg/kg

COBALT(III) FLUORIDE

[10026-18-3]
Formula: CoF_3; MW 115.93
Synonyms: cobaltic fluoride; cobalt trifluoride

Uses

Cobalt(III) fluoride is used as a fluorinating agent for fluorination of hydrocarbons (Fowler process).

Physical Properties

Light brown hexagonal crystal; density 3.88 g/cm^3; moisture sensitive; stable in dry air; melts at 927°C; reacts with water.

Preparation

Cobalt(III) fluoride may be prepared by reaction of elemental fluorine with cobalt(II) fluoride, cobalt(II) chloride or cobalt(III) oxide at 300 to 400°C.

$$2CoF_2 + F_2 \xrightarrow{300-400^\circ C} 2CoF_3$$

$$2CoCl_2 + 3F_2 \xrightarrow{300-400^\circ C} 2CoF_3 + 2Cl_2$$

It should be stored in a sealed glass ampule, free from moisture.

Electrolytic oxidation of cobalt(II) fluoride in 40% hydrofluoric acid yields hydrated cobalt(III) fluoride, $CoF_3 \cdot 3.5H_2O$ (3.5 is the stoichiometric amount of water per CoF_3 molecule in the crystal lattice).

Reactions

Cobalt(III) fluoride reacts with water forming a finely divided black precipitate of cobalt(III) hydroxide, $Co(OH)_3$.

When heated with hydrogen at 400°C, it is reduced first to cobalt(II) fluoride and then to cobalt metal.

Heating with oxygen at 400 to 500°C converts the fluoride to oxide:

$$4CoF_3 + 3O_2 \xrightarrow{400-500^\circ C} 2Co_2O_3 + 6F_2$$

Anhydrous cobalt(III) fluoride reacts with many nonmetallic and metalloid elements including bromine, iodine, sulfur, phosphorus, carbon, arsenic, and silicon. It fluorinates these elements, and is reduced to Co^{2+}.

Analysis

Elemental composition: Co 50.83%, F 49.17%. Cobalt (III) fluoride may be digested with nitric acid and the resulting acid extract diluted with water and analyzed for cobalt by various instrumental techniques (see Cobalt). The compound may be identified from its reaction with water forming a black powder material.

Toxicity

Due to its high affinity for moisture, skin contact can cause irritation.

COBALT(II) HYDROXIDE

[21041-93-0]
Formula: $Co(OH)_2$; MW 92.95
Synonyms: cobaltous hydroxide; cobaltous hydrate

Uses

Cobalt(II) hydroxide is used as a drier for paints and varnishes and is added to lithographic printing inks to enhance their drying properties. Other applications are in the preparation of cobalt salts; as a catalyst; and in storage battery electrodes.

Physical Properties

Two forms occur, a rose-red powder (more stable) and a bluish-green powder less stable than the red form; rhombohedral crystals; density 3.597 g/cm^3; decomposes on heating; practically insoluble in water 3.2 mg/L; K_{sp} 1.0×10^{-15}; soluble in acids and ammonia; insoluble in dilute alkalis.

Thermochemical Properties

$\Delta H_f°$	–129.0 kcal/mol
$\Delta G_f°$	–108.6 kcal/mol
S°	19.0 cal/degree mol

Preparation

Cobalt(II) hydroxide is obtained as a precipitate when an alkaline hydroxide is added to an aqueous solution of cobalt(II) salt:

$$CoCl_2 + 2NaOH \rightarrow Co(OH)_2 + 2NaCl$$

$$Co(NO_3)_2 + 2NaOH \rightarrow Co(OH)_2 + 2NaNO_3$$

Reactions

Thermal decomposition to cobaltous oxide, CoO, occurs at 168°C in a vacuum.

Cobalt(II) hydroxide is oxidized by air and other oxidizing agents, forming cobalt(III) hydroxide, $Co(OH)_3$. Reactions with mineral acids produce corresponding Co^{2+} salts.

Analysis

Elemental composition: Co 63.40%, H 2.17%, O 34.43%. Cobalt(II) hydroxide is dissolved in nitric acid and the acid extract is analyzed for cobalt metal by AA, ICP or other instrumental techniques following appropriate dilution (see Cobalt).

COBALT(II) IODIDE

[15238-00-3]
Formula: CoI_2; MW 312.74; also forms a hexahydrate, $CoI_2 \cdot 6H_2O$, MW 420.83
Synonyms: cobaltous iodide; cobalt diiodide

Uses

Cobalt(II) iodide is used for analysing water in organic solvents; and as a color indicator to determine moisture and humidity.

Physical Properties

Exists in two isomorphous forms, α– and ß–forms; both modifications highly hygroscopic. The α–form is black hexagonal crystal; density 5.58 g/cm^3; turns dark green in air; melts at 560°C; disolves in water giving pink coloration. The α–forms sublimes in vacuo, partly forming an isomorous yellow modification–the anhydrous β–form.

The β–modification is a yellow powder; density 5.45 g/cm^3; converts to the α–form when heated to 400°C; absorbs moisture from air, the yellow powder becoming green droplets; dissolves readily in water forming a colorless solution which turns pink on heating.

The hexahydrate is red hexagonal crystals; density 2.90 g/cm^3; loses water at 130°C giving anhydrous iodide; soluble in water, ethanol, acetone, chloroform and ether, forming colored solutions, (while the aqueous solution is red below 20°C and green above this temperature; the salt forms blue solution in ethanol, chloroform and ether).

Thermochemical Properties

$\Delta H_f°$	–21.20 kcal/mol

Preparation

Cobalt(II) iodide is prepared by heating cobalt powder in a stream of hydrogen iodide at 400 to 450°C:

$$Co + 2HI \xrightarrow{400-450^\circ C} CoI_2 + H_2$$

The product obtained is the black crystalline α–form.

Cobalt(II) iodide also may be made by heating cobalt powder with iodine vapor.

Analysis

Elemental composition: Co 18.84%, I 81.16%. CoI_2 may be identified from its varying colors in different solvents. Under varying conditions, its aqueous solution may be analyzed for cobalt by AA, ICP or other instrumental techniques after appropriate dilution (see Cobalt). Iodide anion may be analyzed in sufficiently diluted aqueous phase by ion chromatography. Also, the analysis of the compound dissolved in chloroform or acetone at low ppm concentration may be performed by GC/MS. The presence of characteristic iodide anion mass, 127 amu, in the mass spectra serves as a further confirmatory test.

COBALT(II) NITRATE

[10141-05-6]
Formula: $Co(NO_3)_2$; MW 182.94; occurs in common hexahydrate form, $Co(NO_3)_2 \cdot 6H_2O$ [10026-26-9], MW 291.03

Uses

Cobalt nitrate is used in the decoration of porcelain and stones; in the manufacture of invisible inks and cobalt pigments; in hair dyes; in animal feeds; as an additive to soils; in catalysts preparation; and in vitamin supplements.

Physical Properties

The hexahydrate is red monoclinic crystal; deliquescent in moist air; density 1.87 g/cm^3; decomposes at 55°C, losing three molecules of water; decomposes to green cobalt(II) oxide on further heating at 74°C; very soluble in water (134 g/100mL at 0°C); also soluble in alcohols and acetone.

The anhydrous salt is pale red powder; density 2.49 g/cm^3; decomposes around 100°C; soluble in water.

Thermochemical Properties

$\Delta H_f°$	–100.50 kcal/mol

Preparation

Cobalt(II) nitrate is prepared by treating the metal, or its oxide, hydroxide or carbonate with dilute nitric acid. The solution on evaporation yields red crystals of hexahydrate:

$$Co + 2HNO_3 \rightarrow Co(NO_3)_2 + H_2$$

$$Co(OH)_2 + 2HNO_3 \rightarrow Co(NO_3)_2 + 2H_2O$$

$$CoCO_3 + 2HNO_3 \rightarrow Co(NO_3)_2 + CO_2 + H_2O$$

Analysis

Elemental composition (anhydrous salt): Co 32.33%, N 15.31%, O 52.47%. The aqueous solution may be analyzed for cobalt by AA or ICP or other instrumental methods. The nitrate anion may be measured by ion chromatography or nitrate ion-selective electrode. The solutions may require sufficient dilution for all these measurements.

Toxicity

The compound is toxic by oral, subcutaneous, and intravenous routes.

LDL_O oral (rabbit): 250 mg/kg

LDL_O subcutaneous (rabbit): 75 mg/kg

COBALT OCTACARBONYL

[10210-68-1]
Formula: $Co_2(CO)_8$; MW 341.95
Synonyms: dicobalt octacarbonyl; cobalt carbonyl; cobalt tetracarbonyl dimer

Uses

Cobalt octacarbonyl is used as a catalyst in the Oxo process (see Carbon Monoxide). It also is used as a catalyst for hydrogenation, isomerization, hydrosilation and polymerization reactions. The compound is also a source of producing pure cobalt metal and its purified salts.

Physical Properties

Orange crystals; density 1.78 g/cm³; melts at 5l°C; decomposes above this temperature; insoluble in water; soluble in most organic solvents including alcohol, ether, carbon disulfide.

Preparation

Cobalt octacarbonyl is prepared by the reaction of finely divided cobalt with carbon monoxide under pressure:

$$2Co + 8CO \rightarrow Co_2(CO)_8$$

The compound may be prepared in a similar way from cobalt(II) iodide. Also, it may be prepared by thermal decomposition of cobalt carbonyl hydride:

$$2HCo(CO)_4 \xrightarrow{40^\circ C} Co_2(CO)_8 + H_2$$

Reactions

Cobalt octacarbonyl forms complexes with many types of ligands, replacing one or more CO groups.

Reaction with potasium cyanide forms a cyano derivative that probably has the structure $K_3[Co(CN)_5(CO)]$.

Reaction with ammonia forms ammine salt, $[Co(NH_3)_6][Co(CO)_4]_2$ liberating carbon monoxide (Hieber, W. and H. Schulten. 1937. *Z. Anorg. Allgem. Chem.*, 236, p. 17). In a strongly alkaline solution, cobalt octacarbonyl undergoes hydrolysis, forming cobalt carbonyl hydride. This hydride, used in organic synthesis as a catalyst, may be prepared in a solution of hexane or toluene by adding octacarbonyl to dimethylformamide (DMF), followed by acidification:

$$3Co_2(CO)_8 + 12DMF \rightarrow 2Co(DMF)_6[Co(CO)_4]_2 + 8CO$$

$$Co(DMF)_6[Co(CO)_4]_2 + 2HCl \rightarrow 2HCo(CO)_4 + 6\ DMF + CoCl_2$$

Metal derivatives of cobalt carbonyl hydride such as $Tl[Co(CO)_4]$, $Zn[Co(CO)_4]_2$, or $Cd[Co(CO)_4]_2$ are formed upon reaction of cobalt octacarbonyl with these metals in the presence of carbon monoxide under pressure. Reaction with halogens (X) produces cobalt carbonyl halides, $Co(CO)X_2$.

Cobalt octacarbonyl decomposes when treated with nitric acid, forming cobalt nitrate. A similar reaction occurs with sulfuric acid or hydrochloric acid, but at a slower rate.

Analysis

Elemental composition: Co 32.47%, C 28.10%, O 37.43%. Cobalt octacarbonyl may be digested with nitric acid, diluted appropriately, and analyzed by AA, ICP, or other instrumental methods (see Cobalt). The compound may be dissolved in methanol and the solution analyzed by GC/MS.

Toxicity

Cobalt octacarbonyl is toxic by ingestion, inhalation, and other routes of exposure.

LD_{50}` intraperitoneal (mice): 378 mg/kg

COBALT(II) OXIDE

[1307-96-6]
Formula: CoO; MW 74.932
Synonyms: cobaltous oxide; cobalt monoxide

Uses

Cobalt(II) oxide is used as a pigment for ceramics and paints; for drying paints, varnishes and oils; for coloring glass; as a catalyst; and for preparation of other cobalt salts. The commercial product is a mixture of cobalt oxides.

Physical Properties

The commercial product is usually dark grey powder, but the color may vary from olive geeen to brown depending on particle size; density 6.44 g/cm^3, which also may vary between 5.7 to 6.7 g/cm^3, depending on the method of preparation; melts around 1,830°C; insoluble in water; soluble in acids and alkalis.

Thermochemical Properties

$\Delta H_f°$	–56.86 kcal/mol
$\Delta G_f°$	–51.19 kcal/mol

S°	12.67 cal/degree mol
C_ρ	13.19 cal/degree mol

Preparation

Cobalt(II) oxide is prepared by heating cobalt(II) carbonate, $CoCO_3$, cobalt(III) oxide, Co_2O_3 or tricobalt tetroxide, Co_3O_4, at high temperatures in a neutral or slightly reducing atmosphere:

$$C_0CO_3 \xrightarrow[\text{helium}]{\text{elevated temperature}} C_0O + CO_2$$

Reactions

Cobalt(II) oxide readily absorbs oxygen at ordinary temperatures. Heating at low temperatures with oxygen yields cobalt(III) oxide.

Cobalt(II) oxide reacts with acids forming their cobalt(II) salts. Reactions with sulfuric, hydrochloric and nitric acids yield sulfate, chloride and nitrate salts, respectively, obtained after the evaporation of the solution:

$$CoO + H_2SO_4 \rightarrow CoSO_4 + H_2O$$

$$CoO + 2HCl \rightarrow CoCl_2 + H_2O$$

Reactions with alkali hydroxide yield cobalt(II) hydroxide. Cobalt(II) oxide is readily reduced by hydrogen, carbon or carbon monoxide to cobalt:

$$CoO + H_2 \xrightarrow{heat} Co + H_2O$$

$$CoO + CO \xrightarrow{heat} Co + CO_2$$

It combines with silica in molten states under electrothermal heating to produce silicate, $CoO{\cdot}SiO_2$.

Analysis

Elemental composition: Co 78.65%, O 21.35%. The commercial product generally contains 76% Co. The powder is digested with nitric acid and the acid extract, after dilution, is analyzed for Co by various instrumental techniques (see Cobalt). Cobalt(II) oxide may be analyzed by x-ray directly, without acid digestion.

Toxicity

Cobalt(II) oxide is moderately toxic by ingestion and subcutaneous and intratracheal routes.

LD_{50} oral (rat): 202 mg/kg

COBALT(III) OXIDE

[1308-04-9]
Formula: Co_2O_3; MW 165.86
Synonyms: cobaltic oxide; cobalt trioxide; dicobalt trioxide; cobalt sesquioxide

Uses

Cobalt(III) oxide is used as a pigment; for glazing porcelain and pottery; and for coloring enamels.

Physical Properties

Grayish black powder; density 5.18 g/cm³; decomposes at 895°C; insoluble in water; soluble in concentrated mineral acids.

Preparation

Cobalt(III) oxide is prepared by heating cobalt compounds at low temperatures in air.

Reactions

Heating with hydrogen, carbon or carbon monoxide reduces the oxide to cobalt metal.

$$Co_2O_3 + 3H_2 \xrightarrow{heat} 2Co + 3H_2O$$

$$Co_2O_3 + 3CO \xrightarrow{heat} 2Co + 3CO$$

$$2Co_2O_3 + 3C \xrightarrow{heat} 4Co + 3CO_2$$

Strong heating in air converts cobalt(III) oxide to tricobalt tetroxide.

Reactions with mineral acids produce their Co^{3+} salts:

$$Co_2O_3 + 6HCl \rightarrow 2CoCl_3 + 3H_2O$$

Analysis

Elemental Composition: Co 71.06%, O 28.94%. Cobalt may be analyzed in acidified solutions by various instrumental techniques (see Cobalt).

COBALT(II) SULFATE

[10124-43-3]
Formula: $CoSO_4$; MW 155.00; the commercial form is heptahydrate, $CoSO_4 \cdot 7H_2O$ [10026-24-1]; also forms a monohydrate, $CoSO_4 \cdot H_2O$ [13455-34-0]

Synonym: cobaltous sulfate

Uses

Cobalt(II) sulfate is used in storage batteries and electroplating baths for cobalt. It also is used as a dryer for lithographic inks; in pigments for decorating porcelains; in ceramics, glazes and enamels to protect from discoloring; and as a additive to soils.

Physical Properties

The anhydrous salt of cobalt(II) sulfate is a red orthogonal crystal; density 3.71g/cm³; melts above 700°C; the monohydrate is red orthogonal crystal having a density of 3.08 g/cm³; the heptahydrate is a pink salt, monoclinic prismatic crystals, density 2.03 g/cm³; heptahydrate dehydrates to hexahydrate at 41°C and converts to monohydrate at 74°C; the anhydrous salt and heptahydrates are soluble in water; monohydrate slowly dissolves in boiling water.

Thermochemical Properties

$\Delta H_f°$	–212.3 kcal/mol
$\Delta G_f°$	–187.0 kcal/mol
S°	28.2 cal/degree mol

Preparation

Cobalt(II) sulfate is prepared by dissolving cobalt(II) oxide, hydroxide or carbonate in dilute sulfuric acid, followed by crystallization:

$$CoO + H_2SO_4 \rightarrow CoSO_4 + H_2O$$

$$Co(OH)_2 + H_2SO_4 \rightarrow CoSO_4 + 2H_2O$$

$$CoCO_3 + H_2SO_4 \rightarrow CoSO_4 + CO_2 + H_2O$$

Crystallization yields the commercial product, pink heptahydrate. Further oxidation of this salt in dilute H_2SO_4 with ozone or fluorine produces hydrated cobalt(III) sulfate, $Co_2(SO_4)_3 \cdot 18H_2O$. This blue octadecahydrate, $Co_2(SO_4)_3 \cdot 18H_2O$ also is obtained by electrolytic oxidation of cobalt(II) chloride or any cobalt(II) salt solution in 8M sulfuric acid.

Analysis

Elemental composition: Co 38.03%, S 20.68%, O 41.29%. Solid cobalt(II) sulfate is brought to aqueous phase by acid digestion, appropriately diluted, and analyzed for cobalt by flame or furnace AA or ICP. It also may be determined in the solid crystalline form by x-ray methods. The sulfate anion may be measured by dissolving an accurately measured small amount of salt in measured quantities of water and analyzing the solution by ion chromatography.

COBALT SULFIDES

Occurrence and Uses

Cobalt forms four sulfides: (1) cobalt(II) sulfide or cobaltous sulfide, CoS, MW 91.00, CAS [1317-42-6]. (2) cobalt(III) sulfide or cobaltic sulfide, or cobalt sesquisulfide, Co_2S_3, MW 214.06, CAS [1332-71-4] (3) cobalt disulfide, CoS_2, MW 123.05. (4) tricobalt tetrasulfide, Co_3S_4, MW 305.04

Among these sulfides, only the ordinary cobalt(II) sulfide, CoS has commercial applications. It is used as a catalyst for hydrogenation or hydrodesulfurization reactions. Cobalt(II) sulfide is found in nature as the mineral sycoporite. The mineral linneite is made up of Co_3S_4, tricobalt tetrasulfide.

Physical Properties

Cobalt(II) sulfide is reddish brown to black octahedral crystal; density 5.45 g/cm^3; melts above 1,100°C; practically insoluble in water (3.8 mg/L); slightly soluble in acids.

Cobalt(III) sulfide is a grayish-black crystalline substance; density 4.80 g/cm^3; insoluble in water; decomposes in acids.

Cobalt disulfide is a black cubic crystal; density 4.27 g/cm^3; insoluble in water; soluble in nitric acid.

Tricobalt tetrasulfide has a reddish color; density 4.86 g/cm^3; decomposes at 480°C; insoluble in water.

Preparation

Cobalt sulfides are found in minerals, sycoporite and linneite, in different forms. Also, they may be readily prepared in the laboratory. A black precipitate of CoS is obtained by passing hydrogen sulfide through an alkaline solution of Co(II) salt, such as $CoCl_2$. Also, the compound is produced by heating cobalt metal with H_2S at 700°C. Heating CoS with molten sulfur for a prolonged period yields cobalt difulfide, CoS_2 as a black powder. The disulfide may decompose and lose sulfur if heated at elevated temperatures.

Heating cobalt metal at 400°C with H_2S yields tricobalt tetrasulfide, Co_3S_4. The temperatures must be well controlled in these preparative processes to obtain a specific sulfide. As the temperatures near 700°C the metal yields CoS, and above 700°C, it produces a sulfide that probably has the composition Co_9S_8.

Analysis

The stoichiometric compositions may be determined from cobalt analysis of nitric acid extract of the solid material by AA, ICP, or other instruments. The structural form of sulfides and their composition may be analysed by x-ray diffraction or fluorescence methods.

TRICOBALT TETROXIDE

[1308-06-1]
Formula: Co_3O_4; MW 240.80
Synonyms: cobaltic cobaltous oxide; cobalto cobaltic oxide; cobaltosic oxide; tricobalt tetraoxide

Uses

Tricobalt tetroxide is a minor component of commercial cobalt oxides. It is used in ceramics, pigments, and enamels. Other applications are in grinding wheels, in semiconductors, and for preparing cobalt metal.

Physical Properties

Black cubic crystal; density 6.11 g/cm^3; decomposes above 900°C, losing oxygen; insoluble in water; soluble in acids and alkalis

Thermochemical Properties

$\Delta H_f°$	–212.95 kcal/mol
$\Delta G_f°$	–184.99 kcal/mol
S°	24.5 cal/degree mol
C_ρ	29.5 cal/degree mol

Preparation

Tricobalt tetroxide is obtained when cobalt(II) carbonate, cobalt(II) or cobalt(III) oxide, or cobalt hydroxide oxide, CoO(OH) is heated in air at temperatures above 265°C. The temperature must not exceed 800°C (see decomposition temperature above).

Reactions

Heating above 900°C expels oxygen out of the molecule forming cobalt(II) oxide:

$$2Co_3O_4 \xrightarrow{>900^\circ Ct} 6CoO + O_2$$

Tricobalt tetroxide absorbs oxygen at lower temperatures, but there is no change in the crystal structure.)

The oxide is reduced to its metal by hydrogen, carbon or carbon monoxide.

$$Co_3O_4 + 4H_2 \xrightarrow{heat} 3Co + 4H_2O$$

$$Co_3O_4 + 4CO \xrightarrow{heat} 3Co + 4CO_2$$

Analysis

Elemental composition: Co 73.42%, O 26.58%. The nitric acid extract of the oxide may be analyzed for cobalt by various instrumental methods (see Cobalt). Additionally, the solid crystalline product may be characterized by x-ray techniques.

COPPER

[7440-50-8]
Symbol Cu; atomic number 29; atomic weight 63.546; a Group IB (Group 11) metal; electron configuration $[Ar]3d^{10}4s^1$; (electron configuration of Cu^+, $[Ar]3d^{10}$ and Cu^{2+} $[Ar]3d^9$); most common valence states +1, +2; two natural isotopes, Cu-63 (69.09%), Cu-65 (30.91%).

Occurrence and Uses

The use of copper dates back to prehistoric times. The metal, its compounds, and alloys have numerous applications in every sphere of life–making it one of the most important metals. Practically all coinages in the world are made out of copper or its alloys. Its alloys, bronze and brass, date from ancient times. More modern alloys such as monel, gun metals, and beryllium-copper also have wide applications. The metal is an excellent conductor of electricity and heat and is used in electric wiring, switches and electrodes. Other applications are in plumbing, piping, roofing, cooking utensils, construction materials, and electroplated protective coatings. Its compounds, namely the oxides, sulfates, and chlorides, have numerous of commercial applications.

Copper is distributed widely in nature as sulfides, oxides, arsenides, arsenosulfides, and carbonates. It occurs in the minerals cuprite, chalcopyrite, azurite, chalcocite, malachite and bornite. Most copper minerals are sulfides or oxides. Native copper contains the metal in uncombined form. The principal copper minerals with their chemical compositions and percentage of copper are listed below:

chalcopyrite	$CuFeS_2$	34.5
chalcocite	Cu_2S	79.8
enargite	$Cu_3As_5S_4$	48.3
covellite	CuS	66.4
bornite	Cu_5FeS_4	63.3
azurite	$2CuCO_3 \cdot Cu(OH)_2$	55.1
malachite	$CuCO_3 \cdot Cu(OH)_2$	57.3
cuprite	Cu_2O	88.8
tenorite	CuO	79.8
atacamite	$CuCl_2 \cdot 3Cu(OH)_2$	59.4
tennantite	$Cu_3As_2S_7$	57.0
tetrahedrite	$Cu_8Sb_2S_7$	52.1
native copper	Cu	100

Physical Properties

Reddish brown metal; face-centered cubic crystal; density 8.92 g/cm^3; Mohs hardness 2.5 to 3.0; Brinnel hardness 43 (annealed); electrical resistivity 1.71 microhm-cm at 25°C; Poisson's ratio 0.33; melts at 1,083°C; vaporizes at 2,567°C; insoluble in water; dissolves in nitric acid and hot sulfuric acid; slightly soluble in hydrochloric acid; also soluble in ammonium hydroxide, ammonium carbonate and potassium cyanide solutions.

Thermochemical Properties

$\Delta H_f°$(cry)	0.0
S° (cry)	7.92 cal/degree mol
C_ρ (cry)	5.84 cal/degree mol
$\Delta H_f°$(g)	80.86 kcal/mol
$\Delta G_f°$ (g)	71.37 kcal/mol
S° (g)	39.7 cal/degree mol
ΔH_{fus}	3.11 kcal/mol
Coeff. Linear expansion	16.6×10^{-6}/°C at 25°C
Thermal conductivity	3.98 watts/cm°C

Production

In general, copper metal is extracted from its ores by various wet processes. These include leaching with dilute sulfuric acid or complexing with ligands (e.g., salicylaldoximes), followed by solvent extraction. The solution is then electrolyzed to refine copper.

In most industrial processes, copper is produced from the ore chalcopyrite, a mixed copper-iron sulfide mineral, or from the carbonate ores azurite and malachite. The extraction process depends on the chemical compositions of the ore. The ore is crushed and copper is separated by flotation. It then is roasted at high temperatures to remove volatile impurities. In air, chalcopyrite is oxidized to iron(II) oxide and copper(II) oxide:

$$2CuFeS_2 + 3O_2 \rightarrow 2FeO + 2CuS + 2SO_2$$

Then the roasted ore is combined with sand, powdered limestone, and some unroasted ore (containing copper(II) sulfide), and heated at 1,100°C in a reverberatory furnace. Copper(II) sulfide is reduced to copper(I) sulfide. Calcium carbonate and silica react at this temperature to form calcium silicate, $CaSiO_3$ The liquid melt of $CaSiO_3$ dissolves iron(II) oxide forming a molten slag of mixed silicate:

$$CaSiO_3\,(l) + FeO\,(s) + SiO_2\,(s) \xrightarrow{1100^\circ C} CaSiO_3 \bullet FeSiO_3\ (l)$$

Lighter mixed silicate slag floats over the denser, molten copper(I) sulfide. Slag is drained off from time to time. Molten Cu_2S is transferred to a Bessmer converter where it is air oxidized at elevated temperatures producing metallic copper and sulfur dioxide:

$$Cu_2S\ (l) + O_2\ (g) \xrightarrow[\text{temperattures}]{\text{elevated}} 2Cu\ (l) + SO_2\ (g)$$

Metallic copper obtained above is purified by electrolytic refining. The electrolytic cell consists of a cathode made of thin sheets of very pure copper connected to the negative terminal of a direct-current generator, and a lump of extracted impure copper from the ore serving as an anode. A solution of copper(II) sulfate in sulfuric acid is used as electrolyte. Electrolysis causes transfer of copper from the anode to the electrolyte solution, and from there to the cathode. Pure copper is deposited on the cathode which grows longer and larger in size. The impure copper anode correspondingly becomes smaller and smaller in size. Also, a sludge, known as anode mud, collects under the anode. The mud contains ore impurities, such as silver, gold, and tellurium, which are more difficult to oxidize than copper. Copper-plating on other metals is done by similar methods.

Reactions

Copper forms practically all its stable compounds in +1 and +2 valence states. The metal oxidizes readily to +1 state in the presence of various complexing or precipitating reactants. However, in aqueous solutions +2 state is more stable than +1. Only in the presence of ammonia, cyanide ion, chloride ion, or some other complexing group in aqueous solution, is the +1 valence state (cuprous form) more stable then the +2 (cupric form). Water-soluble copper compounds are, therefore, mostly cupric unless complexing ions or molecules are present in the system. The conversion of cuprous to cupric state and metallic copper in aqueous media (ionic reaction, $2Cu^+ \rightarrow Cu^\circ + Cu^{2+}$) has a K value of 1.2×10^6 at 25°C.

Heating the metal in dry air or oxygen yields black copper(II) oxide which on further heating at high temperatures converts to the red cuprous form, Cu_2O.

Copper combines with chlorine on heating forming copper(II) chloride. This dissociates into copper(I) chloride and chlorine when heated to elevated temperatures.

$$Cu + Cl_2 \xrightarrow{heat} CuCl_2$$

$$2CuCl_2 \xrightarrow[\text{temperatures}]{\text{elevated}} Cu_2Cl_2 + Cl_2$$

A similar reaction occurs with bromine; at first copper(II) bromide is formed which at red heat converts to copper(I) bromide. Fluorination yields CuF_2. Heating the metal with iodine and concentrated hydriodic acid produces copper(I) iodide. When copper is heated in an atmosphere of hydrogen sulfide and hydrogen, the product is copper(I) sulfide, Cu_2S.

The standard electrode potentials, E° for the half-reactions are:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu\ (s) \qquad +0.34\ V$$

$$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq) \qquad +0.15\ V$$

The metal is not strong enough to reduce H^+ from acids to H_2. Therefore, under ordinary conditions, copper metal does not liberate hydrogen from mineral acids. Copper can reduce Ag^+, Au^{3+}, and Hg^{2+} ions that have greater positive E° values for reduction half reactions, thus displacing these metals from their aqueous solutions.

$$Cu(s) + Hg_2Cl_2 \rightarrow Cu_2Cl_2 + 2Hg \qquad E° \text{ cell } = 0.51V$$

Similarly, copper displaces silver from silver nitrate solution:

$$Cu(s) + AgNO_3\,(aq) \rightarrow Cu(NO_3)_2\,(aq) + Ag\,(s)$$

Copper liberates nitric oxide from nitric acid:

$$3Cu\,(s) + 2NO_3^{-}\,(aq) + 8H^{+}\,(aq) \rightarrow 3Cu^{2+}\,(aq) + 2NO\,(g) + 4H_2O\,(l)$$

Copper(II) ion readily forms complexes with various ligands. It slowly forms a deep blue solution in aqueous ammonia. Its ammonia complex, $Cu(NH_3)_4^{2+}$ is very stable, the formation constant, K being $5.6x10^{11.}$

Analysis

Copper may be analyzed readily at trace concentration levels by flame-AA, furnace-AA, ICP emission spectrophotometry, ICP-MS, neutron activation analysis, and the wavelength dispersive x-ray fluorescence method. Also, the metal may be determined by colorimetry. In colorimetric methods, aqueous solutions of copper salts are reduced to Cu^+ ions by hydroxylamine hydrochloride. The solution is treated with neocuproine (2,9-dimethyl-1,10-phenanthroline) to form a yellow complex or with bathocuproine (2,9-dimethyl-4,7,-diphenyl-1,10-phenanthroline) to form an orange product, the absorbance of which may be measured using a spectrophotometer or a filter photometer at 457 and 484 nm, respectively. The most sensitive wavelength for flame or furnace AA measurement is 324.7 nm. Suggested wavelengths for ICP measurement are 324.75 and 219.96 nm. ICP-MS offers a much lower detection limit than any other method. Copper imparts a deep green (parrot green) color to flame.

Toxicity

Although the toxicity of metallic copper is very low, many copper(II) salts may have varying degrees of toxicity. Inhalation of dusts, mists or fumes of the metal can cause nasal perforation, cough, dry throat, muscle ache, chills and metal fever. Copper in trace amounts is a nutritional requirement, used metabolically in plant and animal enzymes and other biological molecules. It can be either a toxicant or a nutrient within a concentration that may be in the same order of magnitude.

COPPER(II) ACETATE

[142-71-2]

Formula: $Cu(C_2H_3O_2)_2$; MW 181.64; also forms a monohydrate $Cu(C_2H_3O_2)_2 \cdot H_2O$ [6046-93-1], MW 199.65.

Synonyms: cupric acetate; copper acetate; cupric diacetate; crystallized verdigris; neutralized verdigris; crystals of Venus.

Uses

Copper(II) acetate is used as a pigment for ceramics; in the manufacture of Paris green; in textile dyeing; as a fungicide; and as a catalyst.

Physical Properties

Bluish-green fine powder; hygroscopic. The monohydrate is dimeric; density 1.88 g/cm^3; melts at 115°C; decomposes at 240°C; soluble in water and ethanol; and slightly soluble in ether.

Preparation

Copper(II) acetate is prepared by treatment of copper(II) oxide, CuO, or copper(II) carbonate, $CuCO_3$, with acetic acid, followed by crystallization:

$$CuO + 2CH_3COOH \rightarrow (CH_3COO)_2Cu + H_2O$$

Analysis

Elemental composition: Cu 34.98%, C 26.45%, H 3.33%, O 35.24%. Copper(II) acetate is digested with nitric acid, diluted appropriately and analyzed for copper by various instrumental techniques (see Copper).

Toxicity

Copper(II) acetate is moderately toxic by ingestion and possibly other routes of administration.

LD_{50} oral (rat): c. 600 mg/kg

COPPER ACETATE, BASIC

[52503-64-7]
Formula: $Cu(C_2H_3O_2)_2 \cdot CuO \cdot 6H_2O$; MW 369.27; the formula varies–several compositions are known at different ratios of copper acetate to copper oxide/hydroxide. The composition of blue verdigris is $Cu(C_2H_3O_2)_2 \cdot CuO \cdot 5H_2O$; green verdigris $2Cu(C_2H_3O_2)_2 \cdot CuO \cdot 5H_2O$. Other compositions are $Cu(C_2H_3O_2)_2 \cdot 3CuO \cdot 2H_2O$ and $Cu(C_2H_3O_2)_2 \cdot 2CuO$.
Synonyms: cupric acetate, basic; cupric subacetate

Uses

The basic copper acetate is used as a mordant in dyeing and printing; in the manufacture of Paris green and other pigments; and as a fungicide and insecticide.

Physical Properties

Color and form varies from blue crystals to greenish powder; slightly soluble in water and ethanol; soluble in dilute acids and ammonium hydroxide.

Preparation

The basic acetates are obtained by the treatment of copper with acetic acid followed by air oxidation.

Analysis

The compositions of the basic acetates with varying copper acetate-copper hydroxide-water ratios may be determined by elemental analyses of carbon, hydrogen, oxygen and copper. X-ray and thermogravimetric analyses should provide further information on their compositions.

COPPER(I) ACETYLIDE

[1117-94-8]
Formula: Cu_2C_2; MW 151.11

Structure: $\mathrm{Cu}^{+}\,\overline{\mathrm{C}}\equiv\overline{\mathrm{C}}\,\mathrm{Cu}^{+}$
Synonyms: cuprous acetylide; cuprous carbide

Uses

Copper(I) acetylide is used in a diagnostic test for CH unit; to prepare pure copper powder; in purification of acetylene; and as a catalyst in the synthesis of acrylonitrile and 2-propyn-1-ol.

Physical Properties

Red amorphous powder; explodes on heating; insoluble in water; soluble in acids.

Preparation

Copper(I) acetylide is prepared by passing acetylene gas over an aqueous solution of ammoniacal copper salt:

$$\mathrm{HCCH + 2Cu(NH_3)_2OH \rightarrow CuCCCu + 4NH_3 + 2H_2O}$$

Also, the compound may be obtained by reacting acetylene with a soluble copper(I) salt solution.

Reactions

Copper(I) acetylide oxidizes in air forming copper(II) acetylide, CuC_2:

$$\mathrm{2Cu_2C_2 + O_2 \rightarrow 2CuC_2 + CuO}$$

Reactions with dilute mineral acids liberate acetylene and form the corresponding cuprous salts:

$$\mathrm{Cu_2C_2 + H_2SO_4 \rightarrow Cu_2SO_4 + HCCH}$$

Copper(I) acetylide forms a highly explosive mixture containing silver acetylide when mixed with silver nitrate:

$$Cu_2C_2 + 2AgNO_3 \rightarrow Ag_2C_2 + CuNO_3$$

Hazard

In the dry state, the compound is highly sensitive to shock, exploding on impact. Also, it explodes when heated above 100°C. Spontaneous ignition occurs in chlorine, bromine or iodine vapors.

COPPER(II) ACETYLIDE

[12540-13-5]
Formula: CuC_2; MW 87.568
Structure: $(CuCC)_n$
Synonyms: cupric acetylide; cupric carbide

Uses

Copper(II) acetylide is used as a detonator.

Physical Properties

Brownish black powder; insoluble in water.

Preparation

Copper(II) acetylide may be prepared by passing alkyl acetylene vapors over aqueous solution of ammoniacal copper salt.

Hazard

Copper(II) acetylide is highly sensitive to impact, friction or heat. Mild impact or heating can cause a violent explosion. In the dry state it is flammable and is more sensitive to impact or friction than copper(I) acetylide.

COPPER CARBONATE, BASIC

[12069-69-1]
Formula: $CuCO_3 \cdot Cu(OH)_2$; MW 221.12
Synonyms: copper carbonate hydroxide; cupric carbonate basic; Bremen green; Bremen blue; mineral green.

Uses

Basic copper carbonate is used as a pigment in paint and varnish; as a fungicide for seed treatment; as an insecticide; in pyrotechnics; and in the manufacture of other copper salts. The compound is also added in small quantities to animal and poultry feed to supply nutritional copper requirements.

Basic copper carbonate occurs in nature as minerals, malachite and azurite. While the carbonate to hydroxide molar composition ratio in natural malachite is 1:1, the ratio in azurite [$2CuCO_3 \cdot Cu(OH)_2$] is 2:1.

Physical Properties

Natural malachite is a dark green crystalline solid; monoclinic crystals; density 4.0 g/cm^3; refractive index 1.655; decomposes at 200°C; insoluble in cold water and alcohols; decomposes in hot water; soluble in acids, ammonium hydroxide and potassium cyanide solutions.

Natural azurite is blue monoclinic crystal; density 3.88 g/cm^3; refractive index 1.730; decomposes at 220°C; insoluble in cold water; decomposes in hot water; soluble in ammonium hydroxide and hot sodium bicarbonate solutions.

Preparation

Basic carbonate is obtained from its naturally occurring minerals. It also may be prepared by mixing a solution of copper sulfate with sodium carbonate. The precipitate is then filtered and dried.

Analysis

Elemental composition: Cu 57.47%, C 5.43%, H 0.91%, O 36.18%. Both malachite and azurite may be identified by x-ray analysis and analyzed qualitatively using physical properties such as refractive index and density. For quantitative analysis, the compound may be digested in nitric acid and analyzed for copper by various instrumental methods (see Copper.)

COPPER(I) CHLORIDE

[7758-89-6]
Formula: CuCl (dimeric, Cu_2Cl_2, in vapor state); MW 98.99; zinc blende structure consisting of tetrahedrally coordinated Cu^+; Cu–Cl bond length 2.16Å.
Synonym: cuprous chloride

Uses

Copper(I) chloride is used as a catalyst in the production of chlorine by oxygenation of hydrogen chloride. Other important applications are in the petroleum industry as a desulfurization and decolorizing agent; as a condensing agent for fats and oils; as a fungicide; and as an absorbent for carbon monoxide in gas analysis. It occurs in nature as mineral nantokite.

Physical Properties

White cubic crystal which turns blue when heated at 178°C; density 4.14 g/cm^3; the mineral nantokite (CuCl) has density 4.14 g/cm^3, hardness 2.5 (Mohs), refractive index 1.930; melts at 430°C becoming a deep, green liquid; vaporizes around 1,400°C; vapor pressure 5 torr at 645°C and 400 torr at 1,250°C; low solubility in water (decomposes partially); K_{sp} 1.72×10^{-7}; insoluble in ethanol and acetone; soluble in concentrated HCl and ammonium hydroxide.

Thermochemical Properties

$\Delta H_f°$	–32.79 kcal/mol
$\Delta G_f°$	–28.66 kcal/mol
S°	20.60 cal/degree mol
Cρ	11.59 cal/degree mol
ΔH_{fus}	2.438 kcal/mol

Preparation

Copper(I) chloride is prepared by reduction of copper(II) chloride in solution:

$$2CuCl_2 + H_2 \xrightarrow{heat} 2CuCl + 2HCl$$

Alternatively, it can be prepared by boiling an acidic solution of copper(II) chloride with copper metal, which on dilution yields white CuCl:

$$Cu + CuCl_2 \xrightarrow{acid} 2CuCl$$

Copper(I) chloride dissolved in concentrated HCl absorbs carbon monoxide under pressure forming an adduct, CuCl(CO). The complex decomposes on heating releasing CO.

Copper(I) chloride is slightly soluble in water. However, in the presence of Cl^- ion, it forms soluble complexes of discrete halogeno anions such as, $CuCl_2^-$, $CuCl_3^{2-}$, and $CuCl_4^{3-}$.

Formation of complexes and organocopper derivatives as outlined below are not confined only to copper(I) chloride, but typify Cu^+ in general.

Reaction with ethylenediamine (en) in aqueous potassium chloride solution forms Cu(II)-ethylenediamine complex, while Cu^+ ion is reduced to its metallic state:

$$2CuCl + 2en \rightarrow [Cuen_2]_2^+ + 2Cl^- + Cu°$$

It dissolves in acetonitrile, CH_3CN forming tetrahedral complex ion $[Cu(CH_3CN)_4]^+$ which can be precipitated with large anions such as ClO_4^- or PF_6^-.

Reactions with alkoxides of alkali metals produce yellow copper(I) alkoxides. For example, reaction with sodium ethoxide yield copper(I) ethoxide, a yellow compound that can be sublimed from the product mixture:

$$CuCl + NaOC_2H_5 \rightarrow CuOC_2H_5 + NaCl$$

Copper(I) chloride forms complexes with ethylene and other alkenes in solutions that may have compositions such as $[Cu(C_2H_4)(H_2O)_2]^+$ or $[Cu(C_2H_4)(bipy)]^+$. (bipy = bipyridyl)

Reactions with lithium or Grignard reagent yield alkyl or aryl copper(I) derivatives, respectively. Such organocopper compounds containing Cu–Cu bonds are formed only by Cu^+ and not Cu^{2+} ions.

Analysis

Elemental composition: Cu 64.18%, Cl 35.82%. Copper(I) chloride is dissolved in nitric acid, diluted appropriately and analyzed for copper by AA or ICP techniques or determined nondestructively by X-ray techniques (see Copper). For chloride analysis, a small amount of powdered material is dissolved in water and the aqueous solution titrated against a standard solution of silver nitrate using potassium chromate indicator. Alternatively, chloride ion in aqueous solution may be analyzed by ion chromatography or chloride ion-selective electrode. Although the compound is only sparingly soluble in water, detection limits in these analyses are in low ppm levels, and, therefore, dissolving 100 mg in a liter of water should be adequate to carry out all analyses.

Toxicity

Copper(I) chloride is moderately toxic by ingestion and possibly other routes of entry into the body. The oral LD_{50} in mouse is reported to be 347 mg/kg; and subcutaneous LD_{50} in guinea pigs is 100 mg/kg.

COPPER(II) CHLORIDE

[7447-39-4]
Formula: $CuCl_2$; MW 134.45; forms a dihydrate $CuCl_2 \cdot 2H_2O$ [10125-13-0] MW 170.48
Synonyms: cupric chloride; cupric dichloride

Uses

Copper(II) chloride is used as a mordant in dyeing and printing of fabrics; as an ingredient of isomerization and cracking catalysts; and as a desulfurizing and deodorizing agent in petroleum industry. Other important applications are in copper plating of aluminum; in tinting-baths for iron and tin; in pigments for ceramics and glasses; as a fixer and desensitizer reagent in photography; in mercury extraction from ores; in laundry-marking and invisible inks; and in manufacture of several copper salts.

Physical Properties

The anhydrous form constitutes yellow to brown monoclinic crystals. It is hygroscopic; forms dihydrate on exposure to moist air; density 3.40 g/cm^3; melts around 630°C with decomposition; soluble in water, ethanol and acetone.

The dihydrate exists as greenish blue orthorhombic crystals; density 2.51 g/cm^3; decomposes at 100°C; is very soluble in water and ethanol (solubility greater than anhydrous salt in these solvents); also soluble in acetone; insoluble in ether.

Thermochemical Properties

$\Delta H_f°$	–52.61 kcal/mol
$\Delta G_f°$	–41.99 kcal/mol
S°	25.84 cal/degree mol
C_ρ	17.18 cal/degree mol
ΔH_{fus}	4.88 kcal/mol

Preparation

Copper(II) chloride may be synthesized by heating elemental copper with chlorine:

$$Cu + Cl_2 \xrightarrow{heat} CuCl_2$$

Alternatively, it may be prepared by treating copper carbonate with hydrochloric acid followed by crystallization:

$$CuCO_3 + 2HCl \rightarrow CuCl_2 + CO_2 + H_2O$$

In the above preparation, the hydrate of the salt crystallizes, precipitates, and may be dehydrated by heating under vacuum.

Reactions

When heated above 300°C, copper(II) chloride partially decomposes to copper(I) chloride and chlorine:

$$2CuCl_2 \xrightarrow{>300^\circ C} 2CuCl + Cl$$

Also, it is reduced to CuCl and elemental copper when treated with reducing agents.

Fluorination with fluorine produces copper(II) fluoride, CuF_2. Adding potassium ferrocyanide to $CuCl_2$ aqueous solution precipitates out reddish brown cupric ferrocyanide. Reaction with caustic soda forms blue cupric hydroxide:

$$CuCl_2 + 2NaOH \rightarrow Cu(OH)_2 + 2NaCl$$

Black copper(II) sulfide, CuS, is obtained when hydrogen sulfide is passed through dissolved $CuCl_2$.

$CuCl_2$ forms several copper(II) complexes with several types of ligands in aqueous solutions.

Analysis

Elemental composition: Cu 47.26%, Cl 52.74%. Aqueous $CuCl_2$ may be analyzed for copper by various instrumental methods (see Copper) and the chloride anion may be analyzed by ion chromatography, chloride ion-selective electrode, or by titration with a standard solution of silver nitrate.

COPPER(II) CHROMATE

[13548-42-0]
Formula: $CuCrO_4$; MW 179.54; several basic copper chromates are known in combination with copper(II) hydroxide at varying ratios of $CuCrO_4$ to $Cu(OH)_2$; $CuCrO_4 \cdot Cu(OH)_2$, $CuCrO_4 \cdot 2Cu(OH)_2$, and $2CuCrO_4 \cdot 3Cu(OH)_2$. Their colors vary.
Synonyms: neutral cupric chromate; copper chromate neutral

Uses

The neutral and basic forms of copper(II) chromate are used as mordants in dyeing textiles; as fungicides; to protect textiles from damage by microorganisms and insects; and as wood preservatives.

Physical Properties

The neutral form is a reddish-brown crystalline solid; decomposes slowly to copper(II) chromite when heated above 400°C; insoluble in water; soluble in acids.

The basic chromates are crystals having colors that vary from yellow to chocolate-brown to lilac, depending on their compositions and chromate to hydroxide molar ratios. They lose water when heated at 260°C, are insoluble in water, and are soluble in nitric acid.

Preparation

Neutral copper(II) chromate may be prepared by treating copper(II) carbonate, $CuCO_3$, with aqueous solutions of sodium chromate, Na_2CrO_4 and chromium(VI) oxide, CrO_3.

Basic copper(II) chromate may be obtained by treating copper(II) hydroxide, $Cu(OH)_2$ with an aqueous solution of chromium(VI) oxide.

Analysis

Elemental composition (neutral CuCrO4): Cu 35.39%, Cr 28.97%, O 35.64%. These chromates are analyzed by x-ray, thermogravimetic analysis (the basic form loses water around 260°C) and metal analysis. Copper and chromium may be analyzed by digesting the compound(s) with nitric acid, diluting appropriately with water, followed by AA, ICP, or other instrumental analysis. (see Chromium and Copper).

COPPER(II) CHROMITE

[12018-10-9]
Formula: $CuCr_2O_4$; MW 231.54
Synonyms: cupric chromite; cupric chromate(III)

Uses

Copper(II) chromite or its mixture with copper(II) oxide is used as a catalyst for selective hydrogenation of olefinic double bonds; or for the hydrogenolysis of methyl esters of fatty acids (at high temperatures and pressures) to produce fatty alcohols.

Physical Properties

Grayish-black tetragonal crystals; density 5.4 g/cm^3. When heated to elevated temperatures (above 900°C) copper(II) chromite decomposes to cupric chromate(II), $CuCrO_2$ and chromium (VI) oxide, CrO_3. Copper(II) chromite is insoluble in water and dilute acids.

Preparation

Copper(II) chromite is obtained by heating copper chromate, $CuCrO_4$ at 400°C. The Adkin catalyst, a mixture of copper oxide and copper chromite, is prepared by mixing aqueous solutions of copper nitrate, sodium dichromate and ammonium hydroxide; the orange precipitate of copper ammonium chromate formed is dried and then heated below 400°C.

Analysis

The elemental composition of $CuCr_2O_4$: Cu 27.44%, Cr 44.92%, O 27.64%.

The catalyst is analysed by measurement of surface area and pore volume; also by differential thermal analysis, thermogravimetric analysis and x-ray studies.

COPPER(I) CYANIDE

[544-92-3]
Formula: CuCN; MW 89.564
Synonyms: cuprous cyanide; cupricin

Uses

Copper(I) cyanide is used in copper plating of nickel, chromium, zinc alloys, steel, and other metals or alloys. Such copper plating imparts brightness, smoothness, hardness, and strength. The cyanide solution employed for copper electroplating consists of copper cyanide and sodium cyanide. Other applications of this compound are as an insecticide, a catalyst in polmerization, and as an antifouling agent in marine paints.

Physical Properties

Cream-colored powder or green orthorhombic or red monoclinic crystals; density 2.90 g/cm^3; melts at 474°C; decomposes at higher temperatures; practically insoluble in water, ethanol, and cold dilute acids; dissolves in ammonium hydroxide and potassium cyanide solutions.

Preparation

Copper(I) cyanide is a precipitate obtained by adding potassium cyanide solution to an aqueous solution of Cu^{2+} salt:

$$2CuCl_2 + 4KCN \rightarrow 2CuCN + C_2N_2 + 4KCl$$

The Cu^{2+} to CN^- molar ratio should be 1:2. The precipitate dissolves in an excess of cyanide, forming soluble ions $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$.

Analysis

Elemental composition: Cu 70.95%, C 13.41%, N 15.64%. Copper(I) cyanide is decomposed in nitric acid and the acid extract diluted appropriately and analyzed for copper by various instrumental methods (see Copper).

Toxicity

The compound is a poison by ingestion and other routes of exposure.

COPPER(II) FLUORIDE

[7789-19-7]
Formula: CuF_2; MW 101.54; also forms a dihydrate, $CuF_2 \cdot 2H_2O$ [13454-88-1], MW 137.57
Synonym: cupric fluoride

Uses

Copper(II) fluoride is used in cathodes in nonaqueous galvanic cells, such as high energy batteries. It also is used as a fluorinating agent. The dihydrate is used in welding and brazing fluxes and is added to cast iron to improve its strength. Another application of this compound is as opacifier in ceramics, glasses and enamels.

Physical Properties

The anhydrous fluoride is a white crystalline solid; monoclinic crystals; turns blue in moist air; density 4.23 g/cm^3; melts at 836°C; vaporizes at 1,676°C; sparingly soluble in water (hydrolyzes in hot water). The dihydrate is blue monoclinic crystal; density 2.934 g/cm^3; decomposes at 130°C; slightly soluble in water.

Thermochemical Properties

$\Delta H_f°$	–129.71 kcal/mol
ΔH_{fus}	13.15 kcal/mol

Preparation

Copper(II) fluoride is prepared by direct fluorination of copper at high temperatures:

$$Cu + F_2 \xrightarrow{heat} CuF_2$$

It also may be prepared by passing hydrogen fluoride gas over copper(II) oxide at 400°C:

$$CuO + 2HF \xrightarrow{400^\circ C} CuF_2 + H_2O$$

Alternatively, it may be made by treating copper carbonate with hydrofluoric acid followed by crystallization.

$$CuCO_3 + 2HF(aq) \rightarrow CuF_2 + H_2O + CO_2$$

Reactions

Copper(II) fluoride loses fluorine as it melts. At 950°C it converts to copper(I) fluoride (cuprous fluoride), CuF:

$$2CuF_2 \xrightarrow{950^\circ C} 2CuF + F_2$$

Also, when it is heated at 1,200°C in an atmosphere of hydrogen fluoride, copper(I) fluoride is produced.

Reaction with water is slow, forming a hydrate. The product decomposes slowly at ambient temperature with liberating hydrogen fluoride, leaving a basic fluoride, CuFOH. The dihydrate hydrolyzes to oxyfluoride $Cu(OF)_2$ in hot water.

Analysis

Elemental composition: Cu 62.58%, F 37.42%. Copper(II) fluoride acid extract is analyzed for copper by instrumental methods. Powder may be analyzed by the x-ray diffraction method. Aqueous solution (in cold water) may be analyzed for fluoride ion using a fluoride ion-selective electrode or by ion chromatography.

Toxicity

Copper(II) fluoride is moderately toxic by ingestion and other routes of exposure.

COPPER(II) HYDROXIDE

[20427-59-2]
Formula: $Cu(OH)_2$; MW 97.56
Synonyms: cupric hydroxide; copper hydrate; hydrated copper oxide

Uses

Copper(II) hydroxide is used as a mordant in pigments; for staining paper; as an additive to cattle feed; as a catalyst; as a fungicide; and in the preparation of several copper salts.

Physical Properties

Blue crystalline powder or gelatinous mass; density 3.36 g/cm^3; decomposes on heating; insoluble in cold water; K_{sp} 2.20x10^{-20}; decomposes in hot water; soluble in acids, ammonium hydroxide and potassium cyanide.

Thermochemical Properties

$\Delta H_f°$(cry)	–107.5 kcal/mol
$\Delta H_f°$(aq)	–94.46 kcal/mol
$\Delta G_f°$ (aq)	–59.53 kcal/mol

Preparation

Copper(II) hydroxide is precipitated by treating a soluble copper(II) salt such as, $CuCl_2$ or $CuSO_4$ with caustic soda or caustic potash:

$$CuCl_2 + NaOH \rightarrow Cu(OH)_2 + 2NaCl$$

Reactions

Thermal decomposition yields copper(II) oxide. Reactions with mineral acids yield the corresponding copper(II) salts:

$$Cu(OH)_2 + 2HCl \rightarrow CuCl_2 + H_2O$$

$$Cu(OH)_2 + 2HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O$$

Copper(II) hydroxide dissolves in concentrated alkali hydroxides forming deep blue anions of $[Cu(OH)_4]^{2-}$ and $[Cu(OH)_6]^{4-}$.

Reaction with hydrofluosilicic acid followed by crystallization yields blue crystals of hydrated cupric fluosilicate, $CuSiF_6 \cdot 4H_2O$.

When heated with abietic acid, the product is a green salt, cupric abietate, $Cu(C_{20}H_{29}O_2)_2$, a metal paint and fungicide.

Analysis

Elemental composition: Cu 65.13%, H 2.07%, O 32.80%

Copper is determined by AA or ICP spectrophotometry of copper(II) hydroxide nitric acid extract. Heating the solid hydroxide dehydrates to CuO. The moles of water loss may be measured by gravimetric analysis. The black CuO residue may be identified by x-ray analysis and physical tests.

Toxicity

Copper(II) hydroxide is low to moderately toxic by ingestion. LD_{50} oral (rat): 1,000 mg/kg.

COPPER(I) IODIDE

[7681-65-4]
Formula: CuI; MW 190.45

Synonym: cuprous iodide

Uses

The iodide salt is used as a source of dietary iodine in table salt and animal feed; in cloud seeding; as a coating in cathode ray tubes; as a temperature indicator; and as a catalyst in organic reactions.

Copper(I) iodide is found in nature as mineral marshite.

Physical Properties

White powder; cubic crystals; the mineral marshite is a red-brown crytal; density 5.67 g/cm^3 ; refractive index 2.346; hardness 2.5 Mohs; melts at 606°C; vaporizes around 1,290°C; insoluble in water and dilute acids; soluble in aqueous solutions of ammonia and alkali salts of cyanide, iodide and thiosulfate ions.

Thermochemical Properties

$\Delta H_f°$	–16.20 kcal/mol
$\Delta G_f°$	–16.61 kcal/mol
S°	23.11 cal/degree mol
C_ρ	12.93 cal/degree mol

Preparation

Copper(I) iodide is prepared by heating copper with iodine and concentrate hydriodic acid, HI. Another preparation route is precipitation of the salt by mixing aqueous solutions of potassium or sodium iodide with copper sulfate or any soluble copper(II) salt:

$$CuSO_4 + 2KI \rightarrow CuI_2 + K_2SO_4$$

The unstable CuI_2 formed rapidly dissociates into insoluble copper(I) iodide and iodine

$$2CuI_2 \rightarrow 2CuI + I_2$$

Analysis

Elemental composition: Cu 33.36%, I 66.64%. Either compound or mineral copper(I) iodide is identified by x-ray diffraction or fluorescence method. Copper may be analyzed in nitric acid extract of copper(I) iodide by various instrumental techniques (see Copper).

COPPER(II) NITRATE

[3251-23-8]

Formula: $Cu(NO_3)_2$; MW 187.56; two hydrates are known, namely, copper nitrate trihydrate $Cu(NO_3)_2 \cdot 3H_2O$ [10031-43-3], MW 241.60 and copper nitrate hexahydrate, $Cu(NO_3)_2 \cdot 6H_2O$ [13478-38-1] MW 295.65.

Synonyms: cupric nitrate; copper dinitrate

Uses

Copper(II) nitrate is used in light-sensitive reproduction papers; as a mordant in dyeing and printing of fabrics; as a coloring reagent for ceramics; for coloring copper black; as a burnishing agent for iron; in nickel-plating baths; in pyrotechnic compositions; and in paints, varnishes, and enamels. Other applications are as an oxidizing agent; nitrating agent for aromatics; as a catalyst; and an analytical standard for copper.

Copper nitrate trihydrate occurs in nature as the mineral gerhardite.

Physical Properties

Blue-green orthorhombic crystals; deliquescent; density 2.05 g/cm^3; melts at 255°C; sublimes; readily dissolves in water, alcohols and dioxane.

The trihydrate and hexahydrate are blue rhombohedral crystals; hygroscopic; density 2.32 g/cm^3 (trihydrate), 2.07 g/cm^3 (hexahydrate); melts at 114°C (trihydrate); trihydrate decomposes at 170°C; hexahydrate decomposes to trihydrate at 26.4°C; both the hydrates are very soluble in water and ethanol.

Thermochemical Properties

$\Delta H_f°$ –72.39 kcal/mol

Preparation

Copper(II) nitrate is made by action of copper or copper(II) oxide with nitric acid. The solution is evaporated and the product is obtained by crystallization

$$CuO + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O$$

The nitrate salt prepared by this method is hydrated. It cannot be dehydrated fully without decomposition. Anhydrous $CuNO_3$ may be prepared by dissolving copper metal in a solution of dinitrogen tetroxide, N_2O_4, in ethyl acetate. Upon crystallization, an N_2O_4 adduct of $Cu(NO_3)_2$ that probably has the composition $[NO^+][Cu(NO_3)_3]$ is obtained. This adduct, on heating at 90°C, yields blue anhydrous copper(II) nitrate which can be sublimed in vacuum at 150°C and collected.

Reactions

Thermal decomposition of copper(II) nitrate produces copper oxides and nitrogen oxides.

In aqueous solutions, copper(II) nitrate undergoes many double decomposition reactions with soluble salts of other metals, forming precipitates of insoluble copper salts.

When H_2S is passed through its aqueous solution, black CuS precipitates.

Copper(II) nitrate reacts with ether forming a complex.

Analysis

Elemental composition: Cu 33.88%, N 14.94%, O 51.18%. Copper(II) nitrate aqueous solution with appropriate dilution may be analyzed for copper by various instrumental methods (see Copper). After appropriate dilution, the nitrate anion in the aqueous solution may be measured by ion chromatography or nitrate ion-selective electrode.

Hazard

Copper(II) nitrate is moderately toxic by ingestion. Skin or eye contact can cause irritation.

LD_{50} oral (rat): 940 mg/kg.

Copper(II) nitrate, being an oxidizing agent, can undergo violent reactions with readily oxidizable substances. Reaction with acetic anhydride is violent, and heating with potassium or ammonium ferrocyanide at 220°C may cause an explosion. It can ignite paper on prolonged contact.

COPPER(I) OXIDE

[1317-39-1]
Formula: Cu_2O; MW 143.09
Synonyms: cuprous oxide; copper suboxide; copper oxide red; copper protoxide; copper hemioxide

Uses

An important application of copper(I) oxide is in antifouling paints for steel, wood, and other materials exposed to sea water. Other applications include manufacture of ruby-red glass and preparation of miscellaneous copper salts. It also is used as a reducing agent in brazing pastes; as a fungicide; in photocells; and as a catalyst.

Copper(I) oxide occurs in nature as the mineral cuprite.

Physical Properties

Reddish-brown cubic crystals; density 6.0 g/cm^3; Mohs hardness 3.8; melts at 1,235°C; decomposes around 1,800°C; insoluble in water; soluble in ammonium hydroxide.

Thermochemical Properties

$\Delta H_f°$	–40.30 kcal/mol
$\Delta G_f°$	–34.89 kcal/mol
S°	22.25 cal/degree mol
C_ρ	15.20 cal/degree mol

Preparation

Copper(I) oxide is found in nature as the mineral cuprite. Copper(I) oxide can be prepared by several methods, which include:

(1) Reduction of a copper(II) oxide with coper at elevated temperatures in a furnace:

$$CuO + Cu \xrightarrow{\text{elevated temperatures}} Cu_2O$$

(2) Thermal decomposition of copper(II) oxide:

$$4CuO \xrightarrow{>800^\circ C} 2Cu_2O + O_2$$

(at elevated temperatures Cu_2O is more stable than CuO)
(3) Controlled reduction of an alkaline solution of a Cu^{2+} salt with hydrazine, N_2H_4. In this method, Cu_2O is produced as a yellow powder.
(4) Oxidation of finely divided copper.
(5) Thermal decomposition of copper ammonium carbonate:

$$2CuNH_4CO_3 \xrightarrow{heat} Cu_2O + 2CO_2 + 2NH_3 + H_2O$$

(6) Reaction of alkali hydroxide with copper(I) chloride:

$$2CuCl + 2NaOH \rightarrow Cu_2O + 2NaCl + H_2O$$

(7) Reduction of copper(II) hydroxide, $Cu(OH)_2$ with sulfur dioxide, glucose, or another reducing agent.

(8) Electrolyzing an aqueous solution of NaCl using copper electrodes.The technical grade product should contain minimum 97% Cu_2O for use in pigments.

Reactions

Oxidation produces copper(II) oxide, CuO. Heating with hydrogen reduces the oxide to metallic copper:

$$Cu_2O + H_2 \xrightarrow{heat} 2Cu + H_2O$$

The oxide reacts with HCl forming CuCl:

$$Cu_2O + 2HCl \rightarrow 2CuCl + H_2O$$

CuCl dissolves in excess HCl.

Copper oxide reacts with dilute sulfuric and nitric acids forming copper(II) sulfate and copper(II) nitrate, respectively, and precipitating metallic copper:

$$Cu_2O + H_2SO_4 \rightarrow CuSO_4 + Cu + H_2O$$

$$Cu_2O + 2HNO_3 \rightarrow Cu(NO_3)_2 + Cu + H_2O$$

Heating with alkali metal oxides such as Na_2O and K_2O produces alkali metal oxocuprates that have the compositions $Na_4Cu_4O_4$ or $K_4Cu_4O_4$ containing oxocuprate, $[Cu_4O_4]^{4-}$ rings:

$$2Cu_2O + 2Na_2O \xrightarrow{heat} Na_4Cu_4O_4$$

Reaction with trifluoromethanesulfonic anhydride in benzene yields copper(I) trifluoromethanesulfonate, $[Cu(O_3SCF_3)]_2 \cdot C_6H_5$, a white crystalline, air-sensitive complex (Cotton, F. A., G. Wilkinson, C. A. Murillo and M. Bochmann. 1999. *Advanced Inorganic Chemistry*, 6th ed. pp. 857-858. New York: Wiley Interscience) Olefins can displace benzene in the above compound readily, forming a variety of olefin complexes.

Analysis

Elemental composition: Cu 88.42%, O 11.18%. The oxide may be dissolved in excess hydrochloric acid, diluted appropriately and analyzed by AA or ICP techniques (see Copper). The mineral cuprite may be identified nondestructively by various x-ray methods.

Hazard

Copper(I) oxide is moderately toxic by ingestion.

LD_{50} oral (rat): 470 mg/kg

Violent reaction can occur when copper(I) oxide is heated with aluminum

COPPER(II) OXIDE

[1317-38-0]
Formula: CuO; MW 79.545
Synonyms: cupric oxide; copper oxide black

Uses

Copper(II) oxide is used as pigments for coloring glass, ceramics, porcelain and artificial gems; in batteries and electrodes; in antifouling paints; in electroplating; in welding fluxes for bronze; in the production of rayons; for removal of sulfur from oils; in phosphor mixtures; for polishing optical glass; and as a catalyst. It also is used to prepare various copper compounds.

Copper(II) oxide is found in nature as the minerals tenorite and paramelaconite. They differ in crystalline structure: tenorite exists as triclinic crystals while paramelaconite consists of tetrahedral cubic crystals.

Physical Properties

Black powder or monoclinic crystals; density 6.31 g/cm^3; melts at 1,446°C; insoluble in water and alcohols; soluble in dilute acids and ammonium hydroxide.

Thermochemical Properties

$\Delta H_f°$	–37.60 kcal/mol
$\Delta G_f°$	–31.00 kcal/mol
S°	10.18 cal/degree mol

C_ρ	10.11 cal/degree mol
ΔH_{fus}	2.82 kcal/mol

Preparation

Copper(II) oxide occurs in nature as the mineral tenorite. It may be prepared by pyrolysis of copper nitrate, copper carbonate or another oxo copper salt

$$CuNO_3 \xrightarrow[]{\substack{\text{elevated}\\ \text{temperatures}}} CuO + NO_2$$

$$CuCO_3 \xrightarrow[]{\substack{\text{elevated}\\ \text{temperatures}}} CuO + CO_2$$

Also, copper(II) oxide may be prepared by adding alkali hydroxide to a cupric salt solution; the bulky blue slurry of hydroxide obtained is then dehydrated by warming:

$$Cu(NO_3)_2 + 2NaOH \rightarrow Cu(OH)_2 + 2NaNO_3$$

$$Cu(OH)_2 \xrightarrow{heat} CuO + H_2O$$

Reactions

Heating above 800°C converts copper(II) oxide into copper(I) oxide. Also, when the black oxide is heated with copper metal, copper(I) oxide is formed:

$$CuO + Cu \xrightarrow{heat} Cu_2O$$

Copper(II) oxide reacts with dilute sulfuric acid and nitric acid forming copper(II) sulfate and copper(II) nitrate, respectively.

These salts are obtained following evaporation of the solution and crystallization:

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

The oxide is reduced to metallic copper when heated at high temperatures with hydrogen and other reducing agents.

Heating with hydrogen fluoride at 400°C yields copper(II) fluoride, CuF_2:

$$CuO + 2HF \xrightarrow{400^\circ C} CuF_2 + H_2O$$

Analysis

Elemental composition: Cu 79.88%, O 20.12%. Copper(II) oxide is dissolved in nitric or sulfuric acid and copper content may be determined by AA or ICP spectrometry following appropriate dilution of the acid extract. It may be alternatively analyzed nondestructively by x-ray methods.

COPPER(II) SULFATE

[7758-98-7]
Formula: $CuSO_4$; MW 159.61; also exists as a pentahydrate, $CuSO_4 \cdot 5H_2O$ [7758-99-8], MW 249.69
Synonyms: cupric sulfate; blue vitriol; blue copperas; blue stone

Uses

Copper(II) sulfate is probably the most important of all copper compounds. It is used extensively in agriculture as a soil additive to improve crop yields. Other applications are as a feed additive to prevent copper deficiency; a mordant in textiles; in pigments; in electric batteries; in copper plating; as a fungicide (such as Bordeaux mixture); as a wood preservative; in lithography and process engraving; in medicine; as a dehydrating agent (anhydrous salt); and in the manufacture of other copper compounds.

The pentahydrate occurs in nature as the mineral, chalcanthite; the anhydrous sulfate occurs as mineral, hydrocyanite.

Physical Properties

The anhydrous salt is greenish-white rhombohedral crystals or amorphous powder; hygroscopic; density 3.60 g/cm^3; decomposes above 560°C; soluble in water; insoluble in ethanol.

The pentahydrate is large blue triclinic crystal or light-blue amorphous powder; refractive index 1.514; density 2.28 g/cm^3; loses water on heating—two molecules at 30°C, becomes a monohydrate at 110°C and anhydrous at 250°C; very soluble in water; moderately soluble in methanol; slightly soluble in ethanol.

Thermochemical Properties

$\Delta H_f°$	–184.37 kcal/mol
$\Delta G_f°$	–158.27 kcal/mol
S°	26.1 cal/degree mol

Reactions

Thermal decomposition of copper(II) sulfate produces copper(II) oxide and sulfur trioxide.

When heated with rosin oil, a green precipitate of copper(II) resinate is obtained. Similarly, with sodium stearate, $C_{18}H_{35}O_2Na$, and sodium oleate, $C_{18}H_{33}O_2Na$, it precipitates as light blue cupric stearate, $(C_{18}H_{35}O_2)_2Cu$ and greenish-blue copper oleate $Cu(C_{18}H_{33}O_2)_2$, respectively. It forms copper carbonate, basic $Cu_2(OH)_2CO_3$ and basic copper sulfate (varying compositions) with sodium carbonate. With caustic soda, the reaction product is copper(II) hydroxide, $Cu(OH)_2$.

When dissolved in ammonium hydroxide and treated with ethanol dark blue complex, copper amino sulfate is obtained:

$$CuSO_4 + 4NH_3 + H_2O \rightarrow Cu(NH_3)_4SO_4 \cdot H_2O$$

Reaction with oxalic acid produces bluish-white copper(II) oxalate, CuC_2O_4.

When mixed with a solution of borax a blue-green solid of indefinite composition, copper(II) borate, precipitates.

Reaction with potassium cyanide yields green copper(II) cyanide, $Cu(CN)_2$.

Analysis

Elemental composition ($CuSO_4$): Cu 39.81%, S 20.09%, O 40.10%. Aqueous solution of copper(II) sulfate may be analyzed for copper by instrumental techniques (see Copper). The sulfate anion may be determined by ion chromatography. The crystal may be characterized by x-ray techniques and other physical tests.

Toxicity

Copper(II) sulfate is toxic to humans by ingestion and other routes of exposure. Symptoms of ingestion include gastritis, diarrhea, nausea, vomiting, kidney damage and hemolysis (Lewis (Sr.), R. N. 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed. New York: Van Nostrand Reinhold).

LD_{50} oral (rat): 300 mg/kg

COPPER(II) SULFATE, BASIC

[1332-14-5]

Occurrence and Uses

The formula varies; several salts with variable compositions of $CuSO_4$ and $Cu(OH)_2$ or CuO are known. Some of them occur in nature as minerals:

Copper hydroxide sulfate or cupric subsulfate is found in nature as the mineral dolerophane; formula: $CuSO_4 \cdot CuO$

Copper sulfate dibasic occurs in nature as mineral antlerite; formula: $CuSO_4 \cdot 2Cu(OH)_2$

Copper sulfate tribasic occurs in nature as mineral brochantite: formula: $CuSO_4 \cdot 3Cu(OH)_2$

Copper sulfate tribasic hydrate is also found in nature as mineral langite; formula: $CuSO_4 \cdot 3Cu(OH)_2 \cdot H_2O$

These basic salts of copper(II) sulfate are light-to-deep blue crystals of fine particle size; density in the range 3.5 to 4.0 g/cm^3; practically insoluble in water; dissolve in acids. They may be prepared by various methods depending on the nature of the product desired; i.e., mixing solutions of $CuSO_4$ and Na_2CO_3 yields Burgundy mixtures, or $CuSO_4$ with $Ca(OH)_2$ yields Bordeaux mixture.

Basic copper sulfate salts are used as fungicides for plants.

COPPER(I) SULFIDE

[22205-45-4]
Formula: Cu_2S; MW 159.16; slightly copper deficient, the probable composition $Cu_{1.8}S$
Synonym: cuprous sulfide

Uses

Copper(I) sulfide is used in luminous paints; antifouling paints; in solid-lubricant mixtures; in solar cells; in electrodes; and as a catalyst.

The compound occurs in nature as the mineral chalcocite (copper glance) with varying colors.

Physical Properties

Dark-blue or black orthogonal crystals; density 5.6 g/cm^3; hardness 2.8 Mohs; melts at about 1,100°C; insoluble in water; slightly soluble in hydrochloric acid; decomposed by nitric acid and concentrated sulfuric acid; moderately soluble in ammonium hydroxide; dissolves in potassium cyanide solutions.

Thermochemical Properties

$\Delta H_f°$	–19.00 kcal/mol
$\Delta G_f°$	–20.60 kcal/mol
S°	28.90 cal/degree mol
C_ρ	18.24 cal/degree mol

Preparation

Copper(I) sulfide is available in nature as the mineral chalcocite. It also may be made by heating copper(II) sulfide with hydrogen, in the presence of small amounts of sulfur.

Alternatively, copper(I) sulfide may be prepared by heating copper with hydrogen sulfide and hydrogen; or by heating the metal with sulfur in an atmosphere of carbon dioxide and methanol vapor.

Reactions

When heated in air, copper(I) sulfide oxidizes forming copper(II) oxide, and sulfur dioxide:

$$Cu_2S + 2O_2 \xrightarrow{heat} 2CuO + SO_2$$

Heating in the absence of air produces copper(II) sulfide and copper:

$$Cu_2S \xrightarrow{heat} CuS + Cu$$

When heated with nitric acid, copper(I) sulfide decomposes forming copper nitrate and hydrogen sulfide. The compound dissolves in aqueous solutions containing cyanide ions forming soluble copper-cyanide complexes.

Copper(I) sulfide reacts with polysulfide anions in aqueous solutions forming soluble copper polysulfides.

Analysis

Elemental composition: Cu 79.85%, S 20.15%.

Copper(I) sulfide may be analyzed by x-ray analyses. The copper concentration in nitric acid extract may be measured by various instrumental techniques (see Copper).

COPPER(II) SULFIDE

Formula: CuS; MW 95.61; structurally complex, the compound probably consists of S_2^{-2} and S^{-2} ions, as well as Cu_2^+ and Cu^{2+} ions.
Synonym: cupric sulfide

Uses

Copper(II) sulfide is used in antifouling paints; in aniline black dye for dyeing of fabrics; and in the preparation of catalysts for organic reactions. It occurs in nature as the mineral covellite.

Physical Properties

Black monoclinic or hexagonal crystals or powder; density 4.6 g/cm^3; refractive index 1.45; hardness 1.8 Mohs; decomposes at 220°C; insoluble in water, ethanol and alkalis. K_{sp} 8.0×10^{-34}; soluble in nitric acid, ammonium hydroxide and potassium cyanide solutions; also soluble in hot hydrochloric and sulfuric acids.

Thermochemical Properties

$\Delta H_f°$	–12.7 kcal/mol
$\Delta G_f°$	–12.8 kcal/mol
S°	15.9 cal/degree mol
C_ρ	11.43 cal/degree mol

Preparation

Copper(II) sulfide is produced from its natural mineral covellite. In the laboratory it is prepared by passing hydrogen sulfide into an aqueous solution of copper(II) salts:

$$CuCl_2 + H_2S \rightarrow CuS + 2HCl$$

Reactions

Copper(II) sulfide oxidizes to copper(II) sulfate in moist air. The compound, however, is stable in dry air at ordinary temperatures.

When heated strongly in the absence of air, it loses sulfur, forming copper(I) sulfide:

$$2CuS \xrightarrow[\text{temperatures}]{\text{elevated}} Cu_2S + S$$

When heated with hydrogen below 600°C, it produces copper(I) sulfide. The presence of a small amount of sulfur enhances the yield of copper(I) sulfide.

Analysis

Elemental composition: Cu 66.46%, S 33.54%.

The compound may be identified by x-ray analysis. The copper content may be analyzed by AA, ICP, or x-ray fluorescence techniques.

CURIUM

[7440-51-9]
Symbol: Cm; atomic number 96; atomic weight 247; a radioactive transuranium actinide series element; electron configuration [Rn]$5f^76d^17s^2$; most stable valence state +3; most stable isotope Cm-247. Curium isotopes, half-lives and decay modes are:

Isotope	Half-Life	Decay Mode
Cm-238	2.5 hr	electron capture, alpha decay
Cm-239	3 hr	electron capture
Cm-240	26.8 days	alpha decay
Cm-241	35 days	alpha decay
Cm-242	163 days	alpha decay
Cm-243	32 yr	alpha decay
Cm-244	18.1 yr	alpha decay
Cm-245	9,320 yr	alpha decay
Cm-246	5,480 yr	alpha decay
Cm-247	1.67×10^7 yr	alpha decay
Cm-248	4.7×10^5 yr	alpha decay
Cm-249	65 min	beta decay

History, Occurrence, and Uses

Curium was discovered by Seaborg, James, and Ghiorso in 1944 during chemical fractionation of plutonium irradiated with alpha particles (32 MeV). The element was isolated in hydroxide form by Werner and Perlman in 1947 in microgram amounts, and later in 1950 by Crane, Wallmann, and Cunningham in elemental form. Crane *et al.* also studied its magnetic susceptibility and assigned $5f^7$ electron configuration to this element, analogous to $4f^7$ configuration of the element gadolinium in the lanthanide series. This man-made element was named curium in honor of Marie and Pierre Curie.

Curium does not occur in nature. Even if it had occured in the primordial age of earth, its longest lasting isoptope, Cm-247 (half-life of 17 million years), would almost have fully disintegrated during the more than three billion years of earth's existence.

The element does not have any important commercial applications. Its isotopes Cm-242 and Cm-244 have potential applications to generate thermoelectric power for operation of instruments in space ships.

Physical Properties

Silvery metal; density 13.51 g/cm^3 (calculated); atomic volume 18 cm^3/mole; melts in the range 1,300 to 1,380°C; magnetic susceptibility 12.2×10^{-8}cgs units/mole at 25°C; dissolves in mineral acids.

Production

Curium can be synthesized in a nuclear reactor by several methods. The first synthesis involved alpha particle bombardment of plutonium-239:

$$^{239}_{94}Pu + ^{4}_{2}He \xrightarrow{32MeV} ^{242}_{96}Cm + ^{1}_{0}n$$

It may be synthesized by several other methods. Curium isotopes of lower mass numbers may be obtained by charged particle bombardments of plutonium-239:

$$^{239}_{94}Pu + ^{4}_{2}He \xrightarrow{50MeV} ^{238}_{96}Cm + 5^{1}_{0}n$$

Curium-244 isotope may be obtained by irradiation of plutonium-239 by thermal neutrons:

$$^{239}_{94}Pu + ^{1}_{0}n \rightarrow ^{240}_{94}Pu + \gamma \longrightarrow 3^{1}_{0}n\ ^{243}_{94}Pu + \gamma$$

$$^{243}_{94}Pu \xrightarrow{(\beta^- - decay)} ^{243}_{95}Am + e^-$$

$$^{243}_{95}Am + ^{1}_{0}n \rightarrow ^{244}_{95}Am + \gamma$$

$$^{244}_{95}Am \xrightarrow{(\beta^- - decay)} ^{244}_{96}Cm + e^-$$

Curium-242 isotope may be obtained in the same way from plutonium-239 by successive neutron capture and β^- decay:

$$^{243}_{94}Pu + ^{1}_{0}n \rightarrow \ldots\ldots ^{241}_{94}Pu + \gamma$$

$$^{241}_{94}Pu \xrightarrow{(\beta^- - decay)} ^{241}_{95}Am + e^-$$

$$^{241}_{95}Am + ^{1}_{0}n \rightarrow ^{242}_{95}Am + \gamma$$

$$^{242}_{95}Am \xrightarrow{(\beta^{-}-decay)} ^{242}_{96}Cm + e^{-}$$

Also, higher isotopes of curium may be produced from curium-242 by neutron capture reactions.

The heavier isotopes of the element may result from rapid neutron capture process caused by intense neutron fluxes from thermonuclear explosions, followed by a series of β⁻decay (Cunningham, B.D. 1968. Curium. In *Encyclopedia of Chemical Elements*, ed. C. A. Hampel, pp. 173–177. New York: Reinhold Book Corp.)

$$^{238}_{92}U + 8\,^{1}_{0}n \rightarrow ^{246}_{92}U \xrightarrow{\beta^{-}} ^{246}_{93}Np \xrightarrow{\beta^{-}} ^{246}_{94}Pu \xrightarrow{\beta^{-}} ^{246}_{95}Am \xrightarrow{\beta^{-}} ^{246}_{96}Cm$$

Chemical Properties

Most properties are similar to the rare-earth analog gadolinium that has 7*f* electrons. The trivalent oxidation state (Cm^{3+}) is most stable. The metal is reactive, being more electropositive than aluminum.

Curium metal is stable at ambient temperature, but oxidizes on heating to curium(III) oxide, Cm_2O_3.

When curium is heated with fluorine at 400°C, the product is CmF_4, a tetravalent curium compound. However, heating with other halogens yields trivalent halides, CmX_3. Similarly, when heated with hydrogen chloride gas at 500°C, the product is curium(III) chloride, $CmCl_3$.

Curium metal liberates hydrogen from dilute acids, forming the trivalent, Cu^{3+} ion in the solution.

Many compounds of curium are known. They include the oxides, CmO_2 and Cm_2O_3, fluorides CmF_4 and CmF_3, other halides, CmX_3; hydroxide, $Cm(OH)_3$, and oxalate $Cm_2(C_2O_4)_3$. The oxide, hydroxide, fluoride, and oxalate salts are insoluble in water and may be obtained by precipitation reactions.

Health Hazard

Curium may be absorbed into the body and can accumulate in the bone. Exposure to its radiation can destroy the red cell-forming mechanism.

CYANIC ACID

[75-13-8]
Formula: HCNO; MW 43.03;
Structure: N≡C–O–H
Synonym: hydrogen cyanate

Uses

The compound has limited applications, primarily in the synthesis of cyanate salts.

Physical Properties

Colorless liquid or gas; pungent odor; density 1.14 g/mL at 20°C; solidifies at –86°C; boils at 23.5°C; dissolves in water (decomposes on standing); soluble in benzene, toluene and ether.

Thermochemical Properties

$\Delta H_f°$	–36.90 kcal/mol
$\Delta G_f°$	–28.0 kcal/mol
S°	34.6 cal/degree mol

Preparation

Cyanic acid is prepared in the laboratory by dry distillation of cyanuric acid, $C_3N_3(OH)_3$.

Reactions

Cyanic acid decomposes on heating. Rapid heating may cause explosion. When heated to high temperatures, it decomposes forming carbon dioxide, water, and nitrogen oxides:

$$4NCOH + 7O_2 \xrightarrow{heat} 4CO_2 + 4NO_2 + 2H_2O$$

It dissolves in water decomposing to carbon dioxide and ammonia. Although the reaction occurs at ordinary temperatures, it is slow in dilute aqueous solutions at ice temperature.

$$NCOH + H_2O \rightarrow CO_2 + NH_3$$

The compound polymerizes on standing, forming cyanuric acid, an oxygen heterocylic compound, 1,3,5-trioxane-2,4,6-triimine, $C_3H_3N_3O_3$.

Analysis

Elemental composition: C 27.91%, H 2.34%, N 32.56%, O 37.19%.

Cyanic acid may be determined in benzene or toluene solution by GC either using an FID or, alternatively, an NPD measuring in nitrogen mode. Also, it may be identified by GC/MS; the molecular ion should have the mass 43.

CYANOGEN

[460-19-5]
Formula: C_2N_2; MW 52.035
Structure: N≡C–C≡N, linear; two isomers have been detected (isocyanogen is C=N–N=C); both are highly unstable.

Synonyms: ethanedinitrile; oxalic acid dinitrile; dicyan; oxalonitrile

Uses

Cyanogen has limited applications, the most important of which are in organic synthesis. Also, it is used in welding metals; as a fumigant; and in some rocket propellants.

Physical Properties

Colorless gas; almond-like pungent odor; burns with a pink flame with bluish tinge; density 2.283 g/L; liquefies at –21.1°C; vapor pressure 635 torr at –25°C; solidifies at –27.9°C; critical pressure 59.02 atm; slightly soluble in water (about 400 mL gas at NTP dissolves in 100 mL water or 0.85 g/100 mL water) soluble in alcohol and ether.

Thermochemical Properties

$\Delta H_f°$	73.84 kcal/mol
$\Delta G_f°$	71.07 kcal/mol
S°	57.8 cal/degree mol
C_ρ	13.6 cal/degree mol
ΔH_{fus}	2.06 kcal/mol

Preparation

Cyanogen is prepared by the slow addition of potassium cyanide solution to a solution of copper(II) salt, such as copper(II) sulfate or chloride:

$$2Cu^{2+} + 4CN^{-} \rightarrow 2CuCN + (CN)_2$$

Cyanogen also may be prepared by the reaction of mercuric cyanide with mercuric chloride. Dry cyanogen gas may be obtained by this process:

$$Hg(CN)_2 + HgCl_2 \rightarrow Hg_2Cl_2 + (CN)_2$$

Cyanogen may be prepared by oxidation of hydrogen cyanide with oxygen, nitrogen dioxide, chlorine, or another suitable oxidizing agent, using various catalysts:

$$4HCN + O_2 \xrightarrow{\text{silver catalyst}} 2(CN)_2 + H_2O$$

$$2HCN + NO_2 \xrightarrow{\text{CaO/ glass}} (CN)_2 + NO + H_2O$$

$$2HCN + Cl_2 \xrightarrow{\text{silica/activated carbon}} (CN)_2 + 2HCl$$

Reactions

Although cyanogen has a positive heat of formation ($\Delta H_f°$ 73.84 kcal/mol), the compound is unusually stable. In aqueous solution it is hydrolyzed slowly forming oxalic acid and ammonia, which combine to form oxamide:

$$(CN)_2 + 4H_2O \rightarrow H_2C_2O_4 + 2NH_3 \rightarrow \underset{\text{(oxamide)}}{H_2N\text{–}C(O)\text{–}C(O)\text{–}NH_2}$$

In basic solution, cyanogen dissociates rapidly, forming cyanide and oxycyanide salts:

$$(CN)_2 + 2KOH \rightarrow KCN + KOCN + H_2O$$

Reaction with ammonia yields 5-cyanotetrazole, a nitrogen heterocyclic ring compound. Reactions with alkyl amine, RNH_2, yield dialkyloxalamidines RNHC(=NH)CH(=NH)NR; with dialkylamine, R_2NH, the product is N,N–dialkylcyanoformamidine:

$$(CN)_2 + 2RNH_2 \rightarrow RNHC(=NH)\text{–}C(=NH)NHR$$

$$(CN)_2 + R_2NH \rightarrow R_2NC(=NH)\text{–}CN$$

Cyanogen can form mixed complexes with several transition metal complexes, partially displacing their ligands:

$$(Ph_3P)_4Pd + (CN)_2 \rightarrow (CN)_2Pd(PPh_3)_2 + 2PPh_3$$

With hydrogen sulfide, the products are thiocyanoformamide, $NCC(=S)NH_2$ and dithiooxamide, $H_2NC(=S)C(=S)NH_2$.

$$(CN)_2 + H_2S \rightarrow NC\text{—}CS\text{—}NH_2$$

$$(CN)_2 + 2H_2S \rightarrow H_2N\text{–}SC\text{–}CS\text{–}NH_2$$

When heated at 500°C, it polymerizes into an insoluble product, paracyanogen $(CN)_n$. On further heating to 850°C paracyanogen decomposes to cyanogen.

Reaction with fluorine yields the fluoroderivate, $F_3CN{=}NCF_3$.

Analysis

Elemental composition: C 46.16%, N 53.84%.

Cyanogen may be absorbed in ethanol or other suitable organic solvent and the solution analyzed by GC or GC/MS. The characteristic mass ions for identification by GC/MS are 52 and 26. Also, the compound may be analyzed by NMR.

Hazard

Cyanogen is a highly flammable gas. It forms explosive mixtures with air, LEL 6.6%, UEL 32% by volume. Reactions with oxygen, ozone, fluorine or other strong oxidizing agents can be explosive. Also, it can explode when exposed to spark, flame or heat.

Cyanogen is moderately toxic by inhalation. Exposure causes irritation of the eyes, nose and respiratory tract. A 10-minute exposure to about 10 ppm of the gas can manifest these irritant action in humans.

LC_{50} (rat): 350 ppm in 1 hour.

CYANOGEN BROMIDE

[506-68-3]
Formula: CNBr; MW 105.92;
Structure: BrCN
Synonyms: bromine cyanide; bromocyan; bromocyanogen; cyanobromide

Uses

Cyanogen bromide is used in organic synthesis, as a rodent poison, and as a reagent for extracting gold as its cyanide salt.

Physical Properties

Colorless needles or cubic crystals; penetrating odor; density 2.015 g/cm^3; melts at 52°C; boils at 61.4°C; soluble in water, alcohol and ether.

Thermochemical Properties

$\Delta H_f°$(cry)	33.58 kcal/mol
$\Delta H_f°$(g)	44.50 kcal/mol
$\Delta G_f°$ (g)	39.51 kcal/mol
S° (g)	59.35 cal/degree mol
C_ρ (g)	11.21 cal/degree mol

Preparation

Cyanogen bromide is obtained by the reaction of bromine with potassium cyanide or sodium cyanide:

$$KCN + Br_2 \rightarrow CNBr + KBr$$

Alternatively, it may be prepared by treating sodium bromide, sodium cyanide, and sodium chlorate with sulfuric acid.

Toxicity

The compound is highly toxic by all routes of exposure.

CYANOGEN CHLORIDE

[506-77-4]
Formula: CNCl; MW 61.47
Synonyms: chlorine cyanide; chlorcyan; chlorocyanogen; chlorocyanide

Uses

Cyanogen chloride is used in organic synthesis and as a tear gas in warfare.

Physical Properties

Colorless gas or liquid; density of the liquid 1.186 g/mL; solidifies at –6°C; boils at 12.7°C; soluble in water, alcohols, and ether.

Thermochemical Properties

$\Delta H_f°$ (l)	26.79 kcal/mol
$\Delta H_f°$ (g)	32.98 kcal/mol
$\Delta G_f°$ (g)	31.31 kcal/mol
S° (g)	56.45 cal/degree mol
C_ρ (g)	10.76 cal/degree mol

Preparation

Cyanogen chloride may be prepared by the action of chlorine with hydrogen cyanide:

$$HCN + Cl_2 \rightarrow CNCl + HCl$$

It also may be prepared by the action of chlorine on a suspension of moist sodium cyanide in carbon tetrachloride at –3°C. The compound formed is purified by distillation.

Another method of preparation involves electrolysis of an aqueous solution of hydrogen cyanide and ammonium chloride.

Reactions

Cyanogen chloride reacts with caustic soda or caustic potash solution forming the alkali metal cyanide and the oxychloride:

$$CNCl + 2KOH \rightarrow KCN + KClO + H_2O$$

It polymerizes on heating forming cyanuric chloride, $C_3N_3Cl_3$, a cyclic triazine compound.

The trimer of cyanogen chloride, $(CNCl)_3$ reacts with fluorine in the presence of arsenic pentafluoride in chlorofluorocarbon solvent forming the complex $[C_3N_3Cl_3F][AsF_6]$.

Analysis

Elemental composition: C 19.54%, Cl 57.68%, N 22.79%. Cyanogen chloride may be analyzed by GC using an ECD or an FID. It may be identified by mass spectrometry. The characteristic mass ions are 60, 62, and 26.

Toxicity

Cyanogen chloride is highly toxic by all routes of exposure. It is a severe irritant to eyes, causing tears. Exposure to its vapors causes irritation of the respiratory tract and pulmonary congestion.

LC_{50} (guinea pig): 5,500 mg/m^3 in 2 minutes
(1 ppm CNCl = 2.5 mg/m^3 at NTP)

CYANOGEN IODIDE

[506-78-5]
Formula: CNI; MW 152.92
Structure: $I–C≡N$
Synonym: iodine cyanide

Physical Properties

Colorless needles; pungent odor; acrid taste; density 1.84 g/cm^3; melts at 146.7°C; vapor pressure 1 torr at 25°C; soluble in water, ethanol and ether.

Thermochemical Properties

$\Delta H_f°$ (cry)	39.72 kcal/mol
$\Delta H_f°$ (g)	53.90 kcal/mol
$\Delta G_f°$ (cry)	44.22 kcal/mol
$\Delta G_f°$ (g)	46.99 kcal/mol
S° (cry)	22.99 cal/degree mol
S° (g)	61.38 cal/degree mol
C_ρ (g)	11.54 cal/degree mol

Preparation

Cyanogen iodide is prepared by the reaction of iodine on sodium cyanide:

$$NaCN + I_2 \rightarrow CNI + NaI$$

Toxicity

The compound is highly toxic by oral and subcutaneous routes. Ingestion can cause convulsion, paralysis, and respiratory failure.

LDL_O oral (cat): 18 mg/kg
LD_{50} subcutaneous (rat): 44 mg/kg

DEUTERIUM

[7782-39-0]

Symbol D or ${}^{2}_{1}H$

An isotope of hydrogen; a stable, non-radioactive isotope; atomic number 1; atomic mass 2.014; molecular weight (for the diatomic heavy hydrogen molecule) 4.028.
Synonym: heavy hydrogen

History, Occurrence, and Uses

Rutherford predicted the existence of this heavy isotope of hydrogen in

1920. It was detected by Urey, Brickwedde and Murphy in 1932. It occurs in all natural compounds of hydrogen including water, as well as in free hydrogen molecules at the ratio of about one part per 6,000 parts hydrogen. The principal application of deuterium is in tracer studies for measuring rates and kinetics of chemical reactions. It also is used in thermonuclear reactions; and as a projectile in cyclotrons for bombardment of atomic nuclei to synthesize isotopes of several transuranium elements. Deuterium oxide, D_2O, or heavy water is used as a neutron moderator in nuclear reactors.

Physical Properties

Colorless, odorless gas; flammable; density of liquid deuterium at –253°C 0.169 g/mL; viscosity 12.6×10^{-5} poise at 27°C; liquefies at –249.5° C; solidifies at –254.4°C at 121 torr; critical temperature –234.75°C; critical pressure 16.43 atm; practically insoluble in water (3.4 mg D_2/L at 20°C).

Preparation

Deuterium may be prepared by several methods. Urey's first method of preparation involved fractional distillation of a very large amount of liquid hydrogen. It also may be produced by electrolysis of heavy water obtained by H_2S/H_2O exchange process. It may be obtained by continued, long-time electrolysis of ordinary water in which light water molecules are split first, thus concentrating deuterated oxygen in the residual liquid. Also, deuterium in high purity may be separated by thermally induced diffusion processes.

Reactions

The chemical reactions are very much similar to hydrogen (see Hydrogen). Deuterium undergoes exchange reactions instantly with hydrogen. Thus, mixtures of heavy water and water immediately form HDO. Similar exchange reactions occur in a number of hydrogen containing solutes dissolved in D_2O or mixtures of $D_2O—H_2O$. Such exchange reactions, however, are very slow in substances that contain carbon-hydrogen bonds.

Analysis

Deuterium may be analyzed from density measurements of waters. A confirmation method recommended here is GC mass spectrometry. Deuterium is burned in oxygen (or air) to form D_2O which may be separated with helium on a GC column (of intermediate polarity) and identified from its mass spectra. The mass to charge ratio of the molecular ion is 20. Additionally, deuterated products obtained by exchange reactions with hydrogen containing substances (other than those containing C—H bonds) may be separated on a capillary GC column and identified by mass spectrometry.

Hazard

Deuterium is a flammable gas. It forms explosive mixtures in air in between 5 to 75% by volume in air. The autoignition temperature is 585°C. Precautionary measures for handling this gas should be similar to those for hydrogen.

DYSPROSIUM

[7429-91-6]
Symbol Dy; atomic number 66; atomic weight 162.50; a lanthanide series, inner transition, rare earth metal; electron configuration $[Xe]4f^95d^16s^2$; atomic volume 19.032 cm^3/g. atom; atomic radius 1.773Å; ionic radius 0.908Å; most common valence state +3.

History, Occurrence, and Uses

Dysprosium was discovered in 1866 by Boisbaudran. It occurs in the earth's crust associated with other rare earth metals. It is found in the minerals, xenotime YPO_4, gadolinite, euxemite and monazite $(Ce, La, Th)PO_4$. The concentration of dysprosium in seawater is 0.9 ng/L and in the earth's crust 5.2 mg/kg.

Dysprosium is used in nuclear reactor fuels to measure neutron flux. It also is used as a fluorescence activator in phosphors.

Physical Properties

Silvery metal; hexagonal crystals; density 8.559 g/cm^3; melts at 1,411°C; vaporizes at 2,561°C; electrical resistivity 92.6 microhm-cm at 25°C; Poisson's ratio 0.243; Young's modulus $0.644x10^6$ kg/cm^2; soluble in dilute acids.

Thermochemical Properties

$\Delta H_f°$	0.0
S°	75.6 J/degree mol
C_ρ	27.7 J/degree mol
ΔH_{fus}	2.58 kcal/mol

Production

Dysprosium is produced mostly from its minerals xenotime, gadolinite, euxenite, and monazite. The metal is obtained as a by-product in the commercial production of yttrium. Finely ground ore is heated with excess concentrated sulfuric acid which converts yttrium and the other rare-earth metals into their sulfates. The water-soluble sulfates are separated from silica and other unreacted minerals with cold water. The solution is then filtered. Yttrium and other rare-earth metals in the aqueous extract are separated by displacement ion exchange techniques. Copper sulfate or zinc sulfate pretreated with 1 *M* H_2SO_4 is used as cation exchange resin and ammonium EDTA solution as eluting agent in the process. The separated fractions are treated with oxalic acid. Insoluble oxalates are obtained. Dysprosium and yttrium oxalates obtained from the fraction containing these metals are decomposed to their oxides by roasting at 800–900°C. The dysprosium sesquioxide, Dy_2O_3, is then converted to dysprosium fluoride, DyF_3, by heating with ammonium hydrogen fluoride:

$$Dy_2O_3 + 6(NH_4)HF_2 \xrightarrow{heat} 2DyF_2 + 6NH_4F + 3H_2O$$

The fluoride salt is reduced to dysprosium by heating above the melting point of dysprosium with calcium in argon atmosphere in a tungsten or tantalum vessel:

$$2DyF_3 + 3Ca \xrightarrow{>1411^\circ C} 2Dy + 3CaF_2$$

Dysprosium obtained this way may contain small quantities of tungsten or tantalum which may leach out of the reaction vessel, dissolving into molten dysprosium.

Minerals such as euxenite, fergusonite, samarskite, polycrase and loparite are highly refractory and complex in nature. These minerals may be opened up by treatment with hydrofluoric acid. While metals such as niobium, tantalum and titanium form soluble fluorides, rare earth elements form an insoluble residue of their fluorides. Such insoluble fluorides are filtered out of solution and digested with hot concentrated sulfuric acid. The rare earth sulfates formed are dissolved in cold water and thus separated from the insoluble mineral impurities. Rare earth elements in the aqueous solution are then separated by displacement ion exchange techniques outlined above.

Dysprosium is often produced from gadolinite, $Be_2Fe(Y)_2Si_2O_{10}$, an important ore of the metal. The pulverized mineral is either digested with a mixture of hot nitric and hydrochloric acids or fused with caustic soda. When digested with acid, the lanthanide elements along with beryllium and iron are extracted into the acid solution leaving behind insoluble siliceous residue. The solution is diluted and filtered. It is then treated with oxalic acid to precipitate out rare earth oxalates, thus separating these elements from iron and beryllium in the solution. The oxalates are now roasted at 800–900°C to form corresponding oxides, which are then redissolved in hydrochloric acid to separate from any siliceous matter present. The filtered chloride solutions of dysprosium and other rare earth metals are subjected to ion exchange separation, as discussed above. If caustic fusion process is applied, gadolinite forms water-soluble sodium silicate and insoluble rare earth hydroxides. The fused melt is treated with water and filtered. The insoluble hydroxides are dissolved in dilute acids and subjected to the displacement ion exchange separation discussed above.

Reactions

At ordinary temperature, dysprosium is relatively stable in air. However, when heated with oxygen it forms dysprosium sesquioxide, Dy_2O_3. With halogens, dysprosium reacts slowly at room temperature forming dysprosium trihalides:

$$2Dy + 3Cl_2 \rightarrow 2DyCl_3$$

The reaction is vigorous above 200°C.

Dysprosium combines with several nonmetals at high temperatures forming binary compounds with varying compositions. Heating with hydrogen produces dysprosium dihydride, DyH_2, and dysprosium trihydride. DyH_3. With sulfur, several sulfides have been synthesized that have the compositions

DyS, DyS_2, Dy_2S_3, and Dy_5S_7. Heating with boron and carbon yields several borides and carbides, respectively, that have compositions DyB_2, DyB_4, DyB_6, DyB_{12}, Dy_3C, and Dy_2C_3. It forms dysprosium nitride, DyN, and dysprosium phosphide, DyP, when heated with nitrogen and phosphorus respectively. Dysprosium also combines with many metals such as gallium, zinc, manganese, indium, arsenic, antimony, selenium, silicon, germanium, platinum, and polonium. It also combines with many metals at elevated temperatures.

Dysprosium dissolves in most mineral acids with the evolution of hydrogen:

$$2Dy + HCl \rightarrow 2DyCl_3 + H_2$$

The action of 1:1 HNO_3 is relatively slow.

Analysis

Dysprosium may be analyzed by AA, ICP, ICP–MS and x-ray fluorescence and diffraction techniques.

Toxicity

Dysprosium has low acute toxicity. Its soluble salts exhibit low toxicity in experimental animals when administered by intravenous route. The effects were degeneration of the liver and spleen.

EINSTEINIUM

[7429-92-7]

Symbol Es; atomic number 99; atomic weight 252; a radioactive transuranium, actinide series, manmade element; electron configuration $[Rn]5f^{11}7s^2$; the most stable isotope Es-254. Isotopes, their half-lives and the mode of decay are as follows:

Isotopes	Half-life	Mode of Decay
Es-245	75 sec	Orbital electron capture, Alpha decay
Es-246	7.3 min	Orbital electron capture, Alpha decay
Es-248	25 min	Orbital electron capture, Alpha decay
Es-249	2 hr	Orbital electron capture, Alpha decay
Es-250	8 hr	Orbital electron capture
Es-251	1.5 days	Orbital electron capture, Alpha decay
Es-252	140 days	Alpha decay
Es-254	276 days	Alpha decay
Es-254m (Metastable isomer)	39.3 hr	Beta decay, Alpha decay
Es-255	39.8 days	Beta decay, Alpha decay

History, Occurrence, and Uses

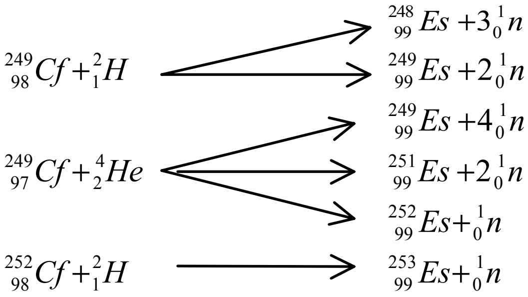
The first isotope of this element having mass number 253 and half-life 20 days was detected in 1952 in the Pacific in debris from the first thermonuclear explosion. The isotope was an alpha emitter of 6.6 MeV energy, chemically analogous to the rare earth element holmium. Isotope 246, having a half-life 7.3 minutes, was synthesized in the Lawrence Berkeley Laboratory cyclotron in 1954. The element was named Einsteinium in honor of Albert Einstein. Only microgram amounts have been synthesized. The element has high specific alpha activities. It may be used as a tracer in chemical studies. Commercial applications are few.

Production

The isotope Es-246 may be synthesized in a cyclotron by bombarding uranium-238 with nitrogen ions:

$$^{238}_{92}U + ^{14}_{7}N \rightarrow ^{246}_{99}Es + 6^{1}_{0}n$$

Isotopes of masses 248, 249, 250, 251 and 252 may be prepared from berkelium-249 or californium-249 by bombardment with alpha particles or deuterium ions:



Heavier isotopes Es-253, Es-254 and Es-255 can be produced in a nuclear reactor by multiple neutron capture reactions that may occur when uranium, neptunium and plutonium isotopes are irradiated under intense neutron flux. These and other isotopes also are produced during thermonuclear explosions.

Separation /Analysis

Einsteinium isotopes are separated on an ion exchange column and eluted with a solution of ammonium citrate. Radioactive isotopes are identified by an activity detector.

ERBIUM

[7440-52-0]

Symbol: Er; atomic number 68; atomic weight 167.26; a rare earth metallic element; lanthanide series, inner-transition metal; electron configuration [Xe]$4f^{11}5d^16s^2$; metallic radius (CN 12) 1.758Å; atomic volume 18.49 cc/mol; naturally occurring stable isotopes and their percent abundances: Er-166 (33.41%), Er-168(27.07%), Er-167(22.94%), Er-170 (14.88%), Er-164(1.56%), Er-162 (0.136%); several radioisotopes have been prepared.

History,Occurrence and Uses

Erbium oxide was separated and obtained from the rare earth oxide, yttrea in 1842 by Mosander. Urbain and James independently separated this oxide from other rare earth oxide mixtures in 1905. The pure metal was produced by Klemm and Bommer in 1934 in powdered form.

Erbium is distributed in nature, commonly occurring as mixtures with other lanthanide elements. A common mineral is gadolinite. Its concentration in the earth's crust is 2.8 mg/kg and in sea water is about 0.9 ng/L.

Physical Properties

Silvery metal; hexagonal, close-packed crystals; dark grey powder; rose colored solution; in lump form the metal is stable at ordinary temperatures; in the finely-divided state it ignites in air; density 9.066 g/cm^3; melts at 1,529°C; vaporizes at 2,863°C; vapor pressure 0.4 torr at its melting point; electrical resistivity 87 microohm-cm at 25°C and 205 microhm–cm at 1,000°C; Poisson's ratio 0.238; Young's modulus 2.96×10^{11} dynes/cm^2; Effective magnetic moment 9.9 Bohr magnetons (at 25°C) (paramagnetic, changes to antiferromagnetic at –189°C and ferromagnetic at –253°C); insoluble in water; soluble in acid.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta G_f°$ (cry)	0.0
S° (cry)	17.49 cal/degree mol
C_ρ (cry)	6.72 cal/degree mol
$\Delta H_f°$ (g)	75.8 kcal/mol
$\Delta G_f°$ (g)	67.1 kcal/mol
S° (g)	46.72 cal/degree mol
C_ρ (g)	4.97 cal/degree mol
ΔH_{fus}	4.757 kcal/mol
Coeff. linear expansion	9.2×10^{-6}/°C (at 25°C)

Production

Erbium metal is produced from rare-earth minerals. Methods of preparation are similar to dysprosium, involving sulfuric acid treatment, ion exchange separation from other lanthanides, roasting, conversion to halide, and finally high temperature reduction with calcium or sodium. (see Dysprosium).

Reactions

In aqueous solution, erbium is always trivalent, Er^{3+}. It forms water-insoluble trivalent salts, such as fluoride, ErF_3, carbonate, $Er_2(CO_3)_2$, hydroxide, $Er(OH)_3$, phosphate, $ErPO_4$, and oxalate $Er_2(C_2O_4)_3$. It also forms water-soluble salts, chloride, $ErCl_3$; bromide, $ErBr_3$; iodide, ErI_3; sulfate, $Er_2(SO_4)_3$; and nitrate, $Er(NO_3)_3$. Evaporation of solutions generally yields hydrated salts.

The metal reacts with acids, forming corresponding salts and liberating hydrogen:

$$2Er + 3H_2SO_4 \rightarrow Er_2(SO_4)_3 + 3H_2$$

When heated in oxygen or air, the metal (in lump form) slowly oxidizes forming erbium sesquioxide, Er_2O_3.

Analysis

Erbium may be analyzed by atomic absorption or emission spectrophotometry. Other instrumental analyses involve ICP–MS and x-ray techniques.

EUROPIUM

[7440-53-1]
Symbol: Eu; atomic number 63; atomic weight 151.97; a lanthanide group inner transition metal; electron configuration $[Xe]4f^65d^16s^2$ (partially filled orbitals); valence states +3 and +2.

History, Occurrence, and Uses

Boisbaudran obtained this rare earth element in 1892 in basic fractions from samarium-gadolinium concentrates, but it was not identified for several years. Demarcay obtained the element in the pure form in 1901. The element was named after Europe. It is found in nature mixed with other rare earth elements. Its concentration, however, is much lower than most other lanthanide elements. The principal rare earth ores are xenotime, monazite, and bastnasite.

Europium is used for the capture of thermal neutrons for nuclear control rods in atomic power stations. Thermal neutron absorption of the natural mixture of europium isotopes is 4,600 barns. While its salts are used in coatings for cathode ray tubes in color televisions, organoderivatives are used in NMR spectroscopy.

Physical Properties

Soft silvery metal; body-centered cubic crystal lattice; density 5.24 g/cm^3; melts at 822°C; vaporizes at 1,596°C; electrical resistivity 81 microhm–cm; reacts with water; soluble in liquid ammonia.

Thermochemical Properties

$\Delta H_f°$(cry)	0.0
S° (cry)	18.6 cal/degree mol
C_ρ (cry)	6.62 cal/degree mol
$\Delta H_f°$(g)	41.90 kcal/mol
$\Delta G_f°$ (g)	33.99 kcal/mol
S° (g)	45.12 cal/degree mol
C_ρ (g)	4.97 cal/degree mol
ΔH_{fus}	2.20 kcal/mol
Coeff. linear expansion	$32x10^{-6}$/°C

Preparation

Europeum generally is produced from two common rare earth minerals: monazite, a rare earth-thorium orthophosphate, and bastnasite, a rare earth fluocarbonate. The ores are crushed and subjected to flotation. They are opened by sulfuric acid. Reaction with concentrated sulfuric acid at a temperature between 130 to 170°C converts thorium and the rare earths to their hydrous sulfates. The reaction is exothermic which raises the temperature to 250°C. The product sulfates are treated with cold water which dissolves the thorium and rare earth sulfates. The solution is then treated with sodium sulfate which precipitates rare earth elements by forming rare earth-sodium double salts. The precipitate is heated with sodium hydroxide to obtain rare earth hydrated oxides. Upon heating and drying, cerium hydrated oxide oxidizes to tetravalent ceric(IV) hydroxide. When the hydrated oxides are treated with hydrochloric acid or nitric acid, all but Ce^{4+} salt dissolves in the acid. The insoluble Ce^{4+} salt is removed.

Acid soluble rare earth salt solution after the removal of cerium may be subjected to ion exchange, fractional crystallization or solvent extraction processes to separate individual rare earths. Europium is obtained commercially from rare earths mixture by the McCoy process. Solution containing Eu^{3+} is treated with Zn in the presence of barium and sulfate ions. The trivalent europium is reduced to divalent state; whereby it coprecipitates as europium sulfate, $EuSO_4$ with isomorphous barium sulfate, $BaSO_4$. Mixed europium(II) barium sulfate is treated with nitric acid or hydrogen peroxide to oxidize Eu(II) to Eu(III) salt which is soluble. This separates Eu^{3+} from barium. The process is repeated several times to concentrate and upgrade europium content to about 50% of the total rare earth oxides in the mixture. Treatment with concentrated hydrochloric acid precipitates europium(II) chloride dihydrate, $EuCl_2 \cdot 2H_2O$ with a yield over 99%.

Several other processes also are applied for the commercial production of europium. In general, all processes are based upon the initial steps involving opening the mineral (bastnasite or monazite) with sulfuric acid or sodium hydroxide, often followed by roasting and solubilization. In one such process after separation of cerium, the soluble rare earth chloride mixture in HCl solution is pH adjusted and treated with bis(2-ethylhexyl)phosphate to obtain europium sesquioxide, Eu_2O_3.

In the Bronaugh process, when the rare earth mixture contains europium in +2 oxidation state while all other lanthanide elements are in +3 state, the mixture is treated with ammonium hydroxide. While europium dissolves in the basic NH_4OH solution, all other metals precipitate as hydrous oxides (hydroxides). The filtrate containing europium is treated with oxalic acid. Europium oxalate formed is calcined to yield europium sesquioxide. High purity Eu_2O_3 may be separated from other rare earths on a cation exchange resin that is eluted with EDTA or other chelating agents.

Europeum metal is prepared from the europium sesquioxide obtained above by the reduction with lanthanum or cerium. The oxide is heated under a vacuum in a tantalum crucible with excess lanthanum turning. Europeum volatilizes and collects as a bright crystalline condensate on the wall of the crucible. It is stored and handled in an inert atmosphere, as the finely divided metal is flammable.

Analysis

Europeum metal may be analyzed by AA, ICP and X-ray methods. The metal or its salts must be digested with nitric acid and brought into aqueous solution prior to analysis by flame or furnace AA or ICP spectrophotometry.

FERMIUM

[7440-72-4]

Symbol Fm; atomic number 100; atomic weight 257; a man-made transuranium radioactive element of the actinide series; electron configuration $[Rn]5f^{12}7s^2$; oxidation state +3; sixteen isotopes are known; most stable isotope Fm-257, $t_{1/2}$ 100.5 days.

The isotopes, their half-lives and decay modes are tabulated below:

Isotopes	Half-lives	Decay Mode
Fm-244	4.5 sec	Alpha decay
Fm-245	3.3 msec	Spontaneous fission
Fm-246	1.6 sec	Alpha decay
Fm-247	35 sec	Alpha decay
Fm-248	0.6 min	Alpha decay
Fm-249	2.5 min	Alpha decay
Fm-250	30 min	Alpha decay
Fm-251	7 hr	Orbital electron capture, Alpha decay
Fm-252	25 hr	Alpha decay, Spontaneous fission
Fm-253	3 days	Orbital electron capture, Alpha decay
Fm-254	3.24 hr	Alpha decay, Spontaneous fission
Fm-255	20 hr	Alpha decay, Spontaneous fission
Fm-256	2.7 hr	Alpha decay, Spontaneous fission
Fm-257	97 days	Alpha decay. Spontaneous fission

History

Fermium was formally discovered in 1954 at the Nobel Institute for Physics in Stockholm. It was synthesized in 1952 in the Material Testing Reactor in Idaho, but the discovery was not announced. The new element was named in honor of Enrico Fermi. There is no commercial application of this element because its yield is in extremely minute quantities. It has been detected in debris from thermonuclear explosion.

Production

Heavier isotopes such as Fm –254, –255, –256, and –257 can be produced in a nuclear reactor by multiple neutron capture reactions when heavy elements are subjected to intense neutron irradiation. Such reactions also occur in thermonuclear explosion.

Isotopes of mass numbers from 250 to 254 have been prepared by alpha particle bombardments of californium –249 and –252:

$${}^{249}_{98}C + {}^{4}_{2}He \rightarrow {}^{253}_{100}Fm$$

$${}^{252}_{98}C + {}^{4}_{2}He \rightarrow {}^{254}_{100}Fm + 2\,{}^{1}_{0}n$$

Lighter isotopes such as Fm –247 and –248 were synthesized by bombarding plutonium –239 and –240, respectively, with carbon –12 ions:

$${}^{239}_{94}Pu + {}^{12}_{6}C \rightarrow {}^{247}_{100}Fm + 4\,{}^{1}_{0}n$$

Fermium –249 was obtained (during its synthesis in 1954) by bombarding uranium –238 with oxygen ions:

$${}^{238}_{92}U + {}^{16}_{8}O \rightarrow {}^{249}_{100}Fm + 5\,{}^{1}_{0}n$$

All these isotopes may also be synthesized by other nuclear processes.

Chemical Properties

The chemical properties of fermium are very similar to those of other trivalent actinide series elements, californium and einsteinium. The element's oxidation state +3 is its only known oxidation state.

FLUORINE

[7782-41-4]
Symbol: F; atomic number 9; atomic weight 37.997; a Group VIIA (Group 17) nonmetallic element; first member of halogen group elements; electron configuration $[He]2s^{2}2p^{5}$; valence –1; electronegativity 4.0; electron affinity 79.5 kcal/g-atom

History, Occurrence, and Uses

The element was identified by Davy in 1813 and named fluorine by Ampere. However, it was prepared successfully first in elemental form by Moissan in 1886. Fluorine is distributed widely in nature and occurs in several minerals. The most common minerals are fluorspar, CaF_2; cryolite, $3NaF{\bullet}AlF_3$; and fluorapatite, $CaF_2{\bullet}3Ca_3(PO_4)_2$. Its concentration in the earth's crust is 585 mg/kg, and is 1.3 mg/kg in sea water.

Fluorine is used in the separation of uranium, neptunium and plutonium isotopes by converting them into hexafluorides followed by gaseous diffusion; then recovering these elements from nuclear reactors. It is used also as an oxidizer in rocket-fuel mixtures. Other applications are production of many fluoro compounds of commercial importance, such as sulfur hexafluoride, chlorine trifluoride and various fluorocarbons.

Physical Properties

Pale yellow gas; occurs as a diatomic gas at ordinary temperatures and pressures; density (of liquid fluorine) at –188°C is 1.108 g/mL; density of the gas at 0°C is 1.696 g/L; liquefies at –188.12°C; solidifies at –219.66°C; critical temperature –129.02°C, critical pressure 51.04 atm; critical volume 66 cm^3/mol; reacts with water.

Thermochemical Properties

$\Delta Hf°$ (F)	–18.88 kcal/mol
$\Delta Gf°$ (F)	–14.80 kcal/mol
S° (F)	37.9 cal/degree mol
C_ρ (F)	5.44 cal/degree mol
$\Delta Hf°$ (F_2)	0.0
$\Delta Gf°$ (F_2)	0.0
S° (F_2)	48.44 cal/degree mol
C_ρ (F)	7.48 cal/degree mol
ΔH_{vap}	1.582 kcal/mol
ΔH_{fus}	0.122 kcal/mol
ΔH_{dissoc}	37.7 kcal/mol

Preparation

Fluorine is manufactured commercially by an electrolysis process which has not changed much since Moissan first isolated it. The electrolytes consist of an aqueous mixture of potassium fluoride and hydrogen fluoride, HF solution, the molar ratio of KF to HF usually being 1:1 or 2:1. Electrolysis of hydrogen fluoride produces fluorine gas at the ungraphitized carbon anode and hydrogen gas at the mild steel cathode. Potassium fluoride makes the solution electrically conductive (pure HF is a nonconductor). In many commercial processes, a KF to HF molar ratio of 2:1 is used. At this composition, the partial pressure of HF over the electrolyte is low, and the temperature of the melt is 70°. However, fluorine produced by this process usually contains about 5 to 10% hydrogen fluoride. HF can be removed by passing fluorine-HF mixture over dry sodium fluoride. HF is retained over sodium fluoride, thus purifying fluorine gas to over 99%.

Fluorine gas is sold commercially in stainless steel or monel cylinders as compressed gas or as liquid fluorine.

Reactions

Fluorine is the most electronegative element in the Periodic Table. It also is the most reactive nonmetal, and the most powerful oxidizing agent:

$$F_2 + 2e^- \rightarrow 2F^- \qquad E° = +3.053 \text{ V}$$

It combines with practically all elements (except helium, neon, and nitrogen) and most compounds. It combines with oxygen at elevated temperatures in an electric furnace. Its' compounds with inert gases xenon, argon, krypton, and radon are known.

Fluorine reacts with gaseous hydrogen forming hydrogen fluoride. Although the reaction is highly exothermic (ΔH_{rxn} = –64 kcal/mol), it requires high temperature or a catalyst for initiation:

$$F_2 + H_2 \xrightarrow[\text{catalyst}]{\text{heat or}} 2HF$$

Reaction with water is complex, producing hydrofluoric acid and oxygen as the main products:

$$F_2 + 2H_2O \rightarrow 4HF + O_2$$

Minor products such as hydrogen peroxide (H_2O_2), oxygen difluoride (OF_2), and ozone (O_3), may form in small yields depending on conditions of the reactions.

Nonmetals, such as sulfur, phosphorus and carbon (amorphous) inflame in fluorine forming their corresponding fluoro compounds, such as sulfur hexafluoride (SF_6), phosphorus pentafluoride (PF_5), and carbon tetrafluoride (CF_4).

Fluorine also reacts with other halogens, forming interhalogen compounds. While with bromine and iodine it reacts vigorously at ordinary temperatures, with chlorine the reaction occurs at 200°C. Such interhalogen products with these halogens include iodine heptafluoride, bromine trifluoride, bromine pentafluoride, and chlorine trifluoride. Metalloid elements, such as arsenic, silicon, selenium, and boron also inflame in a stream of fluorine, forming fluorides.

All metals react with fluorine to form metal fluorides. With alkali metals the reactions are violent and highly exothermic at ordinary temperatures. Other metals react at high temperatures. Many metals in their solid form react with fluorine at ordinary temperatures, forming protective coatings of metal fluorides which prevent any further fluoride formation. Such metals include copper, nickel and aluminum, which mostly are metals of construction. Protective coatings of these metal fluorides have very low volatility, thus preventing further fluorination. However, with certain metals such as titanium, tungsten, and vanadium, such protective fluoride coatings can volatilize readily at high temperatures, allowing the metals to burn vigorously in fluorine.

Reaction of fluorine with an aqueous alkali solution is complex and depends on reaction conditions. A major product of such reaction is oxygen difluoride, OF_2. In cold alkali solution, the products constitute metal fluoride, oxygen difluoride, water, and oxygen:

$$6F_2 + 8NaOH \rightarrow 8NaF + 2OF_2 + 4H_2O + O_2$$

Fluorine reacts with sulfuric acid to yield fluorosulfuric acid, $HFSO_3$, and with nitric acid it forms fluorine nitrate, NO_3F, an explosive gas.

Fluorine reacts with hydrocarbons in vapor phase, producing fluorocarbon compounds in which hydrogen atoms are substituted with fluorine atoms. The strong C—F bond with bond energy in the order of 110 kcal/mol imparts greater stability to such fluorocarbon derivatives in which the fluorine atoms(s) also shield the carbon skeleton from chemical attack. The fluorination of hydrocarbons is, however, more conveniently carried out using hydrogen fluoride, ammonium fluoride, reactive metal fluorides, or by electrolytic fluorination than by using elemental fluorine, with which the reaction is difficult to control.

Analysis

Analysis may be performed by reacting the gas in water (or allowing the contaminated air to bubble through water) and determining the fluoride ion in the solution using a fluoride ion selective electrode, or analyzing the solution by ion chromatography. Solution may require appropriate dilutions prior to measurements. Air may be sampled in a stainless steel or monel canister by repeated evacuation and filling and the contents transported by helium onto a cryogenically cooled GC port. The mixture is separated on a suitable temperature programmed column and measured by a halogen specific detector or by a mass selective detector. The characteristic mass ion for the element is 19. Alternatively, fluorine may be converted into fluorosilicic acid, H_2SiF_6 which may be precipitated either as calcium fluoride or measured by titration with a standard solution of thorium nitrate.

Hazard

Because of its high reactivity, many fluorine reactions are violent and may cause explosion if not carried out under controlled conditions. Reactions with hydrogen, acetylene, ammonia, chlorine dioxide, sulfur dioxide, and a number of organics can be explosive. Also, it forms shock-sensitive products with a number of compounds including perchloric acid, nitric acid, alkali metal nitrates and nitrites, azides and sodium acetate (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances,* 2nd ed., pp. 439-40. New York: Wiley Interscience). Reaction with water is violent even at low temperatures. A large number of inorganic and organic substances ignite in fluorine atmosphere.

Fluorine gas is a severe irritant to eyes, skin, and mucous membranes. Acute exposure can cause respiratory tract irritation and pulmonary edema. Chronic exposure can cause mottling of teeth and injury to lungs, liver and kidney.

FLUORINE NITRATE

[7789-26-6]
Formula: FNO_3; MW 81.003
Synonyms: nitrogen trioxyfluoride; nitroxy fluoride; nitryl hypofluorite.

Uses

Fluorine nitrate is used in rocket propellants as an oxidizing agent.

Physical Properties

Colorless gas; acrid odor; density 3.554 g/L at 25°C; liquefies at –46°C; density of liquid 1.507 g/mL at –46°C; solidifies at –175°C; reacts with water (forming HF, OF_2, HNO_3 and O_2); also reacts with ethanol, ether and aniline; soluble in acetone.

Thermochemical Properties

$\Delta H_f°$	2.486 kcal/mol

Preparation

Fluorine nitrate may be prepared by the action of fluorine on nitric acid:

$$F_2 + HNO_3 \rightarrow FNO_3 + HF$$

Also, it is produced when nitrogeneous compounds are electrolyzed in hydrofluoric acid.

Hazard

Fluorine nitrate is shock sensitive, especially in liquid state. The liquefied material explodes when shaken vigorously or in contact with alcohol, ether, aniline, or grease (Bretherick's *Handbook of Reactive Chemical Hazards*, 5th. Ed., P. Urben (ed.) 1995, pp 1405-6, Oxford, UK: Butterworth-Heinemann). The gas catches fire when mixed with ammonia or hydrogen sulfide.

FRANCIUM

[7440-73-5]
Symbol Fr; atomic number 87; atomic weight 223; heaviest alkali metal element of Group IA (Group 1); a radioactive element; electron configuration $[Rn]7s^1$; oxidation state +1; the most electropositive element; the most stable isotope, Fr-223 ($t_{1/2}$ 21 minutes), also is the only natural isotope. Isotopes, half-lives and their decay modes are shown below:

Isotopes	Half-lives	Decay mode
Fr-203	0.7 sec	Alpha emission
Fr-204	3.3 sec	Alpha emission
Fr-204 (isomer)	2.2 sec	Alpha emission
Fr-205	3.7 sec	Alpha emission
Fr-206	16 sec	Alpha emission
Fr-207	15 sec	Alpha emission
Fr-208	60 sec	Alpha emission
Fr-209	52 sec	Alpha emission
Fr-210	3.2 min	Alpha emission
Fr-211	3.0 min	Alpha emission
Fr-212	19 min	Alpha emission
Fr-213	34 sec	Alpha emission
Fr-218	0.005 sec	Alpha emission
Fr-219	0.02 sec	Alpha emission
Fr-220	27.5 sec	Alpha emission
Fr-221	4.8 min	Alpha emission
Fr-222	15 min	Beta decay
Fr-223	21 min	Beta decay (99%), Alpha decay (0.005%)
Fr-224	2 min	Beta decay

History and Occurrence

Francium occurs in decay products of actinium. It was discovered by French physicist Marguerite Perey in 1939 and named after France. No weighable amount ever has been prepared.

Preparation

Francium-223 is produced from the decay of actinium-227. While the chief decay product is thorium-227 resulting from beta emission, actinium-227 also undergoes alpha emission to an extent of one percent giving francium-223:

$$ {}^{227}_{89}\text{Ac} \xrightarrow{\text{beta decay}} {}^{227}_{88}\text{Th} + \overset{-}{\text{e}} \qquad (99\%) $$

$$ {}^{227}_{89}\text{Ac} \xrightarrow{\text{beta decay}} {}^{223}_{87}\text{Fr} + {}^{4}_{2}\text{He} \qquad (1\%) $$

GADOLINIUM

[7440-54-2]

Symbol Gd; atomic number 64; atomic weight 157.25; a lanthanide series rare earth element; electron configuration $4f^75d^16s^2$; partially filled *f* orbital; common oxidation state +3; six stable natural isotopes: Gd-152 (0.2%), Gd-154 (2.86%), Gd-155 (15.61%, Gd-156 (20.59%), Gd-157 (16.42%), Gd-157 (23.45%)

History, Occurrence, and Uses

Gadolinum is found in minerals bastnasite and monazite, always associated with other rare earth metals. It was isolated from yttria in 1880 by the Swiss chemist Marignac, and discovered independently in 1885 by Boisbaudran. It was named in honor of the Swedish chemist Gadolin. Its abundance in the earth's crust is 6.2 mg/kg and concentration in sea water is 0.7 ng/L.

The most important application of this metal is as control rod material for shielding in nuclear power reactors. Its thermal neutron absorption cross section is 46,000 barns. Other uses are in thermoelectric generating devices, as a thermoionic emitter, in yttrium-iron garnets in microwave filters to detect low intensity signals, as an activator in many phosphors, for deoxidation of molten titanium, and as a catalyst. Catalytic applications include decarboxylation of oxaloacetic acid; conversion of *ortho*- to *para*-hydrogen; and polymerization of ethylene.

Physical Properties

Colorless or light yellow metal; at ordinary temperatures it occurs in hexagonal close-packed crystalline form, known as alpha-gadolinium; alpha form transforms to a body-centered cubic allotropic form, beta-gadolinium upon heating at 1,262°C; density 7.90 g/cm^3; melting point 1,313°C; vaporizes at 3,266°C; vapor pressure 9.0 torr at 1,800°C (calculated); electrical resistivity 134.0 microhm-cm at 25°C; Poisson ratio 0.259; modulus of elasticity 8.15x106 psi; thermal neutron absorption cross section 46,000 barns; insoluble in water; dissolves in acid (reacts).

Thermochemical Properties

$\Delta H_f°$	0.0
$\Delta G_f°$	0.0
S°	16.27 cal/degree mol
C_ρ	8.85 cal/degree mol
ΔH_{fus}	2.34 kcal/mol
ΔH_{vap}	72.0 kcal/mol
Coeff. linear expansion	8.6x10^{-6}/°C

Production

Gadolinium is produced from both its ores, monazite and bastnasite. After the initial steps of crushing and beneficiation, rare earths in the form of oxides are attacked by sulfuric or hydrochloric acid. Insoluble rare earth oxides are converted into soluble sulfates or chlorides. When produced from monazite sand, the mixture of sand and sulfuric acid is initially heated at 150°C in cast iron vessels. Exothermic reaction sustains the temperature at about 200 to 250°C. The reaction mixture is cooled and treated with cold water to dissolve rare earth sulfates. The solution is then treated with sodium pyrophosphate to precipitate thorium. Cerium is removed next. Treatment with caustic soda solution followed by air drying converts the metal to cerium(IV) hydroxide. Treatment with hydrochloric or nitric acid solubilizes all rare earths except cerium. Rare earth salt solution is then treated with magnesium nitrate. The double salts of samarium, europium, and gadolinium nitrate crystallize out. Individual salts are separated by ion exchange methods.

Gadolinium is obtained from its salts, usually its chloride or fluoride, by heating with excess calcium at 1,450°C under argon. The reduction is carried out in a tantalum crucible. Alternatively, fused gadolinium chloride mixed with sodium or potassium chloride is electrolyzed in an iron pot that serves as the anode and using a graphite cathode. Sponge gadolinium may be produced by reducing molten gadolinium chloride with a reducing metal oxide in vaporized state at a temperature below 1,300°C (the melting point of gadolium) at a reduced pressure.

Reactions

The only oxidation state known for this metal is +3. Therefore, all its compounds are trivalent. It reacts with dilute mineral acids forming the corresponding salts. The reaction is vigorous but usually not violent.

$$2Gd + 3H_2SO_4 \rightarrow Gd_2(SO_4)_3 + 3H_2$$

$$2Gd + 6HCl \rightarrow 2GdCl_3 + 3H_2$$

Although the metal is stable in air at ordinary temperature, it burns in air when heated at 150 to 180°C, particularly when present in sponge or powdered form having a large surface area. The product is gadolinium(III) oxide, Gd_2O_3.

Gadolinium is a strong reducing agent. It reduces oxides of several metals such as iron, chromium, lead, manganese, tin, and zirconium into their elements. The standard oxidation potential for the reaction

$$Gd \rightarrow Gd^{3+} + 3e^- \quad \text{is 2.2 volts.}$$

Gadolinium burns in halogen vapors above 200°C forming gadolinium(III) halides:

$$2Gd + 3Cl_2 \xrightarrow{>200^\circ C} 2GdCl_3$$

When heated with sulfur, the product is gadolinium sulfide Gd_2S_3. Similarly, at elevated temperatures, gadolinium combines with other nonmetals such as nitrogen, hydrogen, and carbon forming nitride, hydride, and carbide respectively:

$$2Gd + N_2 \xrightarrow{\text{elevated temperature}} 2GdN$$

$$2Gd + 3H_2 \xrightarrow{\text{elevated temperature}} 2GdH_3$$

Analysis

Gadolinium may be measured in an acidic solution by flame or furnace atomic absorption or ICP atomic emission spectrophotometry. Also, gadolinium may be identified nondestructively and rapidly by x-ray fluorescence methods. It also may be measured by neutron activation analysis, and by various spectrophotometric techniques. The element shows sharp absorption bands in ultraviolet region at 270–280 nm. Other lanthanides also produce bands in this region; however, those are low intensity minor bands.

GADOLINIUM(III) CHLORIDE

[10138-52-0]
Formula: $GdCl_3$; MW 263.61; forms a hexahydrate, $GdCl_3 \cdot 6H_2O$[19423–81–5]

Uses

$GdCl_3$ is used for preparing gadolinium metal.

Physical Properties

White monoclinic crystal; hygroscopic; density 4.52 g/cm^3; melts at 609°C; soluble in water.

Thermochemical Properties

$\Delta H_f°$	–240.9 kcal/degree mol
C_ρ	21.0 cal/degree mol

Preparation

$GdCl_3$ is prepared by heating gadolinium(III) oxide with excess of ammonium chloride above 200°C:

$$Gd_2O_3 + 6NH_4Cl \xrightarrow{200^\circ C} 2GdCl_3 + 6NH_3 + 3H_2O$$

Analysis

Elemental composition: Gd 59.65%, Cl 41.35%. $GdCl_3$ aqueous solution is analyzed for Gd metal by AA or ICP spectrometry, and for chloride ion by ion chromatography, chloride ion selective electrode, or titration with silver nitrate using potassium chromate indicator.

GADOLINIUM(III) OXIDE

[12064-62-9]
Formula: Gd_2O_3; MW 362.50
Synonym: gadolinia

Uses

Gadolinium oxide is used in control rods for neutron shielding in nuclear power reactors. It also is used in filament coatings, ceramics, special glasses and TV phosphor activator. The compound also is used as a catalyst.

Physical Properties

White powder; hygroscopic; density 7.07 g/cm^3; melts at 2,420°C; insoluble in water (K_{sp}=1.8x10^{-23}); soluble in acid.

Thermochemical Properties

$\Delta H_f°$	–434.9 kcal/degree mol
C_ρ	25.5 cal/degree mol

Preparation

Gadolinium oxide is prepared by calcinations of gadolinium carbonate, –hydroxide, –nitrate, or –oxalate:

$$Gd_2(CO_3)_3 \xrightarrow{ignite} Gd_2O_3 + 3CO_2$$

$$2Gd(OH)_3 \xrightarrow{ignite} Gd_2O_3 + 3H_2O$$

Analysis

Elemental composition: Gd 86.76%, O 13.24%. A weighted amount of compound is dissolved in nitric acid, diluted, and analyzed by AA or ICP technique. The solid powder may be characterized nondestructively by x-ray methods.

GADOLINIUM(III) SULFATE OCTAHYDRATE

[13450-87-8]
Formula: $Gd_2(SO_4)_3 \cdot 8H_2O$; MW 746.81

Uses

$Gd_2(SO_4)_3 \cdot 8H_2O$ is used in cryogenic work; and in thermoelectric devices

Physical Properties

Colorless monoclinic crystals; density 3.01/cm^3 (at 15°C); loses water of crystallization at 400°C; density of anhydrous salt 4.14 g/cm^3; decomposes at 500°C; soluble in cold water; solubility decreases with rise in temperature.

Preparation

The hydrated sulfate is obtained by dissolving gadolinium(III) oxide in dilute sulfuric acid followed by crystallization:

$$Gd_2O_3 + 3H_2SO_4 + 5H_2O \rightarrow Gd_2(SO_4)_3 \cdot 8H_2O$$

Analysis

Elemental composition: Gd 42.11%, S 12.88%, H 2.16%, O 42.85%. An aqueous solution of weighted amount of salt is analyzed for gadolinium by AA or ICP spectrometry and sulfate anion by ion chromatography. The water of hydration may be measured by gravimetry, heating a weighted amount of salt at 400°C to expel the water followed by cooling and weighing.

GALLIUM

[7440-55-3]
Symbol Ga; atomic number 31; atomic weight 69.723; a Group IIIA (Group 13) element; electron configuration $[Ar]3d^{10}4s^24\rho^1$; oxidation state +3, also exhibits +2 and +1; ionic radius, Ga^{3+} 1.13Å; two stable natural isotopes: Ga-69 (60.20%), Ga-71 (39.80%).

History, Occurrence, and Uses

The existence of this element was predicted by Mendeleev as a missing link between aluminum and indium during his periodic classification of elements. Mendeleev termed it ekaaluminum. The element was discovered in 1875 by French chemist Lecoq de Boisbaudran while he was carrying out spectroscopic examination of emission lines from Pyrenean zinc blende concentrates. Boisbaudran named this new element gallium, after Gallia, the Latin word for his native France. In the same year, Boisbaudran also separated gallium by electrolysis.

Gallium is widely distributed in nature, mostly found in trace amounts in many minerals including sphalerite, diaspore, bauxite, and germanite. It is found in all aluminum ores. Gallium sulfide occurs in several zinc and germanium ores in trace amounts. It also is often found in flue dusts from burning coal. Abundance of this element in the earth's crust is about 19 mg/kg. Its average concentration in sea water is 30 ng/L.

The most important use of gallium is as a doping agent for semiconductors, transistors, and other solid state devices. It is used to produce semiconducting compounds. Miscellaneous important semiconductor applications include magnetic field sensing, temperature sensing, and voltage amplification. Some gallium compounds, such as gallium arsenide, gallium phosphide, and magnesium gallate have major applications in electroluminescent light emission, microwave generation, and UV activated powder phosphors. Another important use of gallium in oxide form involves spectroscopic analysis of uranium oxide. Gallium also is used to make many low melting alloys. Some other uses for gallium are in high-temperature thermometers as a thermometric fluid; in high vacuum systems as a liquid sealant; as a heat-transfer medium; and to produce mirrors on glass surfaces.

Physical Properties

Gray orthogonal crystal or silvery liquid; the ultrapure material has silver-like appearance; density of solid 5.904 g/cm³ at 29.6°C; specific gravity of liquid 6.095 at 29.6°C; melts near room temperature at 29.6°C; supercools below its freezing point (seeding may be required for solidification); expands on solidification (3.1%); vaporizes at 2,204°C; exists in liquid state in the widest temperature range (i.e., among all elements gallium occurs as liquid in the widest range of temperature); vapor pressure 0.0001 torr at 900°C (lowest vapor pressure for any element in liquid state at this temperature), 0.0008 torr at 1,000°C, 1 torr at 1,350°C, and 5 torr at 1,478°C; surface tension 735 dynes/cm at 30°C; viscosity 1.60 and 0.81 centipoise at 100°C and 500°C, respectively.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (liq)	1.34 kcal/mol
S° (cry)	9.78 cal/degree mol
C_ρ (cry)	6.19 cal/degree mol
H_{vap}	60.71 kcal/mol
Thermal conductivity (30°C)	0.08 cal/sec/cm/°C
Coeff. linear expansion	18×10^{-6}/°C

Production

All gallium minerals contain the element only in very small amounts. It is, therefore, obtained as a by-product during production of aluminum or zinc.

Gallium occurs as a hydrated oxide (hydroxide) in all aluminum minerals including bauxite, clay, and laterite. The ore is digested with a hot solution of caustic soda (Bayer process). This converts aluminum to sodium aluminate and the small quantities of gallium that are present in the ore into sodium gallate. On cooling and seeding the liquor most aluminum salt precipitates along with small quantities of gallum as coprecipitate. After aluminum separates, the supernatant solution becomes richer in gallium. Its concentration even at this stage is not adequate for electrolytic recovery from the solution.

Also, supernatant solution in the Bayer liquor still contains an appreciable amount of soluble aluminum salt that needs to be removed by electrolysis prior to gallium recovery. This may be done either by treating the solution with lime to precipitate out calcium aluminate or by neutralizing the solution with carbon dioxide to precipitate alumina hydrate (Hudson, L.K. 1965. *J. Metals*, 17, pp. 948-51). Removal of most aluminum by these processes enhances the concentration of gallium in the solution to a level of approximately 0.1% whereupon the solution may be electrolyzed using an anode, cathode, and cell made of stainless steel.

Gallium may be recovered from zinc sulfide ores by a series of steps that include oxidation, acid treatments, neutralization, precipitation, alkali treatment, and electrolysis (Foster, L.M. 1968. Gallium. In the *Encyclopedia of Chemical Elements,* ed. C. L. Hampel. pp. 231-237, New York: Reinhold Publishing Corp.). The process is described below.

The sulfide ore is roasted in air to convert it into oxide. The oxide is treated with sulfuric acid. The acid solution now contains zinc sulfate along with sulfates of aluminum, iron, gallium, and other impurity metals. Upon neutralization, iron and aluminum precipitate out along with gallum. The "iron mud" so obtained is treated with caustic soda solution to solubilize gallium and aluminum. Neutralization of this solution yields precipitates of hydrated oxides of aluminum and gallium. The precipitate is dissolved in hydrochloric acid to form gallium chloride and some aluminum chloride. Gallium chloride is highly soluble in ether and, therefore may be separated from the acid solution by ether extraction. The ether extract is treated with caustic soda solution to precipitate out remaining iron impurities. The alkaline solution containing gallium is electrolyzed to recovery the element.

The crude material may be purified by acid wash and fractional crystallization to obtain 99.999% gallium for its semiconductor applications. Gallium is one of the purest elements that may be produced commercially. It is transported in molten state. The element supercools below its normal freezing point. To initiate solidification, molten gallium is 'seeded' with a solid crystal. A small crystal of appropriate orientation in any desired crystallographic axis is brought in contact with the surface of supercooled liquid through a thin layer of dilute hydrochloric acid. The acid removes the thin solid oxide film from the surface. Solidification begins when the seed touches the surface of supercooled liquid gallium, and the crystallographic orientation of the seed is maintained throughout the process.

Chemical Reactions

Chemical properties of gallium fall between those of aluminum and indium. It forms mostly the binary and oxo compounds in +3 oxidation state. It forms a stable oxide, Ga_2O_3 and a relatively volatile suboxide, Ga_2O.

Gallium combines with halogens forming the halides, GaX_3. Similarly, it combines with phosphorus, arsenic and antimony forming the corresponding binary compounds, which exhibit interesting semiconductor properties. With sulfur it forms sulfide. No reaction occurs with bismuth, although Ga dissolves in it. Reaction with nitrogen occurs at high temperatures forming gallium nitride, GaN, which is relatively unstable (decomposes above 600°C). Unlike aluminum, gallium does not form any carbide. Reactions with mineral acids are slow on high purity gallium.

Some lower valence compounds of gallium also are known. These include gallium suboxide, Ga_2O; gallum sulfide, GaS; gallium selenide, GaSe; gallium telluride, GaTe; gallium dichloride, $GaCl_2$; and gallium monochloride, GaCl. The monochloride exists only in vapor state.

Analysis

Gallium may be identified by its physical properties. Its compounds or elemental form may be analyzed by acid digestion followed by dilution of the acid and measurement at ppm to ppb range by atomic absorption, atomic emission, or x-ray fluorescence methods. It also may be identified by neutron activation analysis and ICP-MS techniques.

GALLIUM(III) ARSENIDE

[1303-00-0]
Formula: GaAs; MW 144.64

Uses

Gallium arsenide exhibits semiconductor properties. It is used in transistors, lasers, solar cells and various high-speed microcircuits.

Physical Properties

Gray cubic crystal; density 5.316 g/cm³; melts at 1,227°C; hardness 4.5 Mohs; lattice constant 5.653Å; dielectric constant 11.1; resistivity (intrinsic) at 27°C, 3.7×10^8 ohm-cm.

Thermochemical Properties

$\Delta H_f°$	–16.97 kcal/mol
$\Delta G_f°$	–16.20 kcal/mol
S°	15.34 cal/degree mol
C_ρ	11.04 cal/degree mol
Coeff. linear expansion	5.9×10^{-6}/°C
Thermal conductivity	0.52 $Wcm^{-1}K^{-1}$

Preparation

Gallium arsenide is prepared by passing a mixture of arsenic vapor and hydrogen over gallium(III) oxide heated at 600°C:

$$Ga_2O_3 + 2As + 3H_2 \xrightarrow{600^\circ C} 2GaAs + 3H_2O$$

The molten material attacks quartz. Therefore, quartz boats coated with carbon by pyrolytic decomposition of methane should be used in refining the compound to obtain high purity material.

Gallium arsenide is produced in polycrystalline form as high purity, single crystals for electronic applications. It is produced as ingots or alloys, combined with indium arsenide or gallium phosphide, for semiconductor applications.

Analysis

Elemental composition: Ga 48.20%, As 51.80%. Both As and Ga may be analyzed by various instrumental techniques including flame and furnace AA, ICP spectrometry, and x-ray methods. A weighed amount of solid material is digested with nitric acid, diluted in water and analyzed for these metals. The crystals may be characterized nondestructively by their optical and electronic properties.

GALLLIUM(III) CHLORIDE

[14350-90-3]
Formula: $GaCl_3$; MW 176.08

Uses

Gallium(III) chloride is used to prepare other gallium salts and in solvent extraction. The chloride is highly soluble in solvent ether. This high solubility of metal chloride in ether allows metal extraction from ore.

Physical Properties

Colorless needles or glassy solids; density 2.47 g/cm^3; melts at 77.9°C; vaporizes at 201°C; critical temperature 420.8°C; critical volume 263 cm^3/mol.

Thermochemical Properties

$\Delta H_f°$	–125.40 kcal/mol
$\Delta G_f°$	–108.70 kcal/mol
S°	33.94 cal/degree mol
ΔH_{fus}	2.61 kcal/mol
ΔH_{vap}	5.71 kcal/mol

Preparation

Gallium(III) chloride is prepared by the reaction of gallium with hydrogen chloride. Also, it can be made by direct combination of gallium and chlorine. The reaction is highly vigorous.

Reactions

Reaction with ammonia or caustic soda solution yields a gelatinous precipitate of gallium hydroxide, $Ga(OH)_3$. Reaction of gallium(III) chloride with metallic gallium yields a solid dimeric dichloride, Ga_2Cl_4, having the structure $Ga^I[Ga^{III}Cl_4]$. In the presence of a donor ligand L, molecular adducts of structures $Ga^{II}Cl_4 \cdot 2L$ are formed. In these adducts, gallium exists in the oxidation state +2.

Reaction with lithium hydride in ether produces lithium gallium hydride:

$$4LiH + GaCl_3 \xrightarrow{ether} LiGaH_4 + 3LiCl$$

The corresponding sodium salt has not been synthesized.

Gallium(III) chloride also combines with other metal chlorides such as $CaCl_2$ or $CrCl_3$ to form mixed chlorides that have halogen bridge structures; i.e., $Cl_4Ta(\text{-}Cl)_2$. Many such compounds are volatile.

Analysis

Elemental composition: Ga 39.60%, Cl 60.40%. The compound may be characterized by physical properties, electron diffraction and x-ray methods.

Gallium may be measured in aqueous solution by various instrumental methods (See Gallium), and chloride by ion chromatography.

GALLIUM PHOSPHIDE

[12063-98-8]
Formula: GaP; MW 100.70

Uses

Gallium phosphide is used in making semiconductors.

Physical Properties

Pale orange to yellow transparent cubic crystals or long whiskers; lattice constant 5.450Å; density 4.138 g/cm^3; melts at 1,477°C; dielectric constant 8.4; electroluminescent in visible light.

Preparation

The compound is prepared by vapor phase reaction of gallium suboxide, Ga_2O and phosphorus. It is produced in polycrystalline form or as single crystals or whiskers in high purity grade for use in semiconducting devices.

Analysis

Elemental composition: Ga 69.24%, P 30.76%. Gallium phosphide may be characterized by its physical and electronic properties. It may also be analyzed by various x-ray methods. Gallium may be measured by AA and ICP spectrophotometry following digestion with nitric acid or aqua regia and appropriate dilution (See Gallium).

GALLIUM SESQUIOXIDE

[12024-21-4]
Formula: Ga_2O_3; MW 187.44
Synonyms: gallium(III) oxide; gallia

Uses

The compound is used in spectroscopic analysis and in preparing gallium arsenide for making semiconductors.

Physical Properties

White crystals; exists in three crystalline modifications: alpha-, beta-, and gamma-Ga_2O_3; while the alpha-form is analogous to the corundum form of alumina, the beta-Ga_2O_3 is isomorphous with theta-alumina; alpha-form converts to beta-modification on calcination at high temperatures (600°C); gamma form is stable at low temperatures; density 6.44 g/cm^3 (alpha-Ga_2O_3), 5.88 g/cm^3 (beta- Ga_2O_3); melts at 1,725°C; soluble in most acids.

Thermochemical Properties

$\Delta H_f°$	–260.3 kcal/mol
$\Delta G_f°$	–238.6 kcal/mol
S°	20.32 cal/degree mol
C_ρ	22.01 cal/degree mol

Preparation

Gallium sesquioxide is precipitated in hydrated form upon neutralization of acidic or basic solution of gallium salt. Also, it is prepared by thermal decomposition of gallium salts. Gallium oxide hydroxide, GaOOH [20665-52-5] on calcinations at high temperatures yields beta- Ga_2O_3.

Reactions

Gallium sesquioxide is reduced to gallium suboxide, Ga_2O [12024-20-3] by common reducing agents. Also, heating the sesquioxide with gallium metal yields gallium suboxide. Heating with magnesium reduces the oxide to elemental form in a violent reaction:

$$Ga_2O_3 + 3Mg \xrightarrow{heat} 2Ga + 3MgO$$

Heating with mineral acids yields corresponding gallium salts. When heated with a mixture of hydrogen and arsenic vapors at 600°C, gallium arsenide, GaAs is produced. When heated with alkali metal oxide at 1,000°C, alkali metal gallates, such as $K_2Ga_2O_6$ are formed.

Analysis

Elemental composition: Ga 74.39%, O 25.61%. The compound may be characterized by x-ray methods. Gallium may be analyzed in a diluted acid extract by AA or ICP spectrophotometry (see Gallium).

GERMANIUM

[7440-56-4]
Symbol Ge; atomic number 32; atomic weight 72.61; a GroupIVA (Group 14) metalloid element; electron configuration [Ar]$3d^{10}4s^24p^2$; oxidation states +2 and +4; electonegativity 1.9; covalent radius (tetrahedral, sp^3) 1.22Å; ionic radius: Ge^{2+} 0.93Å, Ge^{4+} 0.53Å; isotopes and their natural abundance: Ge-70 (20.15%), Ge-72 (27.43%), Ge-73 (7.76%), Ge-74 (36.54%), Ge-76 (7.76%).

History, Occurrence, and Uses

The existence of this element was predicted by Mendeleev in 1871 in his periodic scheme. He predicted that it should belong to the carbon group and occupy the position just below silicon. He therefore named it ekasilicon.

Fifteen years later in 1886, the predicted element was discovered by Clemens Winkler who isolated it from the mineral argyrodite. It was named in honor of Germany.

Germanium occurs in nature mostly as sulfide ores. It is found in the minerals germanite, $7CuS \cdot FeS \cdot GeS_2$; argyrodite, $4Ag_2S \cdot GeS_2$; renierite (Cu,Ge,Fe,Zn,As)S; and canfieldite, $4Ag_2S$. It also is found in small quantities in many zinc blende ores from which it is commercially extracted in the United States. Trace quantities of germanium are also found in many coals. Its abundance in the earth's crust is about 1.5 mg/kg and concentration in sea water is 0.05 µg/L.

The most important uses of germanium are in electronic industries. It is a semiconductor material exhibiting an exponential increase of conductivity with increasing temperature. The element can be prepared in extreme purification with a high degree of crystalline perfection so as to yield highly characterized surfaces. Other applications of germanium are in infrared detectors, microscopes and various optical instruments; as a phosphor in fluorescent lamps; as an alloying agent; and as a catalyst.

Physical Properties

Grayish-white cubic crystals; lustrous and brittle; density 5.323 g/cm^3; hardness 6.0 Mohs; melts at 938.2°C; vaporizes at 2,833°C; a poor conductor of electricity; electrical resistivity 47 microhm-cm; dielectric constant 15.7; specific magnetic susceptibility (at 20°C) 0.122×10^{-6}; insoluble in water, dilute acids and dilute alkalies; attacked by concentrated nitric and sulfuric acids, aqua regia and fused alkalies.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (g)	88.9 kcal/mol
$\Delta G_f°$ (g)	79.2 kcal/mol
S° (cry)	7.43 cal/degree mol
S° (g)	40.1 cal/degree mol
C_ρ (cry)	5.57 cal/degree mol
C_ρ (g)	7.38 cal/degree mol
ΔH_{fus}	8.83 kcal/mol
ΔH_{vap}	79.8 kcal/mol
Thermal conductivity (at 25°C)	0.14 cal/sec/cm/°C
Coeff. linear expansion (at 25°C)	6.1×10^{-6}/°C

Production

In the United States, germanium is obtained as a by-product of zinc production from zinc blende ores. The ore is concentrated by the flotation process. Concentrated ore is then roasted, converting zinc and the impurity metals to their oxides. Heating the crude oxides with sodium chloride and coal converts germanium and other impurity metal oxides into their volatile chlorides. The chloride vapors are condensed and germanium chloride, $GeCl_4$, is separated from the condensate by fractional distillation.

Germanium also is recovered from coal that contains this metal at trace concentrations. Coal ash and fine dusts are mixed with sodium carbonate, copper oxide, calcium oxide, and coal dust, and smelted. The crude oxide products are converted to their volatile chlorides. Germanium chloride is isolated from the condensate products by fractional distillation.

High purity (99.9999%) germanium may be produced by fractional distillation of the chloride in the presence of hydrochloric acid and chlorine in quartz stills, followed by hydrolysis of the purified chloride with double distilled water to produce germanium oxide, GeO_2. The oxide is reduced with hydrogen at 1,000°C. Exceedingly high purity germanium for semiconductor applications may be obtained from the high purity grade material by the zone refining process. Impurities present in germanium are more soluble in its melt than the solid metal. Thus, repeated passes of a molten zone along the impure ingot of germanium effectively removes trace impurities from the solid metal ingot.

Doping of the metal for its solid state electronic use may be carried out either by adding trace amounts of doping agents into the melts before a single crystal is grown from the melt or into the prepared single crystal by solid state diffusion. Single crystals up to a few inches in diameter may be prepared from the melt by the Czochralski technique, which involves contacting the melt with a seed crystal under an inert atmosphere and controlled conditions of temperature and seeding.

Reactions

The chemical properties of germanium fall between those of silicon and tin. It forms both the divalent and tetravalent compounds, the oxidation state +4 being more stable than the +2 oxidation state. The metal is stable in air and water at ambient temperatures. However, it reacts with oxygen at elevated temperatures forming divalent and tetravalent oxides, GeO and GeO_2.

While no reaction occurs with dilute mineral acids, the compound is attacked by concentrated HNO_3 and H_2SO_4. Also, no reaction occurs with caustic alkalies.

When heated with carbon dioxide at 800°C, the divalent oxide is formed:

$$Ge + CO_2 \xrightarrow{800^\circ C} GeO + CO$$

The metal also reduces the tetravalent oxide to the divalent oxide upon heating at elevated temperatures:

$$Ge + GeO_2 \xrightarrow{850^\circ C} 2GeO$$

Heating with chlorine at elevated temperatures yields germanium tetrachloride:

$$Ge + 2Cl_2 \xrightarrow{\substack{elevated \\ temperature}} GeCl_4$$

Analysis

The metal or its compounds may be digested with nitric acid, diluted appropriately and analyzed by flame or furnace AA or ICP emission spectrophotometry. It may also be analyzed by various x-ray methods, as well as ICP-MS.

GERMANIUM(IV) CHLORIDE

[10038-98-9]
Formula: $GeCl_4$; MW 214.40
Synonym: germanium tetrachloride

Uses

Germanium(IV) chloride is used in the preparation of many germanium compounds.

Physical Properties

Colorless liquid; density 1.879 g/cm³ at 20°C and 1.844 g/cm³ at 30°C; refractive index 1.464; boils at 86.5°C; solidifies at –49.5°C; decomposes in water; soluble in alcohol, ether, benzene, chloroform and carbon tetrachloride; insoluble in concentrated hydrochloric and sulfuric acids.

Thermochemical Properties

$\Delta H_f°$	–127.1 kcal/mol
$\Delta G_f°$	–110.6 kcal/mol
S°	58.7 cal/degree mol

Preparation

Germanium(IV) chloride is prepared by reacting germanium metal with chlorine; or by treating germanium oxide, GeO_2, with hydrochloric acid:

$$Ge + 2Cl_2 \rightarrow GeCl_4$$

$$GeO_2 + 4HCl \rightarrow GeCl_4 + 2H_2O$$

Germanium(IV) chloride often is obtained as a byproduct of germanium metal production. The process involves heating germanium oxide, GeO_2, with sodium chloride and coal. The vapors of germanium(IV) chloride and other volatile chlorides formed from the impurity metals are condensed. The product is isolated by fractional distillation. Further purification may be achieved by fractional distillation in 8*N* HCl and chlorine, or in the presence of other oxidizing agents in quartz stills.

Germanium(IV) chloride also is obtained by chlorination of germanium(II) chloride at ambient temperature. The reaction is rapid.

$$GeCl_2 + Cl_2 \rightarrow GeCl_4$$

Reactions

Germanium(IV) chloride reacts with water, hydrolyzing to germanium oxide and hydrochloric acid:

$$GeCl_4 + 2H_2O \rightarrow GeO_2 + 4HCl$$

The rate of hydrolysis is slower than the corresponding silicon analog, with hydrolysis occurring only partially. When heated with hydrogen at 1,000°C in a quartz reactor, it is converted into germanium(I) chloride, condensing onto the wall of the reactor:

$$2GeCl_4 + 3H_2 \xrightarrow{1000^\circ C} 2GeCl + 6HCl$$

When vapors of $GeCl_4$ are passed over germanium at elevated temperatures, the product is germanium(II) chloride, $GeCl_2$:

$$GeCl_4 + Ge \xrightarrow{\substack{elevated \\ temperature}} 2GeCl_2$$

Reaction with lithium aluminum hydride in ether forms monogermane, GeH_4:

$$GeCl_4 + LiAlH_4 \xrightarrow{ether} GeH_4 + LiCl + AlCl_3$$

Reactions with antimony trifluoride, SbF_3 in the presence of antimony pentachloride, $SbCl_5$, form mixed halides of compositions: $GeCl_3F$, $GeCl_3F_2$, $GeCl_2F_2$, and $GeClF_3$.

Reactions with alcohols in the presence of an amine yield alkoxides:

$$GeCl_4 + 4CH_3OH + 4C_2H_5NH_2 \rightarrow Ge(OCH_3)_4 + 4C_2H_5N \cdot HCl$$

Germanium forms six coordinate adducts, such as $GeCl_4(L)_2$ with many neutral ligands.

Analysis

Elemental compositions: Ge 33.86%, Cl 66.14%. The compound may be digested with nitric acid, diluted with water, and the diluted acid extract may be analyzed for germanium by AA and ICP spectrophotometry (See Germanium). The compound may be dissolved in a suitable organic solvent and analyzed by GC/MS. It may be identified from its molecular ions 212 and 220.

Toxicity

Fumes of germanium(IV) chloride irritate eyes, nose, and mucous membranes.

GERMANIUM DIOXIDE

[1310-53-8]
Formula: GeO_2; MW 104.61.
Synonym: germanium(IV) oxide

Uses

Germanium dioxide has high refractive index and infrared transmission, for which it is used in industrial glasses. It also is used in preparation of high purity grade germanium.

Physical Properties

Germanium dioxide ccurs in two crystalline and one amorphous modifications: (1) a tetragonal rutile form, refractive index 2.05, density 6.24 g/cm^3 at 20°C. (2) white hexagonal quartz modification, refractive index 1.735, density 4.70 g/cm^3 at 18°C, and (3) a glassy amorphous form, refractive index 1.607, density 3.64 g/cm^3 at 20°C. The tetragonal form is practically insoluble in water, while the hexagonal and the amorphous modifications have low solubilities; 0.45 and 0.52% respectively, at 25°C. Aqueous solutions are acidic due to formation of metagermanic acid, H_2GeO_3. Hexagonal modification converts to a tetragonal crystal system when heated at 350°C in water under pressure. Both crystalline forms convert to a glass-like amorphous GeO_2 when heated at 1,100°C.

Thermochemical Properties

$\Delta H_f°$ (tetragonal)	–188.6 kcal/mol
$\Delta G_f°$ (tetragonal)	–124.6 kcal/mol
S° (tetragonal)	9.49 cal/degree mol
C_ρ (tetragonal)	12.45 cal/degree mol

Preparation

Germanium dioxide is prepared by heating germanium with oxygen at elevated temperatures, or by hydrolysis of germanium(IV) halides:

$$GeCl_4 + 2H_2O \rightarrow GeO_2 + 4HCl$$

It also is prepared by oxidation of germanium(II) sulfide:

$$GeS + 2O_2 \xrightarrow{\text{heat}} GeO_2 + SO_2$$

The product obtained in the above reactions is in the form of hexagonal modification of GeO_2.

Reactions

Germanium dioxide is reduced to germanium metal when heated with hydrogen at 1,000°C:

$$GeO_2 + 2H_2 \xrightarrow{1000^\circ C} Ge + 2H_2O$$

When heated with germanium, the dioxide is reduced to monoxide, GeO:

$$GeO_2 + Ge \xrightarrow{850^\circ C} 2GeO$$

Treatment with hydrochloric acid yields germanium(IV) chloride:

$$GeO_2 + 4HCl \rightarrow GeCl_4 + 2H_2O$$

In a strongly acidic solution, its reaction with hydrogen sulfide yields an amorphous modification of germanium(IV) sulfide, GeS_2.

Melting a mixture of germanium dioxide and metal oxides produces ortho- and metagermanates of the corresponding metals. Aqueous solutions of germanate react with molybdic and tungstic acids forming heteropoly acids of varying compositions.

Analysis

Elemental composition: Ge 69.41%, O 30.59%.

Germanium dioxide may be characterized by x-ray methods. Germanium metal may be analyzed in the acidified aqueous extract of the compound by AA, ICP, and other instrumental techniques (See Germanium).

GERMANIUM HYDRIDES

Germanium forms several tetravalent hydrides that have the general formula Ge_nH_{2n+2} similar to alkanes and silicon hydrides. The formulas and CAS Registry numbers of the three common hydrides are:

Name	**CAS No.**	**Formula**
Monogermane (the tetrahydride)	[7782-65-2]	GeH_4
Digermane	[13818-89-8]	Ge_2H_6
Trigermane	[14691-44-2]	Ge_3H_8

Monogermane is used to produce high purity germanium metal. It also is used as a doping substance for electronic components.

Physical Properties

Monogermane is a colorless gas; density 3.43 g/L at 0°C; liquefies at –90°C; solidifies at –165°C; insoluble in cold and hot waters; soluble in liquid ammonia and sodium oxychloride; slightly soluble in hot hydrochloric acid.

Digermane, Ge_2H_6 is a colorless volatile liquid; density 1.98 g/mL at –100°C; boils at 29°C; decomposes when heated at 215°C; solidifies at –109°C; decomposes in water; soluble in liquid ammonia.

Trigermane is a colorless liquid; density 2.2 g/mL at 30°C; solidifies at –105.6°C; boils at 110.5°C; insoluble in water; soluble in carbon tetrachloride.

Thermochemical Properties

$\Delta H_f°$ (GeH_4(g))	21.70 kcal/mol
$\Delta H_f°$ (Ge_2H_6(l))	32.82 kcal/mol
$\Delta H_f°$ (Ge_2H_6(g)	38.80 kcal/mol
$\Delta H_f°$ (Ge_3H_8(l))	46.30 kcal/mol
$\Delta H_f°$ (Ge_3H_8(g))	54.20 kcal/mol
$\Delta G_f°$ (GeH_4(g))	27.10 kcal/mol
S° (GeH_4(g))	51.87 cal/degree mol
C_ρ (GeH_4(g))	10.76 cal/degree mol

Preparation

Polygermanes may be prepared by the reaction of magnesium germanide, Mg_2Ge, with dilute hydrochloric acid in an atmosphere of hydrogen. Monogermane, GeH_4, may be prepared by various methods, such as: (1) Reduction of germanium tetrachloride, $GeCl_4$, with lithium aluminum hydride in ether, (2) Electrolysis of a solution of germanium oxide, GeO_2, in sulfuric acid using lead electrodes, and (3) Reaction of magnesium germanide and ammonium bromide, NH_4Br, in liquid ammonia.

Reactions

Germanium hydrides are less stable than the corresponding hydrides of carbon and silicon. Thermal decomposition produces germanium and hydrogen. Monogermane decomposes at 350°C, while digermane and trigermane decompose to their elements at 210° and 190°C, respectively, at 200 torr. At elevated temperatures the hydrides dissociate, depositing mirror-like germanium crystals on container surfaces. Heating with oxygen yields germanium oxide. GeO_2:

$$GeCl_4 + 2O_2 \xrightarrow{heat} GeO_2 + 2H_2O$$

Analysis

Germanium hydrides are decomposed by nitric acid, diluted with water, and analyzed for metalic Ge (See Germanium). Monogermane is identified by GC/MS.

Toxicity

Monogermane is moderately toxic. Inhalation causes irritation of the respiratory tract. Chronic exposure can induce kidney and liver damage.

GOLD

[7440-57-5]
Symbol Au; atomic number 79; atomic weight 196.97; a GroupIB (Group 11) coinage metal; electron configuration [Xe]$4f^{14}5d^{10}6s^1$; oxidation states +1 and +3, state +3 is common and more stable; naturally occurring stable isotope Au-196, several radioactive isotopes are known from mass 186 to 203; most long-lived radioisotope is Au-195 ($t_{1/2}$ 200 days).

History, Occurrence, and Uses

Gold has been known to mankind since ancient times, retaining an unique position among all metals and even precious stones in terms of its value, glamour, and allure for possession. Gold is widely distributed in nature but in very low concentrations. Mostly it occurs in native form as metal or alloyed with silver, containing small amounts of copper. A few gold compounds are also found in nature which are mostly the tellurides, such as sylvanite $(Au,Ag)Te_2$, petzite $(Au,Ag)_2Te$, and calaverite, $AuTe_2$. Gold also is found in pyrites and quartzes, as well as in many sands and gravels of riverbeds. Large deposits of gold have been detected on the ocean floor. The average concentration of gold in seawater is 4ng/L and its abundance in the earth's crust is 4µg/kg.

The most important uses of gold are in jewelry and as a monetary standard. The metal has been in use for jewelry, ornaments, and decorative items throughout civilization. Gold bullion and coins have been used as a medium of exchange all over the world. Other uses include electroplating or gold plating of electronic components, such as diodes, heat shields, plugs, and printed circuits, for infrared reflectivity and corrosion resistance. Other uses are in dentistry, brazing alloys, and photography. Certain salts of gold are used in medical treatment.

Physical Properties

Yellow metal; face centered cubic crystals; lattice constant, a at 25°C 4.0786Å; density 19.3 g/cm^3; hardness 2.5–3.0 (Mohs), 18.5 (Brinell); melts at 1,064°C; vaporizes at 2,856°C; electrical resistivity 2.051 microhm-cm at 0°C and 2.255 microhm-cm at 25°C; Young's modulus 11.2×10^6 psi at 20°C (static); Poisson's ratio 0.52; thermal neutron capture cross section 98.8 barns; insoluble in almost all single acids or hydroxide solutions; dissolves in aqua regia.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (g)	87.5 kcal/mol
$\Delta G_f°$ (g)	78.0 kcal/mol
S° (cry)	11.3 cal/degree mol
S° (g)	43.1 cal/degree mol
C_ρ (cry)	6.07 cal/degree mol
C_ρ (g)	4.97 cal/degree mol

ΔH_{fus}	15.22 kcal/mol
Coeff. linear expansion (at 100°C)	14.2×10^{-6}/°C
Thermal conductivity (at 0-100°C)	0.74 cal/cm^2/sec/°C

Production

Recovery of gold mostly involves the combination of several processes, including smelting, flotation, amalgamation and treatment with alkaline cyanide. The ore is crushed, ground, and washed. Quartz rocks that have much lower density than the gold are removed by hydraulic separation. The ground ore is then treated with an alkaline solution of sodium or calcium cyanide. The solution is made alkaline by adding lime. The cyanide concentration may range between 0.01 to 0.05%. Gold dissolves in the solution forming gold(II) cyanide, $Au(CN)_2$. The solution is filtered to remove solid matter, following which it is subjected to electrolysis. Alternatively, gold is recovered from cyanide solution by precipitation with zinc dust or aluminum.

Gold flakes trapped in the ground ore may be recovered by amalgamation. Mercury and water are added to the ore and the mixture is passed over mercury-coated copper plates. Gold forms an amalgam with mercury and the amalgam adheres to the copper plates. Amalgam is scrapped off the copper plates. Mercury is removed by distillation.

Gold obtained by the above method contains copper, silver and other impurity metals. These metals are removed by melting, oxidation, electrolysis or chemical treatment. One such chemical refining is the Miller process in which chlorine gas is bubbled through molten impure gold. Most impurity metals volatilize as chlorides. Silver converts to silver chloride which remains in molten state at this temperature and may be decanted out. This refining process may upgrade gold to 99.5% purity. Other chemical processes for refining scrap and bullion involve precipitation of gold using ferrous sulfate, sulfur dioxide or other reducing agents.

Electrolytic refining yields a higher level of purity, over 99.95%. In electrolytic refining, the electrolyte is gold chloride mixed with HCl (about 5-10% free acid). During melting and oxidation of impure gold, silver alloys with the gold. The gold-silver alloy serves as the anode in electrolysis. An AC current is superimposed on the DC current to prevent any silver chloride buildup on the anode. Gold is deposited on the cathode during electrolysis. Copper, palladium, and platinum dissolve in the electrolyte solution as chlorides. Other impurity metals remain with the silver chloride residue.

Reactions

Gold is relatively inert in comparison to the other two coinage metals of GroupIB; copper and silver. It also is chemically more inert than most other metals in the Periodic Table. It does not combine with oxygen, sulfur or selenium even at elevated temperatures. However, it reacts with tellurium in molten state forming gold telluride.

Gold reacts with chlorine, bromine and iodine at elevated temperatures forming the corresponding halides. Reaction with fluorine is very slow. In the presence of moisture, gold reacts with chlorine, bromine and iodine at ordinary temperatures.

Gold is not attacked by most mineral acids including cold or hot sulfuric acid, phosphoric acid, hydrochloric acid and nitric acid. It dissolves in aqua regia or hydrochloric acid-nitric acid mixtures forming chloroauric acid, $HAuCl_4$. The reaction does occur in hydrochloric-, hydrobromic- or hydriodic acid, in the presence of an oxidizing agent that would liberate nascent halogen, thus forming the corresponding gold halides.

Analysis

Gold may be identified by its physical properties. Trace quantities of gold may be analyzed by flame atomic absorption spectrophotometry (to 1 ppm) or by neutron activation analysis (to 1 ppb). The metal may be dissolved in aqua regia and the solution diluted appropriately prior to analysis. The most sensitive wavelength for this element is 242.8nm.

The following colorimetric analytical method may be applied: The metal is converted to its chloride by reaction with chlorine gas in the presence of moisture. Gold chloride so formed is reduced to colloidal gold by treatment with stannous chloride. Stannous chloride is oxidized to $H_2Sn(OH)_6$, which deposits on the colloidal gold particles producing a beautiful ruby red color. The absorbance may be measured at 380 nm by a spectrophotometer and the concentration then determined from a standard calibration curve. Other color forming reagents, such as rhodanine, rhodamine or malachite green may be used. The colored complex of gold that is formed is separated from impurities in the aqueous solution by an appropriate organic solvent, and the absorbance of the solution is measured at 380nm.

Titrimetric methods also measure gold in solution. Gold(III) may be reduced by excess hydroquinone which may be back titrated with a standard solution of cerium(IV) titrant. Gold(III) may also be determined by iodometric titration.

GOLD(I) CHLORIDE

[10294-29-8]
Formula: AuCl; MW 232.42
Synonyms: aurous chloride; gold monochloride

Physical Properties

Yellow orthorhombic crystals; density 7.6 g/cm^3; decomposes on heating at about 298°C; loses its stoichiometric composition at 170°C; very slightly soluble in cold water; decomposes in hot water; soluble in hydrochloric and hydrobromic acids, and alkali cyanide solutions.

Thermochemical Properties

$\Delta H_f°$	–8.4 kcal/mol

Preparation

Gold(I) chloride is prepared by thermal decomposition of gold trichloride:

$$AuCl_3 \xrightarrow{heat} AuCl + Cl_2$$

Reactions

When heated at 290°C, gold(I) chloride decomposes to gold and chlorine gas:

$$2AuCl \xrightarrow{290^\circ C} 2Au + Cl_2$$

When heated with water, the compound decomposes to metallic gold and gold trichloride:

$$3AuCl \xrightarrow[]{\substack{heat \\ water}} 2\ Au + AuCl_3$$

Reaction with potassium bromide yields potassium auric bromide and potassium chloride with separation of metallic gold:

$$3AuCl + 4KBr \rightarrow KAuBr_4 + 2Au + 3KCl$$

Analysis

Elemental composition: Au 84.76%, Cl 15.24%. Gold(I) chloride is digested in hydrochloric-nitric acid mixture and the acid extract may be diluted and analyzed for gold (see Gold).

GOLD(III) CHLORIDE

[13453-07-1]
Formula: $AuCl_3$; MW 303.33; exists as a dimer, Au_2Cl_6 in solid and vapor state; forms a dihydrate, $AuCl_3 \cdot 2H_2O$
Synonyms: gold trichloride; auric chloride.

Physical Properties

Red monoclinic crystals; deliquesces; density 4.7 g/cm³; sublimes at 180°C (760 torr); highly soluble in water; soluble in alcohol and ether; slightly soluble in liquid ammonia.

Thermochemical Properties

$\Delta H_f°$ ($AuCl_3$)	–28.1 kcal/mol
$\Delta H_f°$ ($AuCl_3 \cdot 2H_2O$)	–170.9 kcal/mol

Preparation

Gold(III) chloride may be produced by the combination of metallic gold with chlorine gas at elevated temperatures:

$$2Au + 3Cl_2 \xrightarrow[\text{temperature}]{\text{elevated}} 2AuCl_3$$

It may be prepared in the laboratory by the reaction of iodine monochloride with metallic gold:

$$2Au + 6ICl \rightarrow 2AuCl_3 + 3I_2$$

The compound should be stored tightly closed and protected from light.

Reactions

When heated at 254°C, gold(III) chloride decomposes to gold(I) chloride and chlorine.

Passing hydrogen sulfide into an ether solution of the compound yields gold(III) sulfide, Au_2S_3.

A similar reaction occurs when alcoholic solutions of gold(III) chloride and hydrogen selenide are mixed, producing gold(III) selenide, Au_2Se_3, a black amorphous solid.

Gold(III) chloride may be reduced readily to metallic gold by common reducing agents. Thus, reduction with stannous chloride in dilute aqueous medium yields colloidal gold in which the atom carries a negative charge. "Cassius purple" is produced from the oxidation of tin to form $H_2Sn(OH)_6$, which protects colloidal gold from coagulation, imparting ruby red color to the solution.

Gold(III) chloride reacts with ammonia forming a gold(III)-nitrogen derivative, an explosive product, known as, "fulminate of gold".

Reaction with Grignard reagent, RMgX in ether yields dialkyl gold(III) chloride, R_2AuCl_3, which may be converted readily to other dialkyl gold(III) complexes by replacement of the chloride anion by a donor ligand.

Analysis

Elemental composition: Au 64.94%, Cl 35.06%. The aqueous solution may be analyzed for gold by AA spectrophotometry (see Gold). Chloride ion may be determined by chloride ion-selective electrode or ion chromatography. The solution must be diluted sufficiently for these measurements. Colorimetric methods are not suitable because the solution itself is colored.

GOLD CHLOROHYDRIC ACID

[16903-35-8]
Formula: $HAuCl_4$; MW 339.81; exists as tetrahydrate, $HAuCl_4 \cdot 4H_2O$; MW 411.85 Synonyms: chloroauric acid; aurochlorohydric acid; hydrochloroauric acid; gold trichloride acid; hydrogen tetrachloroaurate(III).

Uses

Gold chlorohydric acid is used for electroplating of gold; in porcelains and ruby glasses; and in photography.

Physical Properties

Tetrahydrate is golden yellow monoclinic crystals; hygroscopic; density 3.9 g/cm^3; decomposes on strong heating; very soluble in water and alcohol; soluble in ether.

Preparation

Gold chlorohydric acid is prepared by treating gold with hydrochloric acid in the presence of chlorine:

$$2Au + 2HCl + 3Cl_2 \rightarrow 2HAuCl_4$$

Toxicity

Moderately toxic by ingestion. Skin contact can cause blisters.

GOLD(I) CYANIDE

[506-65-0]
Formula: AuCN; MW 222.98
Synonyms: gold monocyanide; aurus cyanide

Physical Properties

Yellow hexagonal crystals; odorless; density 7.14 g/cm^3; decomposes slowly in the presence of moisture or decomposes on heating; insoluble in water, alcohol and ether; also insoluble in dilute acids; soluble in aqueous solutions of potassium-, or sodium cyanide, ammonia, and aqua regia.

Preparation

Gold(I) cyanide may be prepared by boiling sodium aurus cyanide, Na[Au(CN)2] with hydrochloric acid:

$$Na[Au(CN)_2] + HCl \xrightarrow{boiling} AuCN + HCN + NaCl$$

The complex cyanide, $Na[Au(CN)_2]$ is made by dissolving gold in a dilute solution of sodium cyanide in the presence of air; or by dissolution of a gold anode in a solution of sodium cyanide during electrolysis. The solution is evaporated to separate the complex, $Na[Au(CN)_2]$, which is purified by recrystallization from water. Potassium cyanide may be used instead of sodium cyanide to prepare gold(I) cyanide.

Analysis

Elemental composition: Au 88.34%, C 5.38%, N 6.28%. The compound may be digested in nitric acid, diluted with water and the solution analyzed for gold (see Gold).

GOLD(III) FLUORIDE

[14720-21-9]
Formula: AuF_3; MW 253.96; fluoride bridge structure consisting of AuF_4 units.
Synonyms: gold trifluoride; auric fluoride

Physical Properties

Orange-yellow hexagonal crystal; density 6.75 g/cm^3; sublimes at 300°C; decomposes at 500°C.

Thermochemical Properties

$\Delta H_f°$	–86.9 kcal/mol

Preparation

Gold(III) fluoride is prepared by fluorination of gold(III) chloride, $AuCl_3$ (or Au_2Cl_6), at 300°C. Either fluorine gas or hydrogen fluoride may be used as a fluorinating agent.

Analysis

Elemental composition: Au 77.56%, F 22.44%. Gold(III) fluoride may be characterized by x-ray techniques. The concentration of gold may be determined by AA and other instrumental methods following digestion in aqua regia and appropriate dilution.

GOLD(III) HYDROXIDE

[1303-52-2]
Formula: $Au(OH)_3$; MW 247.99
Synonyms: gold trihydroxide; auric hydroxide.

Uses

Gold(III) hydroxide is used for decorating ceramics, porcelains and glasses. It also is used in gold plating solutions.

Physical Properties

Brown powder; decomposes at 100°C; insoluble in water; soluble in acid.

Preparation

Gold(III) hydroxide is precipitated by mixing aqueous solutions of potassium auric chloride and sodium carbonate:

$$2KAuCl_4 + 3Na_2CO_3 + 3H_2O \rightarrow 2Au(OH)_3 + 6NaCl + 2KCl + 3CO_2$$

The product usually contains about three molecules of water of crystallization. It may alternatively be prepared by adding caustic soda solution to sodium auric cyanide:

$$NaAu(CN)_4 + 3NaOH \rightarrow Au(OH)_3 + 4NaCN$$

Reactions

Heating the hydroxide at about 140°C yields gold(III) oxide which on further heating decomposes to metallic gold and oxygen:

$$Au(OH)_3 \xrightarrow{100^\circ C} Au(O)OH + H_2O$$

$$2Au(O)OH \xrightarrow{140^\circ C} Au_2O_3 + H_2O$$

$$2Au\ 2O_3 \xrightarrow{160^\circ C} 4Au + 3O_2$$

It also decomposes to metallic gold on exposure to sunlight.

Reaction with concentrated hydrochloric acid yields gold(III) chloride:

$$Au(OH)_3 + 3HCl \rightarrow AuCl_3 + 3H_2O$$

Reaction with ammonia forms gold fulminate, which explodes when dry.

Analysis

Elemental composition: Au 79.44%, H 1.22%, O 19.35%. The hydrated salt containing three water molecules has 65% gold. The compound may be acid digested, diluted appropriately, and analyzed for gold by various instrumental methods (see Gold).

GOLD(III) OXIDE

[1303-58-8]
Formula: Au_2O_3; MW 441.93
Synonyms: auric oxide; gold trioxide; gold oxide; gold sesquioxide

Physical Properties

Brown powder; decomposes slowly on exposure to sunlight or by heating at 150°C; begins to release oxygen at 110°C; fully decomposes to metallic gold at 250°C; insoluble in water; soluble in hydrochloric and concentrated nitric acids; also soluble in aqueous solutions of sodium- or potassium cyanide.

Preparation

Gold(III) oxide is prepared by heating gold(III) hydroxide, $Au(OH)_3$ at 130 to 140°C:

$$2Au(OH)_3 \xrightarrow{130\text{–}140^\circ C} Au_2O_3 + 3H_2O$$

Analysis

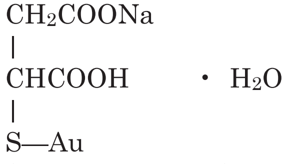
Elemental composition: Au 89.15%, O 10.86%. Gold(III) oxide is acid digested, the acid extract diluted appropriately with water and analyzed for gold by atomic absorption spectrophotometry or other instrumental techniques (see Gold).

GOLD(I) SODIUM THIOMALATE

[12244-57-4]

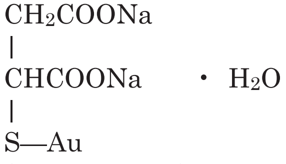
Formula: Gold(I) sodium thiomalate is a mixture of monosodium- and disodium-salts of gold thiomalate; the respective molecular formulas being $C_4H_4AuNaO_4S$ (monosodium salt) and $C_4H_3AuNa_2O_4S$ (disodium salt); a tetrameric structure with S—Au—S linear units.

Structure:



$$\begin{array}{l} CH_2COONa \\ | \\ CHCOOH \qquad \cdot\ H_2O \\ | \\ S\text{—}Au \end{array}$$

(monosodium salt)



$$\begin{array}{l} CH_2COONa \\ | \\ CHCOONa \qquad \cdot\ H_2O \\ | \\ S\text{—}Au \end{array}$$

(disodium salt)

Synonyms: sodium aurothiomalate; mercaptobutanedioic acid monogold (1+) sodium salt; Myochrysine; Mycocrisin; Shiosol

Uses

The compound is a drug for the treatment of rheumatoid arthritis. The mode of transport of this drug in the body involves the exchange of thiomalate ligands *in vivo* and the binding of Au(I) to –SH and S—S units of proteins, such as blood serum albumin.

Physical Properties

White to yellowish white powder; odorless; metallic taste; highly soluble in water; practically insoluble in ethanol and ether.

Preparation

Gold(I) thiomalate is prepared by reacting sodium thiomalate with gold(I) halide. It is stored in the dark and otherwise protected from light.

HAFNIUM

[7440-58-6]
Symbol: Hf; atomic number 72; atomic weight 178.49; a Group IV B (Group 4) transition metal element; atomic radius 1.442Å; electron configuration $[Xe]4f^{14}5d^26s^2$; common valence +4, also exhibits oxidation states +2 and +3; most abundant natural isotope Hf-180; isotopes and their natural abundances: Hf-176 (5.21%), Hf-177 (18.56%), Hf-178 (27.10%), Hf-179 (13.75%), Hf-180 (35.22%), artificial isotopes 157, 158, 168, 173, 175, 181–183.

History, Occurrence, and Uses

Hafnium was discovered in 1922 by Coster and deHevesy. They named it for Hafnia, the Latin word for Copenhagen. It is found in all zirconium ores, such as zircon, ($ZrSiO_4$) and baddeleyite (ZrO_2). It occurs in the earth's crust at about 3 mg/kg. Its average concentration in sea water is 7 ng/L.

Hafnium is used in control rods for nuclear reactors. It has high resistance to radiation and also very high corrosion resistance. Another major application is in alloys with other refractory metals, such as, tungsten, niobium and tantalum.

Physical Properties

Occurs as a close-packed hexagonal alpha-form and a body-centered cubic beta modification; melting point 2,233°C; vaporizes at 4,602°C; electrical resistivity 35.5 microhm-cm at 20°C; magnetic susceptibility 0.42×10^{-6} emu/g at 25°C; thermal neutron absorption cross section 105 barns/atom; work function 3.5 eV; modulus of elasticity 20×10^6 psi; tensile strength 58,000 psi at 25°C; insoluble in water, dilute mineral acids and nitric acid at all concentrations; soluble in hydrofluoric acid, concentrated sulfuric acid and aqua regia.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (g)	148.0 kcal/mo
$\Delta G_f°$ (cry)	0.0
$\Delta G_f°$ (g)	137.8 kcal/mol
S° (cry)	10.41 cal/degree mol
S° (g)	44.64 cal/degree mol
C_ρ (cry)	6.15 cal/degree mol
C_ρ (g)	4.97 cal/degree mol
H_{fus}	6.5 kcal/mol
H_{vap}	72.0 kcal/mol
Coeff. linear expansion	$5.9 \times 10^{-6/}$°C
Thermal conductivity (at 50°C)	0.0533 cal/sec/cm/°C

Production

Hafnium is obtained commercially from mineral zircon, which is zirconium orthosilicate [14940-68-2]. Zircon usually contains hafnium oxide, HfO_2, in an amount that ranges between 1 to 2%. Zircon sand is separated from heavy mineral fractions from alluvial deposits by various electrostatic and magnetic separation processes. The sand is then ground and heated with caustic soda at 600°C or with soda ash at 1,000°C, or fused with lime at elevated temperatures to separate silicates. Alternatively, zircon may be decomposed by heating with chlorine in the presence of coke at 1,100°C. In the caustic fusion process, pulverized fusion cake is washed with water to remove water-soluble sodium silicate and unreacted caustic soda, leaving behind insoluble hydrous zirconium oxide. Hydrous zirconium oxide is soluble in most acids. It is dissolved in hydrochloric acid and filtered to remove unreacted ore and silica. When the chlorination process is applied, the products are zirconium tetrachloride, hafnium tetrachloride, and silicon tetrachloride. Silicon tetrachloride is more volatile than the other two chlorides and, therefore, zirconium tetrachloride and hafnium tetrachloride can be removed from silicon tetrachloride by condensing under controlled heating. The condensed tetrachlorides are dissolved in water and filtered to remove insoluble matter.

Aqueous extracts from caustic fusion or chlorination now contain zirconium and hafnium chlorides. Separation of these metals is carried out by countercurrent liquid-liquid extraction using methyl isobutyl ketone (MIBK). The mixed chlorides are treated with an aqueous solution of ammonium thiocyanate. Oxychlorides of both the metals are formed which complex with thiocyanate ions. Hafnium oxychloride, $HfOCl_2$ is extracted into MIBK phase, leaving $ZrOCl_2$ in aqueous phase. Small amounts of zirconium (~2%) that are extracted with hafnium into the MIBK phase are stripped with HCl. Hafnium is converted to hafnium sulfate by treatment with H_2SO_4 and removed from the organic phase. Hafnium sulfate is treated with NH_4OH to convert it to hafnium hydroxide, $Hf(OH)_4$. The hydroxide is heated in a kiln at 650°C to yield oxide, HfO_2. The oxide is palletized with carbon and chlorinated to the tetrachloride, $HfCl_4$. The $HfCl_4$ is sublimed and purified by passing vapors through a salt bath consisting of NaCl 10%, KCl 10%, and $HfCl_4$ 80%, at 370°C. This removes aluminum, iron and other metal impurities.

Purified $HfCl_4$ is sublimed and reduced with magnesium by passing the vapors through molten magnesium heated in an electric furnace:

$$HfCl_4 + 2Mg \rightarrow Hf + 2MgCl_4$$

The product magnesium tetrachloride and any unreacted magnesium are removed from hafnium sponge produced above by distillation under vacuum. Sodium may be used instead of magnesium in the reduction reaction. Hafnium sponge may be melted in an electric furnace for further refining and the molten material may be electrolyzed to obtain ductile metal. Highly pure metal also can be obtained by reaction with iodine vapor at 600°C and the vapor of the product HfI_4 is decomposed on hafnium wire filament at 1,600°C into the metal and iodine vapor.

Reactions

The chemical properties of hafnium are very much similar to those of zirconium. In aqueous solutions, the metal exists in tetravalent state. The electrode potential for the reaction Hf→ $Hf^{4+} + 4e^-$ is –1.70V. The metal in bulk form does not react with most reagents at ordinary temperatures. However, the powdered metal or hafnium sponge may readily burn in air after ignited with a spark. When heated at 360°C under water pressure, the metal is oxidized to hafnium oxide, forming a thin, protective, surface oxide layer. A similar surface hafnium oxide layer forms in nitric acid, which protects the metal from acid attack.

Reaction with hydrofluoric acid at ordinary temperatures yields hafnium tetrafluoride, HfF_4.

In finely divided form, hafnium is pyrophoric, igniting in air spontaneously. However, bulk metal reacts slowly in oxygen or air above 400°C. The rate of oxidation increases with temperature. The product is hafnium dioxide, HfO_2. It combines with nitrogen, carbon, boron, sulfur and silicon at very high temperatures to form hafnium nitride HfN, hafnium boride HfB, hafnium sulfide $HfSi_2$, respectively. Nitride formation occurs at 900°C.

Reaction with hydrogen occurs around 700°C. Hafnium absorbs rapidly, forming a hydride which probably has a composition $HfH_{1.86.}$

Hafnium metal reacts very slowly in concentrated sulfuric acid at ordinary temperatures. At acid concentration above 70% and under boiling conditions, sulfuric acid readily attacks the metal.

Analysis

Hafnium may be measured by atomic absorption and emission spectroscopy, x-ray fluorescence, ICP-MS methods, and neutron activation. Such instrument methods are faster than wet methods and can measure the metal at trace levels.

HAFNIUM DIOXIDE

[12055-23-1]
Formula: HfO_2; MW 210.49
Synonym: hafnium(IV) oxide; hafnia

Uses

Hafnium dioxide is a high temperature refractory material. It is used for control rods in nuclear reactors. It has high stability and high thermal neutron absorption values. It also is used in special optical glasses and glazes.

Physical Properties

White crystalline solid, when heated at 1,500°C, it transforms into a tetragonal modification with shrinkage; tetragonal form converts to a cubic polymorph with fluorite structure when heated at 2,700°C; density 9.68 g/cm^3; melts at 2,774°C; insoluble in water; dissolves slowly in hydrofluoric acid at ordinary temperatures.

Preparation

Hafnium dioxide may be prepared by heating the metal with air or oxygen at elevated temperatures (above 400°C). Also, the oxide can be obtained by igniting hafnium salts, such as hydroxide, oxalate, sulfate, nitride, carbide, boride or tetrachloride in air. Hafnium carbide converts to dioxide when heated with oxygen at 500°C. The commercial products generally contain about 95-97% hafnium dioxide mixed with small amount of zirconium oxide. The compound can be prepared at 99.9% purity.

Reactions

Hafnium dioxide reacts with chlorine in the presence of carbon at elevated temperatures to yield hafnium tetrachloride, $HfCl_4$. When ammonium hydroxide solution is added to an acid solution of hafnium dioxide, the hydrous oxide, $HfO_2 \cdot xH_2O$ precipitates.

When heated with concentrated sulfuric acid, the product is hafnium sulfate, $Hf(SO_4)_2$.

Reaction with carbon at 1,500°C produces hafnium carbide, HfC.

Reaction with sodium fluorosilicate, Na_2SiF_6 at elevated temperatures yields sodium fluorohafnate, Na_2HfF_6.

Analysis

Elemental composition: Hf 84.80%, O 15.20%. Hafnium may be analyzed in aqueous solution following digestion with hydrofluoric acid–nitric acid, or with aqua regia. The dioxide may be characterized nondestructively by x-ray methods.

HAFNIUM TETRACHLORIDE

[13499-05-3]
Formula: $HfCl_4$; MW 320.30; tetrahedral and mononuclear structure in gas phase, halide bridging polymeric structure in solid phase.
Synonym: hafnium(IV) chloride

Uses

Hafnium tetrachloride is an important intermediate in production of hafnium metal. It also is used to prepare many hafnium compounds.

Physical Properties

White monoclinic crystal; sublimes at 317°C; melts at 432°C at 33 atm (triple point); critical temperature 452.5°C; critical pressure 53.49 atm; critical volume 314 cm^3/mol; hydrolyzes in water.

Thermochemical Properties

$\Delta H_f°$ (cry)	–236.7 kcal/mol
$\Delta H_f°$ (g)	–211.4 kcal/mol
$\Delta G_f°$ (cry)	–215.4 kcal/mol
S° (cry)	45.60 cal/degree mol
C_ρ (cry)	28.80 cal/degree mol

Preparation

Hafnium tetrachloride can be prepared (i) by chlorination of hafnium dioxide in the presence of carbon:

$$HfO_2 + 2Cl_2 + C \rightarrow HfCl_4 + 2CO$$

It also may be prepared by several other methods, such as (ii) reaction of carbon tetrachloride with hafnium dioxide above 450°C; (iii) heating a mixture of hafnium dioxide and carbon above 700°C; and (iv) reaction of chlorine with hafnium at elevated temperatures.

Reactions

Hafnium tetrachloride reacts with water at room temperature, forming hafnium oxide chloride, $HfOCl_2$, and hydrochloric acid:

$$HfCl_4 + 9H_2O \rightarrow HfOCl_2 \cdot 8H_2O + 2HCl$$

When heated with hafnium metal, the tetrachloride forms low-valence chlorides of hafnium, the dichloride and trichloride, $HfCl_2$ and $HfCl_3$.

At elevated temperatures and in vapor phase, the tetrachloride reacts with air or steam forming finely divided hafnium dioxide, HfO_2. When heated with boron trichloride and hydrogen to very high temperatures (above 2,000°C) hafnium diboride, HfB_2, a gray crystalline solid, forms.

Reaction with methane at 2,100°C produces hafnium carbide, a dark-gray, brittle solid, which is not a true stoichiometric compound. It probably is a homogeneous mixture in which carbon impregnates interstitial sites in the face-centered cubic lattice of hafnium.

Hafnium tetrachloride combines with molten sodium chloride, potassium chloride, or other alkali halides to form addition products such as $2NaCl \cdot HfCl_4$, which decompose at higher temperatures.

Hafnium tetrachloride forms many octahedral complexes of structure $HfCl_4L_2$ with neutral donors. For example, with tetrahydrofuran, it forms $HfCl_4(THF)_2$. Mononuclear and dinuclear hafnium chloride ions have been reported, produced by reaction with triphenylchloromethane, CPh_3Cl (Pampaloni, G. O. 1996. *J. Organomet. Chem.* 518, 189).

$$HfCl_4 + Cl^- \rightarrow HfCl_5^-$$

$$HfCl_5^- + THF \rightarrow [HfCl_5(THF)]^-$$

$$2HfCl_5^- \xrightarrow{CH_2Cl_2} [Hf_2Cl_{10}]^{2-}$$

Analysis

Elemental composition: Hf 55.73%, Cl 44.27% The acid extract of hafnium tetrachloride may be analyzed for hafnium by AA or other instrumental methods (See Hafnium).

HAFNIUM TETRAFLUORIDE

[13709-52-9]
Formula: HfF_4; MW 254.48
Synonym: hafnium(IV) fluoride

Physical Properties

White monoclinic crystals; refractive index 1.56; density 7.1 g/cm^3; sublimes at 970°C.

Thermochemical Properties

$\Delta H_f°$	–461.4 kcal/mol
$\Delta G_f°$	–437.5 kcal/mol
S°	27.0 cal/degree mol

Preparation

Hafnium tetrafluoride may be prepared by passing anhydrous hydrogen fluoride over hafnium tetrachloride at 300°C:

$$HfCl_4 + 4HF \xrightarrow{300^\circ C} HfF_4 + HCl$$

Another method of preparation involves thermal decomposition of ammonium fluorohafnate, $(NH_4)_2\ HfF_6$ [16925-24-9] in the absence of air:

$$(NH_4)_2\ HfF_6 \xrightarrow{heat} HfF_4 + 2NH_3 + 2HF$$

Also, HfF_4 can be prepared by treating metallic hafnium with 40% aqueous HF. The monohydrate formed may be heated at 350°C for several days under a flow of fluorine and nitrogen to yield anhydrous HfF_4.

$$Hf + 4HF\ (aq) \rightarrow HfF_4 \cdot H_2O + 2H_2$$

Analysis

Elemental composition: Hf 70.14%, F 29.86%. The compound is digested with aqua regia, the acid extract diluted and analyzed for Hf by various instrumental methods (see Hafnium). The compound may be characterized nondestructively by x-ray methods.

HELIUM

[7440-59-7]
Symbol: He; atomic number 2; atomic weight 4.0026; a Group 0 (Group 18) inert gas element; second lightest element; electron configuration 1s^2; valence 0; no chemical compound known; atomic radius 0.33Å; isotope He-3 is found in trace concentration in He-4; natural abundance of He-3 1.37 ppm; short-lived radioisotopes He-5, He-6, and He-8 are known.

History, Occurrence, and Uses

Janssen and Norman Lockyer in 1868 detected helium gas in the sun's atmosphere from their spectroscopic observation. The element was named helium by Lockyer and Frankland after Helios, the Greek word for sun. Ramsey found the element in 1895 in a sample of cleveite, a uranium mineral, after removing nitrogen and oxygen by treatment with sulfuric acid. Examination of the spectrum showed a yellow line for helium along with the spectral line for argon. Swedish chemists Cleve and Langlet also discovered helium in mineral uranium.

Helium occurs in great abundance in all stars in the universe. Except for hydrogen, it is the second most abundant element in the universe. Stars derive their energy from thermonuclear conversion of hydrogen into helium. Our sun is composed of 20% helium. However, in the earth's atmosphere helium is present only in trace amounts, 5.24 ppm. Its abundance in the earth's crust is only 8g/kg. In seawater, it occurrs at a concentration of 0.007μg/L.

The origin of helium on earth is attributed to alpha decay of uranium, thorium and other radioactive materials in the earth's crust. An alpha particle is a single charged helium ion, He^+, which readily converts into a helium atom in its passage through the earth's crust. Helium occurs in varying concentrations in many natural gas fields. In the United States, some natural gas deposits are found to contain helium at up to 8% by volume, mostly associated with nitrogen and hydrocarbon gases.

Helium has several important industrial applications in analytical chemistry, metallurgy, space research, medicine, and low-temperature supercooling. Liquid helium is used as a cryogenic fluid for supercooling and low temperature cooling baths. Helium-3 is used as a circulating medium in laboratory refrigerators to maintain constant temperatures below 3°K. Gaseous helium is used as a carrier for gas chromatographic analysis and as a purging gas for measuring volatile organics. It is used as a lifting gas in buoyant airships and in most types of balloons, such as weather-, toy-, kite-type-, and advertising balloons. Its lifting power is just slightly less that of hydrogen.

In metallurgy, helium is used to provide an inert atmosphere for growing crystals of high purity silicon and germanium for making transistors and diodes; as an inert shield for arc welding of metals; and to sparge dissolved gas from molten metals during purifications. In nuclear physics, helium ions or alpha particles serve as projectiles in bombarding heavy nuclei to produce energy or to obtain artificial radioisotopes. It also is used for heat transfer and coolant in nuclear reactors. Some other applications of helium include: detecting leaks in pressure containers and high-vacuum equipment; in lasers; in luminous signs for advertising; to fill space between lenses in optical instruments non-reactively; to provide an inert atmosphere for chemical reactions in the absence of air; to displace fuels and oxidizers from storage tanks in rockets or to introduce fuels into combustion chambers under helium pressure; as a non-nitrogen diluent for oxygen in SCUBA diving (so divers avoid the bends); and to mix with oxygen for treatment of respiratory diseases. Liquid helium is used in magnetic resonance imaging (MRI) equipment for diagnosis of cancer and other soft tissue diseases.

Physical Properties

Colorless and odorless gas; refractive index 1.000036 at 0°C and 1 atm; density of the gas at 0°C and 1 atm 0.1785 g/L; density of liquid helium at its boiling point 0.16 g/mL; liquefies at –268.93°C; solidifies at –272.2°C (at 26 atm) to a crystalline, transparent and almost invisible solid having a sharp melting point; cannot be solidified at the atmospheric pressure except by lowering temperatures; critical temperature –267.96°C; critical pressure 2.24 atm; critical volume 57cm^3/mol; very slightly soluble in water; solubility in water 0.0285 mg/L (calculated) at 25°C or 0.174 mL/L at NTP; insoluble in ethanol.

Liquid Helium

Liquid helium exists in two forms, Helium I and Helium II. The gas liquefies at 4.22°K at 1 atm to a colorless liquid known as Helium I. The refractive index of this liquid is 1.026, which is very close to that of the gas, thus making the surface of the liquid difficult to see. Most metal wires when placed in liquid helium or at Helium I temperature exhibit superconductivity; that is, frictionless flow of electrons—flow of electrical current without any resistance whatsoever.

When the temperature of Helium I is further lowered, usually by evacuation of the system to 3.83 torr, an unusual transition occurs at 2.174°K. At this temperature, a liquid called Helium II is obtained. This liquid has many unusual properties that are different from Helium I. While Helium I is a normal fluid exhibiting the boiling of a cryogenic fluid, Helium II is a "superfluid" that has an extremely high thermal conductivity, expands on cooling and can flow rapidly through channels 10^{-6} cm wide. While the viscosity of helium I is about 25.5 micropoise at 2.2°C, that of Helium II is less than 10.5 micropoise. (The viscosity of water at 20°C is about 10,000 micropoise.)

Thermochemical Properties

$\Delta H_f°$	0.0
S°	30.16 cal/degree mol
C_ρ	4.97 cal/degree mol

Production

Helium is produced mostly by extraction from natural gas. The process involves cooling the stream of natural gas at sufficient low temperatures and high pressures to liquefy and separate all hydrocarbons, nitrogen and other gases from gaseous helium. The 'crude' helium gas may be purified further by repeated liquefaction of methane, nitrogen and other impurities under pressure. Trace hydrocarbons may be removed by adsorption on activated charcoal at liquid nitrogen temperature. Water may be removed by drying over a dehydrating agent such as bauxite. Carbon dioxide may be removed by passing helium through a scrubbing solution containing monoethanolamine-ethylene glycol or similar substances. Trace hydrogen may be removed from helium by converting it into water by mixing with oxygen and passing the mix over a palladium catalyst. Final purification may be achieved by adsorbing remaining trace contaminants over activated charcoal at liquid nitrogen temperature.

Alternatively, helium may be separated from natural gas by diffusion through permeable barriers, such as high silica glass or semipermeable membranes. The gas is supplied commercially in steel cylinders or tanks. The United States is the largest producer of helium in the world.

HOLMIUM

[7440-60-0]
Symbol: Ho; atomic number 67; atomic weight 164.93; a lanthanide series rare earth element; electron configuration $[Xe]4f^{11}6s^2$; valence state +3; metallic radius (coordination number 12) 1.767Å; atomic volume 18.78 cc/mol; ionic radius Ho^{3+} 0.894Å; one naturally occurring isotope, Ho-165.

History, Occurrence, and Uses

Soret and Delafontaine identified holmium in 1878 by examination of its spectrum. The following year, Cleve separated its oxide from Marignac's erbia, a mixture of erbium, holmium and thulium oxides. He named this element Holmium, after his native town Holmia (Stockholm). The metal was produced in 1934 by Klemm and Bommer.

Holium occurs in rare-earth minerals, such as monazite, gadolinite, xenotime, euxenite, fergusonite, and bastnasite. Its concentration in monazite is about 0.05%. Its abundance in the earth's crust is 1.3mg/kg.

Currently, holmium metal does not have much commercial application. However, because of its unusual magnetic properties, it is being used in research studies to explore the magnetic and alloying behavior of metals.

Physical Properties

Soft, lustrous metal; silver-like appearance; close-packed hexagonal crystal system; density 8.78 g/cm³; paramagnetic; magnetic moment 11.2 Bohr magnetons; melts at 1,472°C; vaporizes at 2,694°C; electrical resistivity 195 microhm-cm at 25°C; Young's modulus 6.71×10^{11} dynes/cm²; Poisson's ratio 0.255; thermal neutron cross section 64 barns; insoluble in water; soluble in acids (with reactions).

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (g)	71.89 kcal/mol
$\Delta G_f°$ (g)	63.29 kcal/mol
S° (cry)	18.0 cal/degree mol
S° (g)	46.75 cal/degree mol
C_ρ (cry)	6.50 cal/degree mol
C_ρ (g)	4.97 cal/degree mol
ΔH_{fus}	2.81 kcal/mol
Thermal conductivity	0.106 cal/sec/cm/°C
Coeff. linear expansion (at 400°C)	9.5×10^{-6}/°C

Production

Holmium is obtained from monazite, bastnasite and other rare-earth minerals as a by-product during recovery of dysprosium, thulium and other rare-earth metals. The recovery steps in production of all lanthanide elements are very similar. These involve breaking up ores by treatment with hot concentrated sulfuric acid or by caustic fusion; separation of rare-earths by ion-exchange processes; conversion to halide salts; and reduction of the halide(s) to metal (See Dysprosium, Gadolinium and Erbium).

Bulk holmium metal is prepared by reduction of holmium chloride or fluoride by sodium, calcium, or magnesium in a tantalum crucible under argon atmosphere:

$$2H_0F_3 + 3Ca \xrightarrow[\text{argon}]{\text{elevated temperature}} 3Ca\ F^2 + 2H_0$$

Pure holmium metal is obtained by distillation of crude metal at 1,500°C.

Reactions

Holmium forms all its compounds in +3 valence state. The metal forms fluoride, hydroxide, phosphate, oxalate, and carbonate that are insoluble in water. Its water-soluble salts are chloride, bromide, iodide, acetate, nitrate and sulfate.

Reactions with acids yield corresponding salts. Evaporation of the solutions yield water-soluble salts. Treatment with hydrochloric acid followed by evaporation of the solution yields a hexahydrate, $HoCl_3 \cdot 6H_2O$.

When heated with ammonium iodide, it forms holmium iodide, HoI_3.

The bulk metal reacts with oxygen at high temperatures to yield Ho_2O_3. The reaction is slow even at high temperatures. The finely divided metal, however, burns in oxygen at ordinary temperatures, glowing white-hot. It combines with hydrogen at elevated temperatures forming hydride, HoH_3.

Analysis

Holmium may be measured in trace amounts by AA and ICP spectrophotometry, x-ray fluorescence, and neutron activation analysis.

HOLMIUM CHLORIDE

[10138-62-2]
Formula: $HoCl_3$; MW 271.29; also forms a hexahydrate, $HoCl_3 \cdot 6H_2O$, MW 379.38
Synonym: holmium trichloride

Uses

Holmium chloride is an intermediate for preparing holmium metal.

Physical Properties

Yellow monoclinic crystals; hygroscopic; density 3.7 g/cm^3; melts at 718°C; vaporizes at 1,500°C; readily dissolves in water.

Thermochemical Properties

$\Delta H_f°$(cry)	–240.3kcal/mol
$\Delta H_f°$ (g)	–168.0 kcal/mol
$\Delta H_f°$ (hexahydrate)	–687.9 kcal/mol
$\Delta G_f°$ (hexahydrate)	–588.0 kcal/mol
S° (hexahydrate)	97.08 cal/degree mol
S° (g)	40.1 cal/degree mol
C_ρ (cry)	21.0 cal/degree mol
C_ρ (hexahydrate)	83.0 cal/degree mol
ΔH_{fus}	7.0 kcal/mol
ΔH_{vap}	44.0 kcal/mol

Preparation

Holmium chloride is obtained from rare-earth minerals. Recovery steps are discussed above (see Holmium). The rare-earth mineral is cracked by acid attack by heating with hydrochloric acid. The water-soluble chloride salt is filtered and separated from insoluble residues. The hydrated chloride salt is heated at 350°C in a current of hydrogen chloride to yield anhydrous $HoCl_3$. Heating in air in the absence of hydrogen chloride yields holmium oxychloride, HoOCl. Holmium chloride may be purified by distillation or vacuum sublimation.

Holmium chloride also can be prepared by heating holmium oxide with ammonium chloride:

$$Ho_2O_3 + 6NH_4Cl \xrightarrow{heat} 2HoCl_3 + 6NH_3 + 3H_2O$$

HOLMIUM OXIDE

[12055-62-8]
Formula: Ho_2O_3; MW 377.86
Synonym: holmia; holmium sesquioxide

Occurrence and Uses

Holmium oxide occurs in nature, usually associated with small quantities of other rare-earth oxides. Commercial applications of this compound have not been explored fully. It is used in refractories and as a catalyst. Characteristic spectral emission lines of holmium oxide glass are used to calibrate spectrophotometers.

Physical Properties

Yellow cubic crystal; density 8.41 g.cm^3; melts at 2,415°C; insoluble in water; dissolves in acids (with reactions).

Thermochemical Properties

$\Delta H_f°°$	–449.5 kcal/mol
$\Delta G_f°$	–428.1 kcal/mol
S°	37.8 cal/degree mol
C_ρ	27.5 cal/degree mol

Preparation

Holmium oxide is prepared by thermal decomposition of carbonate, oxalate, hydroxide, nitrate, sulfate, or any oxo salt of holmium:

$$Ho_2(CO_3)_3 \xrightarrow{heat} Ho_2O_3 + 3CO_2$$

$$Ho_2(SO_4)_3 \xrightarrow{heat} Ho_2O_3 + 3SO_3$$

The oxide may be obtained by direct combination of elements at elevated temperatures. The element in massive form, however, reacts slowly at high temperatures.

HYDRAZOIC ACID

[7782-79-8]
Formula: HN_3; MW 43.03
Synonyms: azoimide; hydroazoic acid; hydrogen azide.

Physical Properties

Colorless, volatile liquid; pungent disagreeable odor; density 1.09 g/mL; solidifies at –80°C; boils at 37°C; highly soluble in water; soluble in alkalies, alcohol and ether; pK_a 4.6 at 25°C.

Preparation

Hydrazoic acid is prepared by reacting sulfuric acid with sodium azide:

$$H_2SO_4 + NaN_3 \rightarrow HN_3 + Na_2SO_4$$

or by treating hydrazine with nitrous acid:

$$N_2H_4 + HNO_2 \rightarrow HN_3 + 2H_2O$$

or by heating sodium amide with nitrous oxide:

$$NaNH_2 + N_2O \xrightarrow{heat} HN_3 + NaOH$$

Reactions

Hydrazoic acid reacts with mineral acids liberating nitrogen gas:

$$HN_3 + HCl \rightarrow NH_2Cl + N_2$$

Reactions with oxidizing agents yield nitrogen and other products. Reactions with reducing agents yield various products including triazene, H_3N_3, tetrazene, H_4N_4, and ammonia, depending on reaction conditions.

HYDRAZINE

[302-01-2]
Formula: N_2H_4; MW 32.05
Structure: $H_2N—NH_2$, the N—N—H bond angle 112° and the N—N bond length 0.145 nm, sp^3 hybridization, tetrahedral, lone pair of electrons on the vertice of tetrahedron; dipole moment ~1.85;
Synonyms: hydrazine anhydrous; diamine

History and Uses

Hydrazine was isolated first as a sulfate salt by Curtius in 1887. Earlier, in 1875, Fischer prepared and identified the organic derivatives of hydrazine. Raschig in 1906 prepared hydrazine by hypochlorite oxidation of ammonia.

Hydrazine and its derivatives have numerous commercial applications. It was used initially as rocket propellant. During World War II, it was used as a fuel for rocket-powered fighter planes. However, the most important applications of hydrazine and its derivatives at present are: as blowing agents; for insect control; in pharmaceuticals; in water treatment; and in fuel cells. Hydrazine derivatives release nitrogen on decomposition, producing foaming action in polymers to form pores or cells. A large number of hydrazine derivatives are used in agricultural applications as fungicides, herbicides, and pesticides for weed and pest control. A few hydrazide drugs, such as isoniazid [54-85-3] are used extensively for treating tuberculosis. Other applications of hydrazine include its use in fuel cells; and in wastewater treatment for removal of iron; iron removal from hot-water heating systems; reduction of red iron oxide rust into magnetite; and for removal of oxygen to protect against corrosion. It also is used in electrolytic plating of metals on glasses and as a reducing agent. Several hydrazine derivatives are used in azo dyes; as coupling agents in color photography; and in explosives and ammunition primers.

Physical Properties

Colorless, mobile, fuming liquid; ammoniacal odor; density 1.0045 g/mL at 25°C; refractive index 1.46044 at 22°C; solidifies at 2°C to a white crystalline solid; boils at 113.5°C; flash point 52°C; burns with a violet flame; vapor pressure 14.4 torr at 25°C; critical temperature 379.85°C; critical pressure 145 atm; surface tension 66.67 dyne/cm at 25°C; dielectric constant 51.7 at 25°C; viscosity 0.876 centipoise at 25°C; very soluble in water; forms an azeotrope with water at molar composition of 58.5% hydrazine: 41.5% water (71.48%: 28.52% by weight), the azeotrope with water boils at 120.5°C; forms hydrazine hydrate at 1:1 molar concentration in water; soluble in alcohols and other polar solvents; pKa 8.1 at 25°C.

Thermochemical Properties

$\Delta H_f°$ (l)	–12.10 kcal/mol
$\Delta H_f°$(g)	–22.80 kcal/mol
$\Delta G_f°$ (l)	–35.67 kcal/mol
$\Delta G_f°$ (g)	–38.07 kcal/mol
S° (l)	28.97 cal/degree mol
S° (g)	56.97 cal/degree mol
C_ρ (l)	23.63 cal/degree mol
C_ρ (g)	11.85 cal/degree mol
ΔH_{fus}	3.026 kcal/mol
ΔH_{vap}	10.82 kcal/mol
$\Delta H_{combust}$	–148.7 kcal/mol

Production

Hydrazine may be produced by several methods. The most common commercial process is the Raschig process, involving partial oxidation of ammonia or urea with hypochlorite. Other oxidizing agents, such as chlorine or hydrogen peroxide may be used instead of hypochlorite. The reaction steps are as follows.

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$$

$$NH_2Cl + NH_3 + NaOH \xrightarrow{heat} N_2H_4 + NaCl + H_2O$$

$$2NH_3 + NaOH \rightarrow N_2H_4 + NaCl + H_2O$$

While the first partial reaction is rapid, the second reaction is slow at ordinary temperatures and, therefore, requires heating above 120°C.

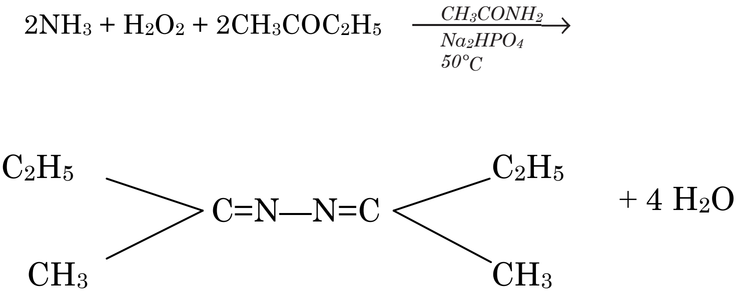
The chloramines formed in the above reaction may further react with the product hydrazine, decomposing the latter to nitrogen.

$$2NH_2Cl + N_2H_4 \rightarrow 2NH_4Cl + N_2$$

The above reaction is catalyzed by copper and other trace metal impurities and can be prevented by adding a suitable complexing agent. In a modification of the Raschig process, what is known as Olin-Raschig process, liquid chlorine feed is continuously absorbed in dilute NaOH solution forming sodium hypochlorite which, similar to the Raschig process, is made to react with excess ammonia. The reaction is rapid. Further addition of large, excess anhydrous ammonia under pressure raises the temperature to about 130°C. This prevents any decomposition of hydrazine by chloramines.

In Ketazine processes, hydrazine derivatives are obtained first. Ammonia is oxidized by chlorine or chloramines in the presence of aliphatic ketones. The products are hydrazones and isohydrazones. These are converted to ketazines with excess ketone. The ketazines or the intermediate hydrazine derivatives may be hydrolyzed to hydrazine after all the oxidizing reactants, such as Cl_2 , NaOCl, or NH_2Cl are consumed. Unlike hydrazine, ketazines do not readily oxidize, and, therefore, the product yield is higher in these processes.

Several other processes have been developed. Most of these are based on oxidation of ammonia, using different oxidizing agents. In one such process, ammonia is oxidized with hydrogen peroxide in the presence of methyl ethyl ketone, acetamide and disodium hydrogen phosphate at 50°C:



$$2NH_3 + H_2O_2 + 2CH_3COC_2H_5 \xrightarrow[Na_2HPO_4\ 50°C]{CH_3CONH_2} (C_2H_5)(CH_3)C{=}N{-}N{=}C(C_2H_5)(CH_3) + 4\,H_2O$$

Hydrazine also may be produced by oxidation of urea, NH_2CONH_2, instead of ammonia.

Reactions

Hydrazine exhibits basic properties because of its lone pair of electrons on each nitrogen atom. Many of its reactions are analogous to those of ammonia.

Anhydrous hydrazine undergoes self-ionization to a small extent, yielding hydrazinium, hydrazide, $N_2H_5^+$, and hydrazide, $N_2H_3^-$ species:

$$2N_2H_4 \rightarrow N_2H_5^+ + N_2H_3^-$$

The magnitude of K value for this self-ionization is in the order of 10^{-25}, which is greater than that for anhydrous ammonia ionizing to ammonium (NH^{4+}) and amide (NH_2^-) ions (K~ 10^{-33}). Anhydrous hydrazine thus forms salts with halide and other anions of the composition $N_2H_5^+ X^-$ which are acids. Similarly, metallic hydrazides, $M^+N_2H_3^-$, are bases in anhydrous hydrazine. Most hydrazine salts are unstable and are sensitive to heat and shock. Reaction with sodium metal yields sodium hydrazide, NaN_2H_3 [13598-47-5] with liberation of hydrogen:

$$2N_2H_4 + Na \rightarrow 2NaN_2H_3 + H_2$$

Reaction with sodium amide also yields the same compound with liberation of ammonia:

$$N_2H_4 + NaNH_2 \rightarrow NaN_2H_3 + NH_3$$

Hydrazide salts of alkaline earth metals, such as MgN_2H_2 and of aluminum, $Al(N_2H_3)_3$ are known and are less sensitive to heat and shock than are alkali metal hydrazides.

Reactions with alkali and alkaline earth metal hydrides also produce the same ionic metallic hydrazides:

$$NaH + N_2H_4 \rightarrow NaN_2H_3 + H_2$$

Many metal alkyls undergo similar reactions forming their metal hydrazides.

Hydrazine reacts with carbon dioxide forming carbazic acid (hydrazinecarboxylic acid) [471-31-8]:

$$N_2H_4 + CO_2 \rightarrow NH_2NHCOOH$$

Oxidation-reduction reactions are probably the most important reactions of hydrazine. The compound can reduce several classes of inorganic substances including the oxidizing agents, metals and hologens. Also, it can reduce a number of organic functional groups such as, carbonyl, nitro and nitrile groups.

Chromate, dichromate, permanganate, chlorate and hypochlorite and other oxidants are readily reduced by hydrazine; for example, removal of chromate from wastewater may be achieved fully by converting water-soluble chromate to insoluble precipitate of chromium hydroxide, $Cr(OH)_3$:

$$CrO_4^{2-} + N_2H_4 \rightarrow Cr(OH)_3 + N_2 + OH^-$$

Hydrazine reduces potassium iodate in hydrochloric acid forming iodine monochloride, a reaction of analytical importance:

$$N_2H_4 + KIO_3 + 2HCl \rightarrow KCl + ICl + N_2 + 3H_2O$$

Hydrazine reduces sodium hypochlorite forming products that depend on molar ratios of the reactants. When hydrazine is in excess, ammonia is one of the products; but when hypochlorite is in excess, no ammonia is formed:

$$2N_2H_4 + NaOCl \rightarrow N_2 + 2NH_3 + H_2O + NaCl$$

$$N_2H_4 + 2NaOCl \rightarrow N_2 + 2H_2O + 2NaCl$$

Hydrazine reacts with halogens forming hydrogen halides:

$$N_2H_4 + 2Cl_2 \rightarrow N_2 + 4HCl$$

$$N_2H_4 + 2I_2 \rightarrow N_2 + 4HI$$

Hydrazine reacts with chloramines to produce ammonium chloride while decomposing to nitrogen. The reaction is catalyzed by metal ions at trace concentrations:

$$N_2H_4 + 2NH_2Cl \rightarrow 2NH_4Cl + N_2$$

A reaction of commercial interest that is applied in many water treatment processes is for protection against corrosion. The reaction involves oxidation of iron to form magnetite that provides a protective coating on the metal surface:

$$3Fe + 4N_2H_4 + 4H_2O \rightarrow Fe_3O_4 + 8NH_3$$

Hydrazine reduces heavy metal oxides and their salts to free metals. These reactions are utilized for plating of metal films on plastics and glass:

$$2Ag_2O + N_2H_4 \rightarrow 4Ag + N_2 + 2H_2O$$

Hydrazine is a strong reducing agent. It reduces oxygen, forming nitrogen and water:

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

The reaction is highly exothermic ($H_{rxn} = -148.6$ kcal/mol) and is employed in rocket propellant engines and fuel cells.

An important reduction reaction is Wolff-Kishner reduction of carbonyl group on aldehydes and ketones to form hydrazone:

$$(CH_3)_2C{=}O + N_2H_4 \rightarrow (CH_3)_2C{=}NNH_2$$

In the presence of a base and upon heating, the hydrazone yields alkane (or alcohols depending on reaction conditions):

$$(CH_3)_2C{=}NNH_2 \xrightarrow[200°C]{NaOH} CH_3CH_2CH_3 + N_2$$

Diaziridines or isohydrazones may be obtained instead of hydrazones by varying the ratio of aldehyde or ketone to hydrazine.

Reduction of several classes of organics may be achieved using hydrazine and appropriate catalysts. It reduces nitro compounds to corresponding amines; e.g., nitrobenzene to aniline:

$$C_6H_5NO_2 \xrightarrow[Ni]{N_2H_4} C_6H_5NH_2$$

Nitro compounds in presence of carbonyl group are selectively reduced to amines in the presence of Raney nickel catalyst. Hydrazine reduces nitriles yielding hydrazones. Under controlled reaction conditions other functional groups, including nitroso and oxime, may be reduced. Many partially hydrogenated derivatives, such as azo-, hydrazo-, and azoxy compounds may be obtained by partial reduction with hydrazine. Reaction with chlorobenzene yields benzene.

Reaction with benzoic acid yields benzoyl hydrazide:

$$C_6H_5COOH + N_2H_4 \rightarrow C_6H_5CONHNH_2 + H_2O$$

The product hydrazide may be sulfonated and decomposed by heating with a base in ethylene glycol to yield benzaldehyde, C_6H_5CHO. Many aromatic aldehydes may be produced by similar routes. The hydrazone derivative of toluenesulfonic acid reacts with an aldehyde or a ketone in the presence of a base catalyst, such as sodium ethoxide, to yield the corresponding olefin (Bamford-Stevens reaction):

$$CH_3C_6H_5SO_2NHNH_2 + RCOCH_2R \rightarrow RC(=N—NH—SO_2C_6H_4CH_3)CH_2R$$

$$\xrightarrow{NaOEt} RCH{=}CHR$$

Reactions with sulfonyl chloride in the presence of ammonia yield sulfonic acid hydrazides:

$$RSO_2Cl + N_2H_4 \xrightarrow{NH_3} RSO_2NHNH_2 + NH_4Cl$$

Hydrazine reacts with carbon disulfide to yield dithiocarbazic acid [471-32-9]:

$$N_2H_4 + CS_2 \rightarrow NH_2NHCSSH$$

In the presence of an alkyl halide and potassium hydroxide, dithiocarbazate ester is obtained. The product is used in many organic syntheses:

$$N_2H_4 + CS_2 + KOH + C_2H_5Cl \rightarrow NH_2NHC(=S)SC_2H_5 + H_2O + KCl$$

Refluxing an aqueous solution of urea and hydrazine yields hydrazodicarboxamide, $H_2NC(=O)NHNHC(=O)NH_2$ [110-21-4], which on chlorination yields azodicarbonamide $H_2NC(=O)N{=}NC(=O)NH_2$, used as a blowing agent for polymers:

$$N_2H_4 + 2NH_2CONH_2 \rightarrow H_2NCONHNHCONH_2$$

Acetone cyanohydrin reacts with hydrazine forming a hydrazo derivative, $(CH_3)_2C(CN)NHNHC(CN)(CH_3)_2$ [6869-07-4], a precursor to azobis(isobutyronitrile), $(CH_3)_2C(CN)N{=}NC(CN)(CH_3)_2$, a blowing agent for PVC foam:

$$(CH_3)_2C(CN)OH + N_2H_4 \rightarrow (CH_3)_2C(CN)NH\text{-}NHC(CN)(CH_3)_2$$

Thermal decomposition of hydrazine can occur by several energetic routes. The most favorable one being:

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \qquad \Delta H = -37.5 \text{ kcal/mol}$$

Under controlled conditions, hydrazine may be decomposed thermally to nitrogen and hydrogen:

$$N_2H_4 \rightarrow N_2 + 2H_2 \qquad \Delta H = -22.8 \text{ kcal/mol}$$

Analysis

Hydrazine may be analyzed by various methods including GC-FID, GC-NPD, HPLC, GC/MS, polarography, colorimetry, and iodometric titrations. The iodometric method is simple and applicable to measure hydrazine quantitatively in water at all concentrations.

Hydrazine reduces iodine to hydrogen iodide. Thus, an excess of standard solution of iodine is added to a measured volume of aqueous hydrazine solution and the excess iodine is back titrated at pH 7.0 to 7.2 (buffered by sodium bicarbonate) against a standard solution of sodium thiosulfate using starch indicator.

Hydrazine solutions may be analyzed by various colorimetric methods. Low concentrations of hydrazine in aqueous samples at ppm level may be determined by treating the sample with an acidified solution of dimethylaminobenzaldehyde and the absorbance of color formed is measured at 485 nm with a spectrophotometer.

Hydrazine may be derivatized with salicylaldehyde to a hydrazone derivative, separated on a suitable HPLC column and determined by a UV detector. Aqueous samples may be directly injected into a polar GC column interfaced to an FID. Anhydrous hydrazine may be appropriately diluted in alcohol or ether and determined by GC/MS. The molecular ion for GC/MS determination by electron-impact ionization is 32.

Hazard

Hydrazine is a flammable liquid, and forms explosive mixtures with air in the range 4.7 to 99% hydrazine (by volume) in air. Violent reactions can occur when combined with oxidizing agents. Exposure to vapors or ingestion of the liquid can cause nausea, vomiting, and convulsion. Direct contact can cause eye damage. It also is a carcinogen and teratogen.

HYDRAZINE HYDRATE

[7803-57-8]
Formula: $N_2H_4 \cdot H_2O$; MW 50.06
Synonym: diamine hydrate

Uses

Hydrazine hydrate is used as a reducing agent in synthetic and analytical reactions and as a solvent for many inorganic compounds. It also is used with methanol as a propellant for rocket engines. Another application is catalytic decomposition of hydrogen peroxide.

Physical Properties

Colorless fuming liquid; faint odor; refractive index 1.4284; density 1.032 g/mL; boils at 119°C; solidifies at –51.7°C; miscible with water and alcohol; insoluble in chloroform, methylene chloride, and ether.

Preparation

Hydrazine hydrate is prepared by treating hydrazine sulfate, $N_2H_4 \cdot H_2SO_4$ with sodium hydroxide. The product is collected by distillation under nitrogen. It also is obtained as a by-product in the Bayer Ketazine process for producing hydrazine in which hydrazine solution is hydrolysed under pressure in a ketazine column.

Reactions

See Hydrazine.

Analysis

Elemental composition: H 12.09%, N 55.95%, O 31.96%. The compound may be identified from its physical properties. Its concentration can be determined by titration (See Hydrazine.)

Toxicity

Hydrazine hydrate is toxic by all routes of exposure. Toxic properties are similar to hydrazine (See Hydrazine.)

HYDRAZINE SULFATE

[10034-93-2]
Formula: $N_2H_4 \cdot H_2SO_4$; MW 130.125

Uses

Hydrazine sulfate is used as a reducing agent; in analytical chemistry for gravimetric measurement of nickel, cobalt, and other metals, and in peptide analysis; in the separation of polonium from tellurium; as an antioxidant in soldering flux for metals; in the preparation of hydrazine hydrate; and in many organic syntheses. It also is used as a fungicide.

Physical Properties

Colorless orthorhombic crystal; density 1.378 g/cm^3; melts at 254°C; sparingly soluble in cold water 1.64% at 0°C and 3.41% at 25°C; more soluble in hot water; practically insoluble in alcohol (0.04% at 25°C).

Preparation

Hydrazine sulfate may be synthesized from aqueous ammonia and sodium hypochlorite solution in a two-step process. In the first stage, aqueous solution of ammonia is boiled with a normal solution of sodium hypochlorite in the presence of 10% gelatin solution to yield hydrazine. In the second stage, the hydrazine solution is ice-cooled followed by slow addition of concentrated sulfuric acid (Adams, R., and B.K. Brown. 1964. In *Organic Synthesis, Collective Volume I*, ed. H. Gilman and A. H. Blatt, 2nd ed. pp 309-310, New York: John Wiley & Sons). The reaction steps are as follows:

$$2NH_3 + NaOCl \rightarrow NH_2NH_2 + H_2O + NaCl$$

$$NH_2NH_2 + H_2SO_4 \rightarrow NH_2NH_2 \cdot H_2SO_4$$

Reactions

Hydrazine sulfate, when distilled with caustic soda under nitrogen, yields hydrazine hydrate. The sulfate salt is used in many organic syntheses. A few synthetic reactions are listed below:

Reaction with 2,4-dinitrochlorobenzene and potassium acetate yields 2,4-dinitrophenylhydrazine:

$$C_6H_3(NO_2)_2Cl + 3CH_3COOK + NH_2NH_2 \cdot H_2SO_4 \rightarrow$$
$$C_6H_3(NO_2)_2NHNH_2 + K_2SO_4 + KCl + 3CH_3COOH$$

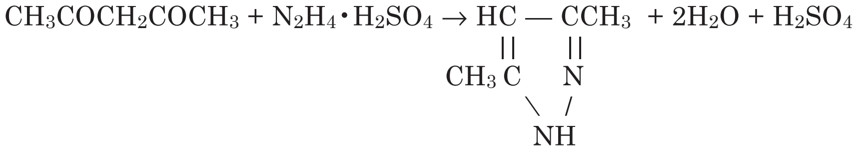
Hydrazine sulfate reacts with benzoyl chloride in basic medium to form dibenzoylhydrazine:

$$2C_6H_5COCl + N_2H_4 \cdot H_2SO_4 \xrightarrow{NaOH} C_6H_5CONHNHCOC_6H_5$$

Reaction with benzaldehyde in ammonia forms benzalazine:

$$2C_6H_5CHO + N_2H_4 \cdot H_2SO_4 \xrightarrow{NH_3} C_6H_5CH{=}N{-}N{=}CHC_6H_5$$

Hydrazine sulfate reacts with acetylacetone to yield 3,5-dimethylpyrazole:



$$CH_3COCH_2COCH_3 + N_2H_4 \cdot H_2SO_4 \rightarrow \text{(3,5-dimethylpyrazole: } HC{-}CCH_3,\ CH_3C{=}, N{=}, NH) + 2H_2O + H_2SO_4$$

Toxicity

Hydrazine sulfate is moderately toxic. Symptoms of ingestion are paresthesia, somnolence, nausea, and vomiting. It also is an irritant to the eye. It is a confirmed carcinogen and an experimental teratogen.

HYDRAZINE HYDROCHLORIDE

[2644-70-4]
Formula: $N_2H_4 \cdot HCl$, MW 68.506
Synonym: hydrazine monochloride

Uses

Hydrazine hydrochloride is used to prepare other hydrazine derivatives.

Physical Properties

White flakes; orthorhombic crystals; density 1.5 g/cm^3; melts at 93°C; decomposes around 200°C; very soluble in water (37 g/100mL at 20°C); slightly soluble in alcohol.

Preparation

Hydrazine hydrochloride is prepared by the reaction of hydrazine with hydrogen chloride.

$$N_2H_4 + HCl \rightarrow N_2H_4 \cdot HCl$$

Toxicity

Hydrazine hydrochloride is moderately toxic by all routes of exposure. The oral LD_{50} in mice is 126 mg/kg.

HYDROGEN

[1333-74-0]
Symbol: H; atomic number 1; atomic weight 1.0079; the lightest of all the chemical elements; the first element in the Periodic Table; Group IA (group 1) nonmetallic gaseous element; occurs as H_2, a diatomic molecule; electron configuration 1s^1; valences +1 and –1; three isotopes: H-1 or protium (99.9844%), H-2 or deuterium (0.0156%), H-3 or tritium (radioactive, $t_{1/2}$ =12.4 yr., in traces

only); molecular hydrogen is a mixture (ratio 3:1)of *ortho*- and *para*-hydrogen, which differ by the spins of their electrons and nuclei.

History, Occurrence, and Uses

The existence of hydrogen has been known since the 16th century. The gas, however, was reported in different ways, such as "inflammable air." Henry Cavendish was the first to elucidate the chemical nature of hydrogen in 1776 and prepared it by several methods. Lavoisier in 1783 named this element hydrogen, which means, "water former." Practically all gaseous hydrogen from earth's atmosphere escaped into outer space during formation of the earth.

Hydrogen is the most abundant element in the universe. All stars primarily are made up of hydrogen, which undergoes nuclear fusion forming helium, and releasing an enormous quantity of energy. The sun constitutes about 80% hydrogen by mass. The concentration of hydrogen in the earth's crust is estimated to be in the range of 1,400 mg/kg. Almost all hydrogen on earth is in the form of compounds. Its concentration in the atmosphere, however, is very small, about 0.00005%. The percentage composition of hydrogen in water, its most abundant compound on earth, is about 10.8% by mass. Although hydrogen is the fifteenth most abundant element on earth in mass, it forms the largest number of chemical compounds, more than any other element, including carbon. It is a component of all mineral acids, ammonia, natural gases and hydrocarbons, and a vast number of organic compounds from simple alcohols and aldehydes to complex proteins, carbohydrates, and chlorophyll.

Some important commercial applications of hydrogen gas include synthesis of ammonia by the Haber process; hydrogenation of vegetable oils, fats, and unsaturates; hydrocracking of petroleum crude; as a reducing agent in chemical reactions; in the manufacture of hydrochloric acid, methanol and metal hydrides; in oxy-hydrogen flame for welding and glass blowing; as a carrier gas in gas chromatography and a component of air-hydrogen flame in the Flame Ionization Detector (FID) in GC, and a filler gas in balloons and airships. It also is used in thermonuclear reactions and as a projectile proton in nuclear reactions. Liquid hydrogen is used as a cryogenic coolant, and in bubble chambers to study subatomic particles.

Physical Properties

Colorless, odorless, tasteless gas; flammable; burns in air with a popping sound; the lower and upper explosive limits are 4 and 75%, respectively, by volume in air; autoignition temperature 574°C; lighter than air; density of the gas at 0°C and 1 atm 0.0899 g/L; density of liquid 70.8 g/L at –253°C, and the density of solid 76.0 g./cm^3 at –262°C; liquefies at –252.9 °C and 1 atm; solidifies at –259.3°C and 1 atm; viscosity 0.0087 centipoise at 15°C and 1atm; critical temperature –240.18°C; critical pressure 12.76 atm; critical volume 65 cm^3/mol; velocity of sound 1,269.5 m/sec at 0°C; diffusion coefficient in air at 0°C 0.634 cm^2/sec; thermal neutron absorption cross section 0.332 barns; slightly soluble in water.

Thermochemical Properties

$\Delta H_f°$ (H_2 gas)	0.0
$\Delta H_f°$ (H gas)	52.10 kcal/mol
$\Delta G_f°$(H gas)	48.59 kcal/mol
S° (H_2 gas)	31.24 cal/degree mol
S° (H gas)	27.41 cal/degree mol
C_ρ (H_2 gas)	6.88 cal/degree mol
C_ρ (H gas)	4.97 cal/degree mol
ΔH_{fus} (H_2)	0.0287 kcal/mol
ΔH_{vap} (H_2)	0.210 kcal/mol
Thermal conductivity (at 0°C)	0.00038 cal/cm²/sec/°C/cm

Production

Hydrogen gas may be produced by several methods. It is commercially obtained by electrolysis of water. It also is made industrially by the reaction of steam with methane or coke:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$C + H_2O \rightarrow CO + H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

The reactions are carried out at about 900 to 1,000°C and catalyzed by nickel, nickel-alumina, or rhodium-alimina catalysts. In the laboratory, hydrogen may be prepared by the reaction of zinc or iron with dilute hydrochloric or sulfuric acid:

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

It also may be prepared by passing water vapor over heated iron:

$$H_2O + Fe \xrightarrow{heat} FeO + H_2$$

Also, it can be generated by reaction of metal hydrides with water:

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$$

Another method of preparation involves heating aluminum, zinc, or other active metals in dilute sodium hydroxide or potassium hydroxide:

$$2Al + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2$$

$$Zn + 2KOH \rightarrow K_2ZnO_2 + H_2$$

Reactions

At ordinary temperatures, hydrogen gas is very stable. It's dissociation is highly endothermic:

$$H_2 \rightarrow 2H \qquad \Delta H_{dissoc} = 108.52 \text{ kcal/mol}$$

However, at higher temperatures or in the presence of a catalyst, it can combine with a number of metals and nonmetals forming corresponding binary compounds; such as H_2O, HF, HCl, HBr, HI, H_2S, NH_3, CH_4, PH_3, AsH_3, SbH_3, SiH_4, B_2H_6, H_2Te, GeH_4, and numerous metal hydrides. Some specific reactions are as follows:

Hydrogen burns in air to form water. The reaction is catalyzed by Fe_2O_3 catalyst:

$$2H_2 + O_2 \xrightarrow{catalyst} 2H_2O$$

Reactions with halogens yield hydrogen halides.

$$H_2 + Cl_2 \xrightarrow{light} 2HCl$$

The reaction is explosive with fluorine and occurs under all conditions. With chlorine and bromine reaction occurs rapidly when exposed to light, undergoing a photochemical chain reaction. With iodine, the reaction is very slow, even at elevated temperatures. Hydrogen is a strong reducing agent. At high temperatures, the gas reduces many metal oxides to lower oxides or metals:

$$WO_3 + 3H_2 \xrightarrow{heat} W + 3H_2O$$

Hydrogen reacts with alkali and alkaline earth metals in the molten state to form their hydrides:

$$Ca + H_2 \rightarrow CaH_2$$

Hydrogen combines with nitrogen forming ammonia (See the Haber process.)

$$3H_2 + N_2 \xrightarrow[\text{high temperature and pressure}]{\text{catalyst}} 2NH_3$$

Reaction with carbon monoxide using copper/zinc oxide catalyst yields methanol:

$$2H_2 + CO \xrightarrow{catalyst} CH_3OH$$

The above reaction is utilized in large-scale industrial production of methanol. Reaction with boron trichloride over a hot tungsten or tantalum filament yields boron and hydrogen chloride:

$$2BCl_3 + 3H_2 \xrightarrow[\text{tungsten}]{>100°C} 2\,B + 6HCl$$

Hydrogen undergoes catalytic hydrogenation adding to unsaturated hydrocarbons, such as alkenes and alkynes forming alkanes. The reaction is catalyzed by nickel, platinum or palladium catalysts at ambient temperature. Hydrogenation of benzene over platinum catalyst yields cyclohexane, C_6H_{12}.

Hydrogen reduces esters into alcohols in the presence of nickel catalysts:

$$RCOOR' + 2H_2 \xrightarrow{Ni} RCH_2OH + R'OH$$

Many transition metal complexes catalyze homogeneous activation of molecular hydrogen in solution, forming hydrido complexes. Such complexes include pentacyanocobaltate(II) anion, $[Co(CN)_5]^{3-}$, many metal carbonyls, and several complexes of rhodium, iridium, and palladium.

Analysis

Hydrogen gas may be analyzed by GC using a thermal conductivity detector (TCD). A molecular sieve 5Å capillary column and helium as the carrier gas should be suitable for analysis. A common method of analyzing hydrogen involves combustion with oxygen to produce water, which is trapped on an adsorbent and determined by gravimetry.

Hazard

Hydrogen is a flammable gas. It combines explosively with oxygen at ordinary temperatures in the presence of finely divided metals. The LEL and UEL are 4 to 74% by volume in air, respectively. It combines with halogens explosively. Explosion of its mixture with chlorine is detonated by sunlight, heat, or a spark.

HYDROGEN BROMIDE

[10035-10-6]

Formula: HBr; MW 80.912. H—Br bond energy 88.0 kcal/mol; internuclear distance 1.41Å; An aqueous solution of hydrogen bromide gas is hydrobromic acid.

Uses

Hydrobromic acid is used in the preparation of inorganic bromide salts. The acid also is used for many organic syntheses, including alkyl bromides from alcohols or olefins, and bromophenols from phenols. The compound also is used as an acid catalyst in many alkylation, selective oxidation, isomerization, and dehydrogenation reactions. Other applications are in extraction of minerals and use as a reducing agent.

Physical Properties

Colorless gas; fumes in moist air; pungent acrid odor; nonflammable; heavier than air; density 2.71 (air=1.0); gas density 3.55 g/L at 25°C; liquefies at –66.4°C; solidifies at –86.8°C; critical temperature 89.8°C; critical pressure 84.5 atm; highly soluble in water (saturated aqueous solution contains 66% HBr at 25°C); forms a constant-boiling azeotrope at 47.5% HBr in solution, boiling at 126°C at atmospheric pressure; soluble in alcohol; a 0.10*M* aqueous solution is 93% ionized to H^+ and Br^- ions at 18°C.

Thermochemical Properties

$\Delta H_f°$	–8.676 kcal/mol
$\Delta G_f°$	–12.763 kcal/mol
S°	47.49 cal/degree mol
C_ρ	6.96 cal/degree mol
ΔH_{fus}	0.576 kcal/mol
ΔH_{vap}	3.03 kcal/mol

Preparation

Hydrogen bromide gas may be produced by combustion of hydrogen in bromine vapor at 37.5°C using a catalyst such as platinized asbestos or platinized silica gel. Unreacted free bromine is removed from the product by passing the gaseous product mixture over hot activated charcoal. Hydrogen bromide formed may be absorbed in water to obtain the acid; or may be cooled and liquefied for shipment in cylinders.

Hydrobromic acid may be prepared in the laboratory by distillation of a solution of potassium bromide with dilute sulfuric acid:

$$2KBr + H_2SO_4 \rightarrow K_2SO_4 + HBr$$

The acid may be prepared by several other methods, as well, including reaction of bromine either with sulfur and water; or with phosphorus and water:

$$2Br_2 + S + 2H_2O \rightarrow 4HBr + SO_2$$

Hydrobromic acid also may be prepared by hydrogen exchange with a sodium or potassium bromide solution when the solution is passed through a cation-exchange resin.

Hydrobromic acid is stored and shipped in drums, tanks, carboys, or bottles, labeled as corrosive materials. The anhydrous gas is stored and shipped in cylinders under its vapor pressure.

Reactions

Hydrobromic acid is a strong acid which neutralizes bases forming salts and water. The most important reactions involve the formation of bromide salts. The acid reacts with most metals, their oxides, hydroxides, carbonates and other salts, forming bromides:

$$2Al + 6HBr \rightarrow 2AlBr_3 + 3H_2$$

$$CuO + 2HBr \rightarrow CuBr_2 + H_2O$$

$$Ca(OH)_2 + 2HBr \rightarrow CaBr_2 + 2H_2O$$

$$Na_2CO_3 + 2HBr \rightarrow 2NaBr + H_2O + CO_2$$

Hydrogen bromide adds to carbon-carbon double bonds, usually the Markovnikov-type addition, forming bromo derivatives:

$$CH_2{=}CHCH_3 + HBr \rightarrow CH_3CH(Br)CH_3$$

Analysis

Elemental composition: H 1.25%, Br 98.75%. The normality of the acid may be measured by titration against a standard solution of a base using a suitable color indicator or by potentiometric titration. The bromide ion, Br^-, may be measured quantitatively by ion chromatography after appropriate dilution. Concentration of HBr gas in air may be measured by passing a known volume of air through water and determining concentration of acid in aqueous solution by titration or ion chromatography. Alternatively, HBr gas may be analyzed by GC or GC/MS. A very polar column should be used for such measurements. An FID or a TCD type detector may be used for GC analysis.

Toxicity

Hydrogen bromide gas is a strong irritant to eyes, nose and respiratory tract. The acid is corrosive to skin.

HYDROGEN CHLORIDE

[7647-01-0]
Formula: HCl; MW 36.461; a polar molecule, dipole moment 1.12D; H—Cl bond energy 105.5 kcal/mol; internuclear distance 1.28Å. Hydrochloric acid is an aqueous solution of hydrogen chloride.
Synonym: muriatic acid

History and Uses

Basilus Valentinus of Italy was first to isolate the acid and reported it under the name spiritus salis in the fifteenth century. Glauber prepared this acid by the reaction of sulfuric acid with common salt in 1648. Lavoisier proposed the name muriatic acid in 1789 after muriate, the term referring to a chlorine-containing inorganic substance. Sir Humphrey Davy proved the gas was composed of only hydrogen and chlorine in 1810. Subsequently, the gas was named hydrogen chloride.

Dilute hydrochloric acid occurs in the stomachs of mammals. Gaseous hydrogen chloride occurs in trace concentrations in the atmosphere.

Hydrochloric acid is one of the most important industrial chemicals and has numerous applications. Both anhydrous hydrogen chloride and aqueous acid are used to produce a large number of chloride salts. The acid also is a common laboratory reagent. Some major applications of hydrochloric acid include processing of ores and extraction of metals from their minerals; in metal cleaning, particularly in steel pickling to dissolve oxide impurities; production of alumina, titanium dioxide, and other metal oxides by various hydrometallurgical processes; production of hydrogen; synthesis of chlorine dioxide; removal of heavy metal impurities from carbon black; activation of bentonite clays; etching of concrete surfaces for finishing operations; and as a catalyst in several organic reactions such as inversion of sugar, hydrolysis of starch to obtain sugar syrup, and esterification of aromatic acids.

Anhydrous hydrogen chloride gas is used to produce phosphonium chloride, PH_4Cl, which is a flame retardant for cotton textiles. Other major applications include manufacture of a number of high purity metal chlorides, ammonium chloride, chlorosulfuric acid; recovery of waste metals; preparation of alkyl chlorides and chloroacetic acids; and as a chlorinating agent in organic syntheses.

Physical Properties

Colorless gas; sharp pungent odor; fumes in air; nonflammable; refractive index of gas at 0°C 1.000446; density of the gas 1.639 g/L (1.268 times heavier than air); density of liquid at –155°C 1.045 g/cm^3; density of solid at –192°C 1.507 g/cm^3; liquefies at –85.05°C to a colorless liquid; freezes to a white crystalline solid at –114.22°C; critical temperature 51.55°C; critical pressure 82.01 atm; critical volume 81 cm^3/mol; triple point –114.25°C; dielectric constant at 25°C 1.0046; electrical conductivity 35.0 micromho/cm at –87.6°C; highly soluble in water 42.02 g/100 g solution (or 72.47 g/100 g water) at 20°C and 1 atm; soluble in alcohols and ethers (47.0 g and 24.9 g/100 g solution at 20°C in methanol and ether, respectively.)

Hydrochloric acid is a colorless to yellowish liquid (the yellow coloration may be due to traces of iron, chlorine or organics contaminants); fumes in air; refractive index of 1.0 N solution 1.3417; density of commercial concentrated acid (37.8 g/100g solution) 1.19 g/mL, and constant boiling solution (20.22 g/100g solution) 1.096 g/mL at 25°C; forms a constant boiling azeotrope with water at HCl concentration 20.22%; the azeotrope boils at 108.6°C; several metal chlorides can be salted out of their aqueous solutions by addition of HCl; the addition of $CaCl_2$ can break the azeotrope; the pH of the acid at 1.0, 0.1 and 0.01 N concentrations are 0.10, 1.1, and 2.02, respectively; a 10.0 M solution ionizes to 92.6% at 18°C.

Thermochemical Properties

$\Delta H_f°$	–22.06 kcal/mol
$\Delta G_f°$	–22.78 kcal/mol
S°	44.67 cal/degree mol

C_ρ	6.955 cal/degree mol
ΔH_{fus}	0.478 kcal/mol
ΔH_{vap}	3.86 kcal/mol
ΔH_{dissoc}	103.16 kcal/mol

Production

Hydrochloric acid can be produced by several methods. It is obtained from the reaction of sodium chloride and sulfuric acid in a cast iron retort at elevated temperature. Although reaction starts at 150°C, the complete reaction occurs at about 600°C:

$$2NaCl + H_2SO_4 \xrightarrow{\text{high temperatures}} Na_2SO_4 + 2HCl$$

Hydrochloric acid also is made by the Hargreaves process in which a mixture of salt, sulfur dioxide, oxygen, and water are heated at elevated temperatures, between 430 to 540°C. The reaction is exothermic and becomes self-sustaining:

$$4NaCl + SO_2 + O_2 + 2H_2O \xrightarrow{\text{elevated temperatures}} 2Na_2SO_4 + 4HCl$$

Hydrochloric acid may be produced by hydrolysis of metal chlorides such as titanium(IV) chloride:

$$TiCl_4 + 2H_2O \xrightarrow{heat} TiO_2 + 4HCl$$

High purity HCl for commerce is made directly from hydrogen and chlorine:

$$H_2 + Cl_2 \xrightarrow{\text{elevated temperatures}} 2HCl$$

The above reaction is highly exothermic. The stoichiometric proportion of gaseous mixture at equilibrium flame temperature is cooled to 200°C, whereupon the elements combine rapidly to form HCl with over 99% yield.

HCl also may be prepared by several other methods including thermal dissociation of aluminum chloride hexahydrate, $AlCl_3 \cdot 6H_2O$, and as a by-product of manufacturing many organic compounds.

Crude HCl gas mixture may be purified by cooling and drying over concentrated sulfuric acid, which also removes organic unsaturated contaminants. Organic contaminants may be removed further by adsorption over molecular sieves, polystyrene foam, active carbon, or scrubbing with a high-boiling point organic liquid.

Commercial grade, concentrated hydrochloric acid is about 37.5% HCl by weight and has a normality of 12 and specific gravity 1.19.

Hydrogen chloride gas may be stored in steel cylinders free of contaminants. Monel, pure nickel, or its alloy, inconel, may also be used for storage and transportation up to 500°C. Hydrochloric acid may be stored in glass bottles or in containers made up of tantalum or tantalum-molybdenum alloys, or other alloys of zirconium, molybdenum, and tungsten.

Reactions

Aqueous hydrochloric acid reacts with most metals and alloys liberating hydrogen and forming their chloride salts:

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

Reactions with highly electropositive elements (e.g. alkali metals) occur with explosive violence. On the other hand, certain metals, such as tantalum or tungsten, show little reactivity at ordinary temperatures.

Hydrochloric acid is a strong mineral acid, the pH of 0.1N HCl is 1.10. In aqueous solutions, it dissociates almost one hundred percent forming hydronium, H_3O^+ and Cl^- ion. The acid undergoes neutralization reactions with bases. With strong bases such as caustic soda solution, the neutralization is complete. The reaction may be written formally as:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

Reactions with metal carbonates liberate carbon dioxide:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

Anhydrous hydrogen chloride combines with ammonia or phosphine to form ammonium or phosphonium chloride:

$$HCl + NH_3 \rightarrow NH_4Cl$$

With silane or germane, the products are SiH_3Cl and SiH_2Cl_2 or GeH_3Cl and GeH_2Cl_2, respectively:

$$SiH_4 + HCl \xrightarrow{AlCl_3} SiH_3Cl + H_2$$

$$SiH_3Cl + HCl \xrightarrow{AlCl_3} SiH_2Cl_2 + H_2$$

Reaction with diborane and other boron hydrides yield boron trichloride:

$$B_2H_6 + 6HCl \xrightarrow{AlCl_3} 2BCl_3 + 6H_2$$

Hydrogen chloride gas reacts with oxygen forming chlorine and water:

$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$$

A similar reaction occurs with hydrogen peroxide:

$$2HCl + H_2O_2 \rightarrow Cl_2 + 2H_2O$$

At elevated temperature HCl gas reacts with metals forming chlorides. At ordinary temperatures the reaction is very slow.

Metal oxides react with hydrogen chloride at elevated temperatures forming corresponding metal chlorides and water:

$$NiO + 2HCl \xrightarrow{\text{elevated temperatures}} NiCl_2 + H_2O$$

$$Fe_2O_3 + 6HCl \xrightarrow{>300^\circ C} 2FeCl_3 + 3H_2O$$

Often at high temperatures the reaction product is an oxychloride, particularly when the reactant is an oxide of a heavy transition metal, such as, hafnium or tungsten.

Reaction with nitric acid liberates chlorine gas:

$$2HCl + HNO_3 \rightarrow Cl_2 + HNO_2 + H_2O$$

HCl forms adducts with anhydrous sulfates of several metals, such as $ZnSO_4 \cdot 2HCl$. HCl combines with sulfur trioxide to produce chlorosulfonic acid:

$$HCl + SO_3 \rightarrow ClSO_3H$$

Hydrogen chloride undergoes addition reactions with carbon-carbon double and triple bonds. Many addition products of olefins and acetylenes are important industrial raw materials. It adds to ethylene forming ethyl chloride:

$$CH_2{=}CH_2 + HCl \rightarrow CH_3CH_2Cl$$

Addition of HCl to acetylene yields vinyl chloride:

$$CH{\equiv}CH + HCl \rightarrow CH_2{=}CHCl$$

The product vinyl chloride can combine with another molecule of HCl to form 1,1-dichloroethane, undergoing Markovnikov addition:

$$CH_2{=}CHCl + HCl \rightarrow CH_3CHCl_2$$

HCl combines with many conjugated dienes forming a variety of addition products.

HCl reacts with methanol in the presence of a catalyst, such as $FeCl_3$ or $ZnCl_2$, forming methyl chloride:

$$CH_3OH + HCl \xrightarrow{\textit{catalyst}} CH_3Cl + H_2O$$

Usually all alcohols undergo such reactions, forming their alkyl halides and eliminating a molecule of water. The reaction is catalyzed by metal chlorides deposited on carbon, alumina or silica gel or by silica-alumina catalysts.

Analysis

The strength of hydrochloric acid solution can be measured by acid-base titration against a standard solution of sodium hydroxide using a color indicator. Alternatively, the end point may be determined by potentiometric titration. Hydrogen chloride gas in air may be analysed by passing a measured volume of air through water containing methyl red or any suitable color indicator. Concentration of HCl in solution may be analysed using colorimetry by measuring absorbance of the solution. Hydrogen chloride in gaseous mixture may be analyzed by GC using a TCD or an FID and a strong polar column. HCl may be identified with a mass spectrometer following separation on a GC column. The characteristic mass ions for HCl should be 36 and 38.

Toxicity

Inhalation of HCl gas pungent-odor can cause coughing, choking, and irritation of the respiratory tract. Chronic exposure to the acid can produce gastritis and bronchitis. Ingestion of the acid can result in corrosion of the mouth and stomach, and diarrhea. Concentrated acid causes skin burn, and contact with eyes can damage vision.

HYDROGEN CYANIDE

[74-90-8]
Formula: HCN; MW 27.03
Structure: H—C≡N, a linear molecule with a carbon-nitrogen triple bond.
Synonyms: hydrocyanic acid; prussic acid; formonitrile

History and Uses

Hydrogen cyanide in pure form was prepared first in 1815 by Gay-Lussac. Earlier, in 1782, Scheel prepared this compound in dilute solution. The most important application of hydrogen cyanide is to produce methyl methacrylate for methacrylate resins and plastics. Other products made from hydrogen cyanide include potassium cyanide, sodium cyanide, adiponitrile, methionine, cyanuric chloride, cyanogen, nitrilotriacetic acid, and several triazine pesticides. The compound also is used in small amounts for extermination of rodents.

Physical Properties

Colorless liquid or gas; odor of bitter almond; burns in air with a blue flame; refractive index 1.2675; autoignition temperature 538°C; vapor density at 31°C 0.947 (air=1); liquid density 0.715 g/mL at 0°C and 0.688 g/mL at 20°C; boils at 25.7°C; melts at 13.24°C; vapor pressure 264 torr at 0°C; critical temperature 183.5°C; critical pressure 53.20 atm; critical volume 139 cm^3/mol dielectric constant 158.1 at 0°C and 114.9 at 20°C; conductivity 3.3 mhos/cm at 25°C; viscosity 0.201 centipoise at 20°C; surface tension 19.68 dyn/cm; readily mixes with water and alcohols; density of a 10% aqueous solution 0.984 g/mL at 20°C; pK_a at 25°C 9.21.

Thermochemical Properties

$\Delta H_f°$ (liq)	26.03 kcal/mol
$\Delta H_f°$ (gas)	32.29 kcal/mol
$\Delta G_f°$ (liq)	29.88 kcal/mol
$\Delta G_f°$ (gas)	29.80 kcal/mol
S° (liq)	26.96 cal/degree mol
S° (gas)	48.23 cal/degree mol
C_ρ (liq)	16.87 cal/degree mol
C_ρ (gas)	8.58 cal/degree mol
ΔH_{fus}	2.01 kcal/mol
$\Delta H_{combustion}$	159.4 kcal/mol

Preparation

Hydrogen cyanide is generally produced in industrial quantities by high temperature catalytic reaction between ammonia, methane, and air (the Andrussow process). The stoichiometry of the process is:

$$2CH_4 + 2NH_3 + 3O_2 \xrightarrow[1100°C]{Pt/Rh} HCN + 3H_2O \quad \Delta H_{rxn} = 230.4 \text{ kcal}$$

The above reaction is endothermic requiring a temperature of 1,100°C and a catalyst such as platinum or rhodium. Other hydrocarbons may be used instead of methane.

The compound may be made by several other methods, which include:

1. Heating methanol and ammonia in the absence of air at elevated temperatures (600 to 950°C) using a catalyst:

$$CH_3OH + NH_3 \xrightarrow[\text{catalyst}]{600\text{-}950°C} HCN + H_2O + H_2$$

2. Thermal decomposition of formamide at elevated temperatures and reduced pressure:

$$HCONH_2 \xrightarrow{\text{elevated temperatures}} HCN + H_2O$$

3. Heating acetonitrile and ammonia at 1,100 to 1,300°C:

$$CH_3CN + NH_3 \xrightarrow{1100\text{–}1300°C} 2HCN + 2H_2$$

4. Reaction of sodium cyanide or potassium cyanide or potassium ferro cyanide with a mineral acid:

$$NaCN + HCl \rightarrow HCN + NaCl$$
$$K_4Fe(CN)_6 + 6HCl \rightarrow 6HCN + 4KCl + FeCl_2$$

Reactions

Hydrogen cyanide is a very weak acid, the pK_a at 25ºC is 9.21

Hydrogen cyanide is oxidized by air when heated at elevated temperatures forming cyanic acid as the major product and cyanogen as a minor product. The reaction is catalyzed by gold and silver catalysts:

$$HCN + O_2 \xrightarrow{300-650^\circ C} 2HOCN$$

$$4HCN + O_2 \xrightarrow{300-650^\circ C} 2(CN)_2 + 2H_2O$$

Oxidative cleavage over silver catalyst yields cyanogen.

Reactions with caustic soda and caustic potash solution yield sodium cyanide and potassium cyanide, respectively:

$$HCN + NaOH \rightarrow NaCN + H_2O$$

Similar reactions occur with some other metal hydroxides forming corresponding cyanides:

$$2HCN + Ca(OH)_2 \rightarrow Ca(CN)_2 + H_2O$$

While treatment with aqueous sulfuric acid hydrolyzes hydrogen cyanide to formic acid, HCOOH, its reaction with concentrated sulfuric acid is violent forming an adduct $HCN{:}H_2SO_4$. The adduct is unstable, decomposing to carbon dioxide, sulfur dioxide and ammonia:

$$HCN + H_2SO_4 \rightarrow HCN\bullet H_2SO_4$$

$$HCN\bullet H_2SO_4 \rightarrow SO_2 + CO_2 + NH_3$$

Hydrogen cyanide undergoes many important organic reactions forming a variety of industrial products. Probably the most important reaction is the addition of the carbonyl (=C=O) group. It adds to the carbonyl groups of aldehydes and most ketones forming cyanohydrins:

$$\underset{\text{(aldehyde)}}{RCHO} + HCN \rightarrow \underset{\text{(cyanohydrin)}}{RCH(OH)CN}$$

$$\underset{\text{(ketone)}}{RCOR'} + HCN \rightarrow \underset{\text{(cyanohydrin)}}{RC(OH)(CN)R'}$$

The above reaction is slow, but is catalyzed by mild bases. Thus, addition of potassium cyanide enhances the rate of reaction dramatically. Cyanohydrins are important intermediates in many organic synthesis.

Reaction with formaldehyde yields glycolic nitrile (a cyanohydrin), but in the presence of aniline the product is N-phenylglycinonitrile:

$$\underset{\text{(formaldehyde)}}{HCHO} + HCN \rightarrow \underset{\text{(glycolic nitrile)}}{H_2C(CN)OH}$$

$$HCHO + HCN + \underset{\text{(aniline)}}{C_6H_5NH_2} \rightarrow \underset{\text{N-phenylglycinonitrile}}{C_6H_5NHCH_2CN} + H_2O$$

Reaction with methanol yields N,N-dimethylformamide:

$$2CH_3OH + HCN \xrightarrow{H^+} HCON(CH_3)_2 + H_2O$$

Reactions with secondary or tertiary alcohols in strongly acidic media yield amides (Ritter reaction):

$$R_3C—OH + HCN \xrightarrow[H_2O]{H^+} HCONHCR_3$$

Similarly, amines may be obtained by the addition of HCN to olefins.

Hydrogen cyanide reacts with phenol in the presence of hydrochloric acid and aluminum chloride, forming 4-hydroxybenzaldehyde:

$$C_6H_5OH + HCN + HCl \xrightarrow{AlCl_3} [HOC_6H_4CH{=}NH\cdot HCl]$$

$$\xrightarrow{H_2O} HOC_6H_4CHO + NH_4Cl$$

Similar reactions occur with aromatic ethers, C_6H_5OR, giving aldehydes ROC_6H_4CHO (Gattermann synthesis).

Analysis

Elemental composition: H 3.73%, C 44.44%, N 51.83%. HCN may be analyzed by GC or GC/MS. The aqueous solution may be directly injected onto the GC column and determined by an FID. For GC/MS determination, an alcoholic solution may be injected into the column. The characteristic mass ions are 27 and 26. The cyanide ion in aqueous solution also may be measured by cyanide ion-selective electrode, titrimetry, and by colorimetric methods (APHA, AWWA, WEF. 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington, DC: American Public Health Association). For colorimetric analysis, the aqueous solution may be treated with a dilute caustic soda solution, followed by treatment with chloramine-T, and then with pyridine-barbituric acid reagent. A red-blue color develops, the absorbance of which is measured by spectrophotometer at 578 nm. The concentration of CN^- is determined from a standard calibration curve using KCN standards.

Titrimetric measurement involves titrating alkaline HCN solution against a standard solution of silver nitrate using a silver sensitive indicator, ρ-dimethylaminobenzalrhodamine. At the end point, color changes from yellow to pink.

Hazard

Hydrogen cyanide is extremely toxic by ingestion, inhalation, skin absorption, and all routes of exposure. An oral dose of 50 mg could be lethal to humans (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed., New York: John Wiley). Symptoms from acute poisoning include labored breathing, shortness of breath, paralysis, unconsciousness, and respiratory failure. Lower doses can cause headache, nausea and vomiting. Oral LD_{50} in mice is 3.7 mg/kg. Amyl nitrite is an effective antidote.

HCN also is a highly flammable compound; closed cup flash point is 0°C. The vapors form an explosive mixture with air: the LEL and UEL are 6 and 41% by volume of air, respectively.

HYDROGEN FLUORIDE

[7664-39-3]
Formula: HF; MW 20.006. A very stable polar covalent diatomic molecule; H—F bond energy 136.1 kcal/mol; at lower temperatures molecules are associated by hydrogen bonding; H—F bond length 0.92Å; partial ionic character 40%; dipole moment 6.10 D; hydrofluoric acid is an aqueous solution of hydrogen fluoride gas.
Synonyms: hydrofluoric acid gas; fluohydric acid gas.

History and Uses

Anhydrous hydrogen fluoride was first prepared by Fremy in 1856. It may have been made earlier in 1670 by Schwankhard in the process of etching glass using fluorspar and acid.

Hydrogen fluoride is the most important fluorine compound, in terms of amounts produced and the vast number of uses. The largest application of this compound is in the manufacture of aluminum fluoride and sodium aluminum fluoride (cryolite) for electrolytic production of aluminum. Another major application is in the manufacture of chlorofluorocarbons, which are used as refrigerants and foaming agents; for making polymers; and for pressurizing gases. Another important application is in the processing of uranium where HF converts uranium dioxide to uranium tetrafluoride and hexafluoride, respectively. Uranium hexafluoride is used to separate isotopes of uranium by diffusion.

Hydrogen fluoride also is used as a catalyst in alkylation of aromatic compounds and for dimerization of isobutene. Other catalytic applications are in isomerization, polymerization, and dehydration reactions. Other uses are in etching and polishing glasses for manufacturing light bulbs and TV tubes; in extraction of ores; in pickling stainless steel; in acidizing oil-wells; to remove laundry stains; for sample digestion in metal analysis; for removal of sand during metal castings; as a stabilizer for rocket propellant oxidizers; and in preparation of a number of fluoride salts of metals.

Physical Properties

Colorless gas or liquid at ambient temperatures; fumes in air; highly irritating; gas density 0.878 g/L at 25°C; liquid density 1.002 g/mL at 0°C; boils at 19.85°C; freezes at –83.55°C; vapor pressure 360 torr at 0°C; critical temperature 187.85°C; critical pressure 63.95 atm; critical volume 69 cm^3/mol; viscosity 0.256 centipoise at 0°C; surface tension $10.1 x 10^{-4}$ dyn/cm at 0°C; dielectric constant 83.6 at 0°C; highly soluble in water and alcohols; forms an azeotrope with water at a composition 38.2 HF: 61.8 H_2O (weight percent); the azeotrope boils at 112.2°C; moderately soluble in benzene (2.55 g/100 g at 5°C).

Hydrofluoric acid is a colorless, fuming liquid which is an aqueous solution of hydrogen fluoride; densities of 20%, 40% and 60% acid at 20°C are 1.070, 1.135, and 1.215 g/mL, respectively; a 70% solution boils at 66.4°C; the same solution freezes at –69°C to a solid phase that has a composition of $HF \cdot H_2O$; vapor pressure of 70% solution at 25°C 150 torr; partial pressures of HF over HF—H_2O solutions at 20°C are 0.412, 12.4 and 115.3 torr, respectively, for 20, 50 and 70% HF solutions by weight; equivalent conductance of 0.01 M and 0.1 M solutions at 20°C, 93.5 and 37.7 mhos-cm^2, respectively; a weak acid, pK_a 3.20 at 25°C; a 0.1M aqueous solution ionized <10%

Thermochemical Properties

$\Delta H_f°$ (gas)	–65.32 kcal/mol
$\Delta H_f°$ (liquid)	–71.65 kcal/mol
$\Delta G_f°$ (gas)	–65.82 kcal/mol
S° (gas)	41.54 cal/degree mol
C_ρ (liquid at 16°C)	12.1 cal/degree mol
C_ρ (gas at 22°C)	109.0 cal/degree mol
ΔH_{vap}	1.80 kcal/mol
ΔH_{fus}	1.095 kcal/mol
ΔH_{soln}	–14.70 kcal/mol

Production

Hydrogen fluoride is produced from mineral fluorspar, CaF_2, which is decomposed by heating with concentrated sulfuric acid. The gaseous products consisting of hydrogen fluoride, sulfur dioxide, silicon tetrafluoride, and water vapor are separated from sulfuric acid mist and solid residues in a precondenser. The separation is carried out in a cyclone countercurrent scrubbing. Water is removed from the scrubbing fluid by the addition of 20% oleum. Hydrogen fluoride vapors are condensed and redistilled to obtain the product at 99.9% purity.

Hydrogen fluoride may be made from silicon tetrafluoride produced from phosphate rocks. A major step in the process involves reaction of silicon tetrafluoride with recycled ammonium fluoride solution:

$$SiF_4 + 2NH_4F \rightarrow (NH_4)_2SiF_6$$

The product ammonium fluorosilicate formed above is neutralized with ammonia solution to precipitate silica and form more ammonium fluoride:

$$(NH_4)_2SiF_6 + 4NH_3 + 2H_2O \rightarrow SiO_2 + 6NH_4F$$

The solution of ammonium fluoride is concentrated by evaporation to a solid residue which also contains a small amount of partially converted ammonium bifluoride, NH_4HF_2. Heating this solid residue at 180°C with 95% sulfuric acid yields hydrogen fluoride:

$$2NH_4F + H_2SO_4 \xrightarrow{180^{\bullet}C} 2HF + (NH_4)_2SO_4$$

$$2NH_4HF_2 + H_2SO_4 \xrightarrow{180^{\bullet}C} 4HF + (NH_4)_2SO_4$$

Hydrogen fluoride may be prepared by direct combination of hydrogen and fluorine at elevated temperatures. In general, HF can be generated by action of a concentrated acid with a fluoride salt.

Hydrofluoric acid must not be stored in glass or silicate ceramic containers. Stainless steel or PTFE are satisfactory for storage and handling. Nonferrous materials such as carbon, bronze, Monel or lead may be used for weaker acids.

Reactions

Although anhydrous hydrogen fluoride is a very strong acid, its aqueous solution, hydrofluoric acid, is weakly acidic, particularly when dilute. The K_a value of aqueous acid at 25°C is 6.46×10^{-4} mol/L. It is an excellent solvent for many inorganic fluorides, forming bifluoride anion:

$$HF + NaF \rightarrow Na^+ + HF_2^-$$

At lower temperatures (below 200°C), HF forms molecular aggregates that are held by hydrogen bonding containing linear chains of –F—H—-F—H—-F—H—-. However, above this temperature the weak hydrogen bond breaks producing monomolecular HF. Thermal dissociation of HF into elements probably occurs only at very high temperatures. Forty to 50% HF probably dissociates around 4,000°C, indicating that it is one of the most stable diatomic molecules.

The most important reactions of HF involve formation of inorganic fluoride salts. HF gas or hydrofluoric acid reacts with oxides, hydroxides, carbonates, chlorides and other metal salts forming the corresponding fluorides. Some examples are:

$$Bi_2O_3 + 6HF \rightarrow 2BiF_3 + 3H_2O$$

$$LiOH + HF \rightarrow LiF + H_2O$$

$$CaCO_3 + 2HF \rightarrow CaF_2 + CO_2 + H_2O$$

$$FeCl_3 + 3HF \rightarrow FeF_3 + 3HCl$$

$$CoCl_2 + 2HF \rightarrow CoF_2 + 2HCl$$

Reaction with potassium dichromate yields chromyl fluoride:

$$K_2Cr_2O_7 + 6HF \rightarrow 2CrO_2F_2 + 2KF + 3H_2O$$

When ammonia gas is bubbled through a 40% ice-cold solution of hydrofluoric acid, the product is ammonium fluoride:

$$NH_3 + HF \rightarrow NH_4F$$

The addition of equimolar amount of NaOH or Na_2CO_3 to 40% HF instantaneously precipitates NaF:

$$NaOH + HF \rightarrow NaF + H_2O$$

Excess HF, however, yields sodium bifluoride, $NaHF_2$:

$$NaOH + 2HF \rightarrow NaHF_2 + H_2O$$

Reaction with phosphorus trichloride yields phosphorus trifluoride; and with phosphoryl fluoride and sulfur trioxide, the product is phosphorus pentafluoride:

$$PCl_3 + 3HF \rightarrow PF_3 + HCl$$

$$POF_3 + 2HF + SO_3 \rightarrow PF_5 + H_2SO_4$$

Analysis

Elemental composition: H 5.04%, F 94.96%. The total acidity of an aqueous HF solution may be measured by titration with a standard solution of base using phenolphthalein or another suitable color indicator. Alternatively, the end point may be determined by potentiometric titration. The fluoride ion may be analyzed using a fluoride ion-selective electrode or by ion chromatography. The HF gas may be analyzed by GC/MS using a GC column having very high polarity.

Toxicity

Both anhydrous hydrogen fluoride gas and hydrofluoric acid are highly corrosive and dangerous. Skin contact by even dilute aqueous HF can be severely injurious, causing deep ulceration with delayed effect. The acid can penetrate the skin and destroy tissues. It also is damaging to eyes, nose and lungs. Inhalation can cause fluorosis and pulmonary edema.

HYDROGEN IODIDE

[10034-85-2]
Formula: HI; MW 127.91; H—I bond energy 71.0 kcal/mol; internuclear distance 1.62Å.
Hydriodic acid is the aqueous solution of hydrogen iodide.

Uses

Hydrogen iodide is used to prepare a number of organic iodides. Hydriodic acid is a reducing agent; and is used in the preparation of inorganic iodide salts. It also is used in pharmaceuticals; disinfectants, and as a reagent in chemical analysis.

Physical Properties

Colorless gas; pungent acrid odor; fumes in moist air; nonflammable; density 5.613 g/L; liquefies at –35.55°C; density of liquid at –4.7°C 2.85 g/mL; solidifies at –50.8°C; critical temperature 150.85°C; critical pressure 82.01 atm; highly soluble in water, 234 g/100 g water at 10°C forming hydriodic acid; forms an azeotrope at 56.9% HI and 43.1% water; the azeotrope boils at 127°C and has density 1.709 g/mL; soluble in organic solvents.

Hydriodic acid is a colorless liquid when pure or freshly prepared; becomes yellowish or brown on exposure to light or air; strong acid odor; pH of 0.1 molar solution, 1.0; a 0.1 M aqueous solution is 95% ionized at 25°C; miscible with alcohols; dissolves iodine.

Thermochemical Properties

$\Delta H_f°$	6.33 kcal/mol
$\Delta G_f°$	0.406 kcal/mol
S°	49.38 cal/degree mol
C_ρ	6.98 cal/degree mol
ΔH_{vap}	4.723 kcal/mol
ΔH_{fus}	0.686 kcal/mol

Preparation

Hydrogen iodide is prepared by direct combination of hydrogen and iodine vapor in the presence of platinum catalyst:

$$H_2 + I_2 \xrightarrow{Pt} 2HI$$

The compound is produced in commercial scale by reaction of iodine with hydrazine or hydrogen sulfide:

$$2I_2 + N_2H_4 \rightarrow 4HI + N_2$$

$$I_2 + H_2S \rightarrow 2HI + S$$

Hydriodic acid may be prepared by dissolving hydrogen iodide gas in water. The acid also may be obtained by electrolysis of iodine solution or by passing hydrogen sulfide into a suspension of iodine in water and boiling to expel excess sulfide. After boiling, the precipitated sulfur is removed by filtration through fritted glass plate or glass wool.

Hydriodic acid in small quantities may be prepared by adding water carefully to a solid mixture of red phosphorus and iodine.

Technical grade hydriodic acid is a 47% HI solution and usually has a brown color due to the presence of free iodine, produced by air oxidation of HI. Hydriodic acid should be stored in the dark to prevent photochemical decomposition, and free from air to prevent oxidation. The addition of 1.5% hypophosphorus acid (H_3PO_2) prevents oxidative decomposition.

Hydriodic acid also is commercially sold at 57% (azeotropic concentration) and 10% aqueous solutions.

Reactions

Hydrogen iodide gas dissociates on heating to hydrogen and iodine.

Hydrogen iodide in gaseous state or in the aqueous solution (hydriodic acid) reacts with most metals and their salts. Hydriodic acid dissolves metals and metal oxides, forming iodide salts:

$$Cu + 2HI \rightarrow CuI_2 + H_2$$

$$CuO + 2HI \rightarrow CuI_2 + H_2O$$

HI also reacts with metal salts, forming iodides:

$$KHCO_3 + HI \rightarrow KI + H_2O + CO_2$$

Hydriodic acid is a strong reducing agent, which readily reduces oxidizing substances. Reaction with oxygen yields iodine:

$$HI + O_2 \rightarrow I_2 + H_2O$$

Hydrogen iodide adds to double bond of alkenes undergoing Markovnikov addition. The reaction is faster than that with other hydrogen halides:

$$CH_2{=}CHCH_3 + HI \rightarrow CH_3CHICH_3$$

HI replaces iodine from organic iodo compounds:

$$CH_3CH_2I + HI \rightarrow C_2H_6 + I_2$$

Reactions with lower alcohols yield alkyl iodides:

$$CH_3CH_2OH + HI \rightarrow CH_3CH_2I + H_2O$$

Analysis

Elemental composition: I 99.21%, H 0.79%

The strength of hydriodic acid may be measured by titrating against a standard solution of base using color indicator, or by potentiometric titration. It can be analyzed by treatment with an oxidizing agent such as chlorine and the liberated iodine is titrated with a standard solution of sodium thiosulfate using starch indicator. The blue color of the solution decolorizes at the end point. Hydrogen iodide gas may be measured by GC-TCD using a very polar column. Also, it may be identified by GC/MS, the molecular ion having mass 127.

Toxicity

The gas is a strong irritant to eyes, nose and mucous membranes. The acid is corrosive to skin.

HYDROGEN PEROXIDE

[7722-84-1]
Formula: H_2O_2; MW 34.015
Structure: H—O—O—H, covalently bound, nonpolar molecule.

Synonyms: hydrogen dioxide; perone; hydroperoxide.

History and Uses

Hydrogen peroxide was prepared first by Thenard in 1818. It has many industrial applications. Aqueous solutions at varying concentrations are used for bleaching fabrics, silks, furs, feathers and hair; as a dough conditioner; and a bleaching and oxidizing agent in foods; for cleaning metals; as a laboratory reagent for oxidation; as an antiseptic; in sewage and wastewater treatment; and in preparation of inorganic and organic peroxides. An 80% concentrated solution is used in rocket propulsion.

Physical Properties

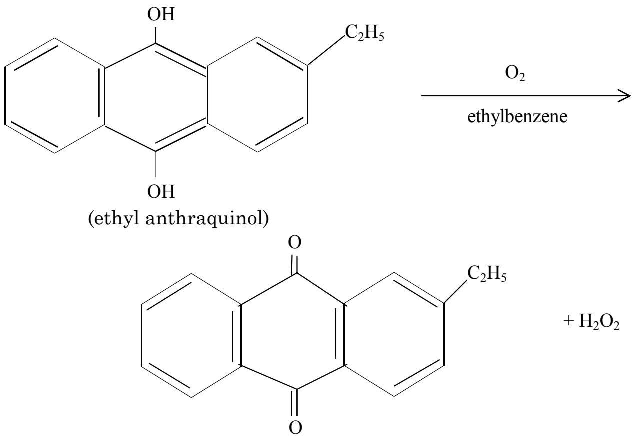
Colorless liquid; pure compound or 90% solution unstable; bitter taste; density 1.463 g/mL; boils at 150.2°C; freezes at –0.43°C; vapor pressure 9.9 torr at 50°C and 121.5 torr at 100°C; viscosity 1.245 centipoise at 20°C; surface tension 80.4 dyn/cm at 20°C; miscible with water in all proportions; soluble in ether; densities of 30%, 70%, and 90% H_2O_2 solutions are 1.1081, 1.2839 and 1.3867 g/mL, respectively, at 25°C; freezing points at these concentrations are –25.7°C, –40.3°C and –11.5°C, respectively; and their boiling points are 106.2°C, 125.5°C and 141.3°C, respectively; decomposed by many organic solvents; pK_a at 25°C is 11.62.

Thermochemical Properties

$\Delta H_f°$ (liq)	–44.885 kcal/mol
$\Delta H_f°$ (gas)	–32.576 kcal/mol
$\Delta G_f°$(liq)	–28.776 kcal/mol
$\Delta G_f°$ (gas)	–25.239 kcal/mol
S° (liq)	55.62 cal/degree mol
S° (liq)	55.62 cal/degree mol
S° (gas)	37.05 cal/degree mol
C_ρ (liq)	10.3 cal/degree mol
ΔH_{vap} (at 25°C)	12.33 kcal/mol
ΔH_{fus}	2.988 kcal/mol
ΔH_{dissoc}	8.20 kcal/mol

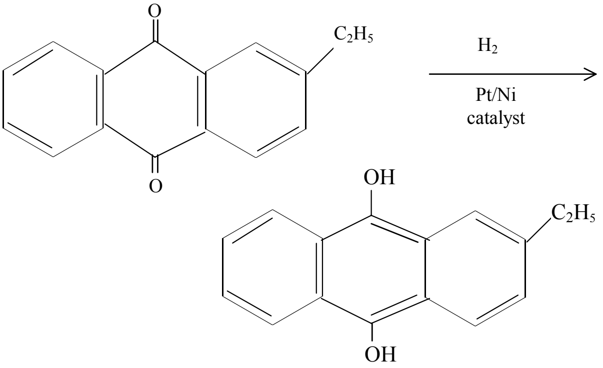
Preparation

Hydrogen peroxide is commercially produced by autooxidation of ethyl anthraquinol in a solvent such as toluene or ethylbenzene. The product ethyl anthraquinone is reduced by hydrogen over supported nickel or platinum catalyst to regenerate back the starting material, ethyl anthraquinol for a continuous production of H_2O_2. The reaction steps are:



(ethyl anthraquinol)

(ethyl anthraquinone)



Hydrogen peroxide may also be made by heating 2-propanol with oxygen at 100°C under 10 to 20 atm pressure:

$$(CH_3)_2CHOH \xrightarrow[10\text{-}20\text{ atm, }100°C]{O_2} (CH_3)_2C(OH)OOH \rightarrow CH_3COCH_3 + H_2O_2$$

Vapor phase partial oxidation of hydrocarbons also yield H_2O_2. However, several by-products are generated, the separations of which make the process difficult and uneconomical.

Hydrogen peroxide may also be prepared by treating barium peroxide with dilute sulfuric acid:

$$BaO_2 + 2H_2SO_4 \rightarrow H_2O_2 + BaSO_4$$

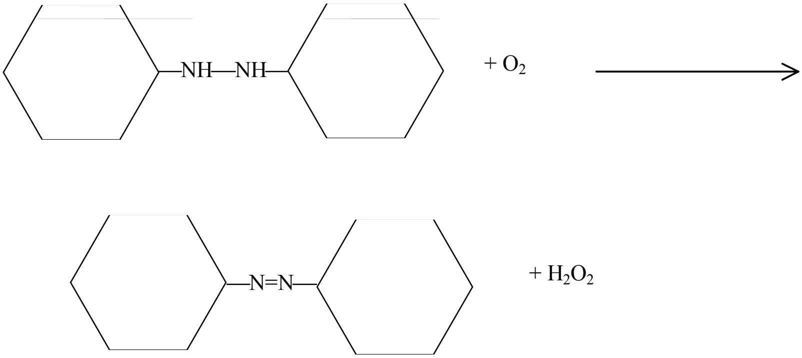
Another preparative method involves electrolytic conversion of aqueous sulfuric acid to peroxydisulfate followed by hydrolysis to H_2O_2 (Weissenstein process). The reaction steps are as follows:

$$2H_2SO_4 \xrightarrow{electrolysis} H_2S_2O_8 + H_2$$

$$H_2S_2O_8 + H_2O \rightarrow H_2SO_4 + H_2SO_5$$

$$H_2SO_5 + H_2O \rightarrow H_2O_2 + H_2SO_4$$

An earlier method, which currently is no longer practiced commercially, involved oxidation of phenyl hydrazine:



Hydrogen peroxide obtained this way may contain many impurities, depending on the process used. Such impurities are removed by ion exchange, solvent extraction, and distillation. Dilute solutions of H_2O_2 may be purified and concentrated by fractional distillation at reduced pressures.

Reactions

The most important reactions of hydrogen peroxide involve oxidation-reduction. It is a powerful oxidizing agent, both in acidic and basic solutions. Usually a 30% aqueous solution of H_2O_2 is used in oxidation. While oxidation with H_2O_2 in basic solution is fast, it is slow in acid solution. The half-reaction in acidic solution is:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2OE° = 1.78V$$

The half-reaction for the basic HO_2^- ion is

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \ E° = 0.87V$$

However, H_2O_2 will behave as a reducing agent only towards a very strong oxidizing agent, such as MnO_4^-:

$$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O$$

$$H_2O_2 + Cl_2 \rightarrow 2H^+ + 2Cl^- + O_2$$

H_2O_2 is more acidic than water in dilute aqueous solution. The equilibrium constant K at 20°C is about 1.5×10^{-12} for dissociation of H_2O_2 to H^+ and HO_2^- The pH of a 50% aqueous solution is 4.3.

Aqueous solution of H_2O_2 decomposes into water and oxygen upon boiling:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The reaction is exothermic, ΔH_{rxn} being –23.66 kcal. In basic solution, such decomposition occurs very rapidly. Also, decomposition is catalyzed rapidly by trace amounts of transition metals. In aqueous media, Fe^{2+} ion decomposes H_2O_2 forming $Fe^{III}(OH)_2^+$ and OH^- ions, while in acetonitrile a "ferryl" ion, FeO_2^{2+} is formed initially, but it reverts to Fe^{2+} ion. The reactions are:

$$Fe^{2+}(aq) + H_2O_2 \rightarrow Fe^{III}OH^{2+}(aq) + OH\bullet$$

$$Fe^{2+} + H_2O_2 \xrightarrow{CH_3CN} FeO^{2+} + H_2O$$

$$FeO^{2+} + H_2O_2 \rightarrow Fe^{2+} + O_2 + H_2O$$

(Cotton, F. A., G. Wilkinson, C. A. Murillo, and F. Bochmann. 1999. *Advanced Inorganic Chemistry*, 6th ed., New York: John Wiley).

Reaction with sulfuric acid yields monoperoxysulfuric acid. Reactions with many alkaline earth compounds yield peroxides of alkaline earth metals:

$$H_2O_2 + BaCl_2 \rightarrow BaO_2 + 2HCl$$

$$H_2O_2 + Ba(OH)_2 \rightarrow BaO_2 + 2H_2O$$

Hydrogen peroxide undergoes substitution reactions with alkyl halides forming an organic peroxy acid or peroxide, depending on reaction conditions and molar ratios of reactants. The mechanism of such reactions are very complex. These reactions may be represented in the following equations:

$$H_2O_2 + RCl \rightarrow ROOH + HCl$$

$$H_2O_2 + 2RCl \rightarrow ROOR + 2HCl$$

Reactions with carboxylic acids yield peroxy acids:

$$\underset{\text{(carboxylic acid)}}{RC({=}O)OH} + H_2O_2 \rightarrow \underset{\text{(peroxy acid)}}{RC({=}O)OOH} + H_2O$$

Reaction with acetyl chloride yields diacetyl peroxide. Similar diacyl peroxides are formed from other acyl chlorides:

$$2CH_3COCl + H_2O_2 \rightarrow CH_3C—O—O—C—CH_3 + 2HCl$$

Reactions with ketones yield ketone peroxides. For example, with methyl ethyl ketone, the product is methyl ethyl ketone peroxide, which probably is a mixture of monomeric and polymeric products of peroxidic structure.

These organic peroxides are sensitive to shock and heat and require careful handling.

Hazard

Hydrogen peroxide is a strong oxidizing agent. Concentrated solutions, even a 30% aqueous solution, should be handled carefully. The compound decomposes violently in the presence of trace impurities. Inhibitors are, therefore, added at trace levels to prevent decomposition. Explosion can occur when concentrated solutions are heated or brought in contact with a number of organic substances that are readily oxidizable or that form organic peroxides, such as alcohols, aldehydes, ketones, anhydrides, and carboxylic acids (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons). Also, reactions with metals, metal alloys, a number of metal salts and oxides, and concentrated mineral acids can proceed to explosive violence.

HYDROGEN SELENIDE

[7783-07-5]
Formula: H_2Se; MW 80.98

Uses

Hydrogen selenide is used in preparation of metal selenides and organoselenium derivatives. It also is used in doping mix for semiconductor applications.

Physical Properties

Colorless gas; disagreeable odor; flammable; gas density 3.553 g/L; liquefies at –41.25°C; liquid density 2.12 g/mL at –42°C; freezes at –65.73°C; critical temperature 137.85°C; critical pressure 88.0 atm; soluble in water, carbon disulfide and phosgene; pK_a 3.89 and 11.0 at 25°C, respectively, for the first and second replaceable hydrogen.

Thermochemical Properties

$\Delta H_f°$	7.10 kcal/mol
$\Delta G_f°$	3.80 kcal/mol
S°	52.34 cal/degree mol
C_ρ	8.29 cal/degree mol
ΔH_{vap}	4.71 kcal/mol

Preparation

Hydrogen selenide may be synthesized directly from elements by heating at elevated temperatures. It is prepared by heating hydrogen at 440°C with either selenium metal in a sealed tube or with selenium vapor over pumice stone:

$$H_2 + Se \xrightarrow{440^\circ C} H_2Se$$

Alternatively, the compound may be prepared by treating an alkali metal selenide with hydrochloric acid during mild heating:

$$NaSe + 2HCl \xrightarrow{heat} H_2Se + NaCl$$

Reactions

Heating with oxygen at elevated temperatures decomposes hydrogen selenide forming selenium oxides and water:

$$2H_2Se + 3O_2 \xrightarrow[\text{}]{\text{elevated temperatures}} 2SeO_2 + 2H_2O$$

$$H_2Se + 2O_2 \xrightarrow{\text{elevated temperatures}} SeO_3 + H_2O$$

Hydrogen selenide reacts with most metals forming metal selenides with the liberation of hydrogen:

$$H_2Se + Zn \rightarrow ZnSe + H_2$$

Metal oxides are converted to metal selenides on heating:

$$H_2Se + ZnO \xrightarrow{heat} ZnSe + H_2O$$

Analysis

Elemental composition: H 2.49%, Se 97.51%. The gas may be analyzed by GC using a TCD, FID or a flame photometric detector. The compound may be identified by GC/MS: the molecular ions have masses 82 and 80. The compound may be absorbed in water and the solution analyzed for elemental selenium by flame or furnace atomic absorption—or by ICP atomic emission spectrophotometry.

Hazard

Dangerously toxic by inhalation. Exposure can cause injury to lungs and liver; pneumonitis, and strong irritant actions on skin, eyes, and mucous membranes. Other effects are garlic odor of breath, nausea and dizziness. A few minutes exposure to 50-100 ppm concentration of this gas in the air can be lethal to humans. LC_{L0} inhalation (rat): 20 mg/m^3/1 hr.

Hydrogen selenide is flammable, forming an explosive mixtures with air.

HYDROGEN SULFIDE

[7783-06-4]
Formula: H_2S; MW 34.08
Synonyms: sulfur hydride; sulfureted hydrogen

Occurrence and Uses

Hydrogen sulfide occurs in natural gas. It also is found in many sewer gases. It is a by-product of many industrial processes. Trace amounts of dissolved H_2S are found in wastewaters in equilibrium with dissolved sulfides and hydrosulfides. It also is found in volcanic eruptions, hot springs and in troposphere. The average concentration of H_2S in the air is about 0.05 ppb.

The most important applications of hydrogen sulfide involve the production of sodium sulfide and other inorganic sulfides. Hydrogen sulfide obtained as a by-product often is converted into sulfuric acid. It also is used in organic synthesis to make thiols or mercaptans. Other applications are in metallurgy for extracting nickel, copper, and cobalt as sulfides from their minerals; and in classical qualitative analytical methods for precipitation of many metals (see Reactions). It also is used in producing heavy water for nuclear reactors.

Physical Properties

Colorless gas; characteristic odor of rotten eggs; odor threshold 1ppm; sweetish taste; fumes in air; flammable gas, burns with a pale blue flame; refractive index at 589.3nm, 1.000644 at 0°C and 1 atm; density 1.539 g/L at 0°C; critical temperature 100.4°C; critical pressure 88.9 atm; liquefies at –60.7°C; solidifies at –85.5°C; velocity of sound 289 m/sec in H_2S gas; slightly soluble in water (0.4% at 20°C); pH of a saturated aqueous solution 4.5; slightly acidic; diffusivity in water at 16°C, $1.77x10^{5}$ cm^2/sec; soluble in carbon disulfide, methanol, acetone; very soluble in N-methylpyrrolidinone and alkanolamines (salt formation occurs: salt dissociates on heating); liquid H_2S dissolves sulfur and SO_2.

Thermochemical Properties

$\Delta H_f°$	–4.93 kcal/mol
$\Delta G°$	–8.02 kcal/mol
$S°$	49.16 cal/degree mol
C_ρ	8.18 cal/degree mol
Thermal conductivity (15°C)	$33.3x10^{-6}$ cal/sec.cm^2.°C/cm

Production

Hydrogen sulfide may be prepared conveniently in the laboratory in a Kipp apparatus by the reaction of iron(II) sulfide or zinc sulfide with dilute hydrochloric or sulfuric acid:

$$ZnS + 2HCl \rightarrow H_2S + ZnCl_2$$

A steady supply of hydrogen sulfide may be maintained by adding acid from time to time.

H_2S is produced in large scale by several processes, which are:

1. Refining crude oil by hydrodesulfurization. The crude oil contains varying amounts of sulfur that may range from 0.05 to about 5%. The sulfur-rich fractions, the coke-distillate and the gas-oil fractions of the crude oil are passed through a fixed-bed catalyst along with hydrogen.
2. It also is produced as a by-product by hydrodesulfurization of coal or liquefaction of coal.
3. It also is obtained by the reaction of methane with sulfur vapor to produce carbon disulfide which on hydrolysis yields H_2S:

$$CH_4 + 2S \xrightarrow{\text{high temperature}} CS_2 + 2H_2$$

$$CS_2 + 2H_2O \xrightarrow{\text{high temperature}} 2H_2S + CO_2$$

4. Heating hydrogen and sulfur vapor at 500°C in the presence of a catalyst, such as, bauxite or cobalt molybdate, which produces a high purity H_2S:

$$H_2 + S \xrightarrow[\text{catalyst}]{500°C} H_2S$$

Reactions

There are four types of H_2S reactions: decomposition, precipitation, oxidation, and organic addition.

Thermal dissociation of H_2S is rapid above 850°C, producing hydrogen and sulfur. The reaction is endothermic.

$$2H_2S \xrightarrow{\rangle 850^\circ C} 2H_2 + S_2$$

The dissociation also is rapid below this temperature (between 450°C to 850°C), however, only in the presence of a catalyst, such as silica, platinum sulfide or cobalt molybdate. Other sulfur species are also produced in the reaction.

Hydrogen sulfide forms precipitates of several metal sulfides when passed through an aqueous solution of metal salts. Under acid conditions, several metals including arsenic, antimony, bismuth, cadmium, copper, lead, mercury, and tin are precipitated as their sulfide; e.g.;

$$Cd^{2+}(aq) + 2Cl^{-}(aq) + H_2S\ (g) \xrightarrow{acid} CdS\ (s) + 2H^{+}(aq) + 2Cl^{-}(aq)$$

Under ammoniacal conditions, iron, cobalt, nickel, zinc and manganese precipitate as sulfides.

$$NaOH + H_2S \xrightarrow{base} NaHS + H_2O$$

$$2NaOH + H_2S \xrightarrow{base} Na_2S + 2H_2O$$

$$Na_2CO_3 + H_2S \xrightarrow{base} NaHS + NaHCO_3$$

In the presence of moisture at ordinary temperatures, H_2S reacts with some metals, such as copper and silver, forming sulfides:

$$4Ag + 2H_2S + O_2 \xrightarrow{moisture} 2Ag_2S + 2H_2O$$

Hydrogen sulfide undergoes thermal or catalytic oxidation with oxidizing agents forming sulfur, sulfur oxides, or sulfur derivatives. The products formed depend on reaction conditions and the nature of oxidizing agents. Combustion in air in the presence of flame primarily produces sulfur dioxide:

$$2H_2S + 3O_2 \xrightarrow{\text{high temperatures}} 2SO_2 + 2H_2O$$

Sulfur trioxide is a minor product in such oxidation:

$$H_2S + 2O_2 \rightarrow SO_3 + H_2O$$

When a mixture of H_2S and SO_2 gases are passed over a catalyst such as silica gel at elevated temperatures, sulfur and water are formed:

$$2H_2S + SO_2 \xrightarrow[\text{high temperature}]{\text{catalyst}} 3S + 2H_2O$$

Stronger oxidizing agents such as hydrogen peroxide or ozone readily oxidize H_2S forming sulfur and various other sulfur products. For example, H_2O_2 reacts with H_2S under neutral conditions forming sulfur and water:

$$H_2S + H_2O_2 \rightarrow S + 2H_2O$$

In alkaline solution however, the reactions are more complex and the products include thiosulfate and sulfate.

Oxidation with ozone in aqueous conditions yields sulfur and sulfuric acid:

$$3H_2S + O_3 \rightarrow 3S + 3H_2O$$

$$S + O_3 + H_2O \rightarrow H_2SO_4$$

In aqueous solution, H_2S and iodine react to form sulfur and hydriodic acid:

$$H_2S + I_2 \rightarrow S + 2HI$$

In gaseous phase, chlorine and H_2S react at equimolar ratio, forming sulfur and hydrogen chloride:

$$H_2S + Cl_2 \rightarrow S + 2HCl$$

In excess chlorine, the product is sulfur dichloride:

$$H_2S + 2Cl_2 \rightarrow SCl_2 + 2HCl$$

In aqueous solution, however, chlorine in higher molar ratios oxidizes H_2S to sulfuric acid:

$$H_2S + 4Cl_2 + 4H_2O \rightarrow H_2SO_4 + 8HCl$$

In aqueous solution nitric acid also oxidizes H_2S to sulfuric acid.

$$H_2S + 2HNO_3 \rightarrow H_2SO_4 + 2HNO_2$$

Reaction with concentrated sulfuric acid yields sulfur and sulfur dioxide:

$$H_2S + H_2SO_4 \rightarrow S + SO_2 + 2H_2O$$

In aqueous solutions, metal ions in their higher oxidation states oxidize H_2S, forming a lower-valence sulfide and sulfur:

$$2CoCl_3 + H_2S \rightarrow 2CoS_2 + S + 6HCl$$

$$2Fe(NO_3)_3 + 3H_2S \rightarrow 2FeS + S + 6HNO_3$$

Hydrogen sulfide also reacts with many types of organic substances. Reaction with methanol at high temperatures in the presence of an acidic catalyst yields methanethiol and dimethylsulfide:

$$H_2S + CH_3OH \xrightarrow[\text{heat}]{\text{acid catalyst}} CH_3SH + H_2O$$

$$CH_3SH + CH_3OH \xrightarrow[\text{heat}]{\text{acid catalyst}} CH_3SCH_3 + H_2O$$

H_2S adds to olefins in the presence of acid catalysts forming thiols (mercaptans):

$$\underset{\text{(propene)}}{H_2S + CH_3CH{=}CH_2} \xrightarrow{\text{acid catalyst}} \underset{\text{(2-propanethiol)}}{(CH_3)_2CHSH}$$

In the presence of a free radical initiator, the product is 1-propanethiol:

$$\underset{\text{(propene)}}{H_2S + CH_3CH{=}CH_2} \xrightarrow[\text{initator}]{\text{free radical}} \underset{\text{(1-propanethiol)}}{CH_3CH_2\,CH_2SH}$$

Reaction with cyanamide in the presence of basic catalyst yields thiourea:

$$H_2S + NH_2CN \xrightarrow{\text{basic alumina}} \underset{\text{(thiourea)}}{NH_2CSNH_2}$$

Under similar conditions, reactions with nitriles yield thioamides:

$$H_2S + CH_3CN \xrightarrow{\text{basic catalyst}} \underset{\text{(thioacetamide)}}{CH_3CSNH_2}$$

Reaction with chlorobenzene at elevated temperatures yields thiophenol as major product and dibenzyl sulfide in smaller amounts:

$$H_2S + C_6H_5Cl \xrightarrow{600^\circ C} \underset{\text{(thiophenol)}}{C_6H_5SH} + HCl$$

$$H_2S + 2C_6H_5Cl \xrightarrow{600^\circ C} \underset{\text{(dibenzyl sulfide)}}{C_6H_5SC_6H_5} + 2HCl$$

Analysis

Elemental composition: H 5.92%, S 94.08. Hydrogen sulfide may be distinguished by its characteristic odor. The gas turns a paper soaked in lead acetate solution black. Many infrared sensors are commercially available for *in-situ* measurements of H_2S. It may be monitored semiquantitatively by Draeger tubes. It also may be analyzed by GC following trapping over molecular sieves and thermal desorption. Either a flame photometric detector or a sulfur chemiluminescence detector may be used for GC analysis. It may be separated on a capillary column such as Carboxen 1006 PLOT ™ or SPB-1 SULFUR™ (*Supelco Catalog 1999*: Supelco Inc., Bellefonte, PA).

Hazard

Hydrogen sulfide is a highly toxic and flammable gas. A 5-minute exposure to 1,000 ppm concentration in air can be fatal to humans (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley). The symptoms are headache, nausea, nervousness, cough, eye irritation, and insomnia. High doses can produce unconsciousness and respiratory paralysis.

Hydrogen sulfide forms explosive mixtures with air; the LEL and UEL are 4.3 and 45.0% by volume in air, respectively. Its autoignition temperature is 260°C. Its reaction with soda-lime in oxygen can be explosive. Reactions with strong oxidizing agents can progress to incandescence.

HYDROGEN TELLURIDE

[7783-09-7]
Formula: H_2Te; MW 129.62

Uses

Hydrogen telluride is used in preparation of telluride salts.

Physical Properties

Colorless gas; strong garlic-like odor; stable to light when dry but undergoes photochemical decompostion in the presence of moisture and dust; density 5.68 g/L; liquefies to a colorless unstable liquid at –2°C, decomposed by light; liquid density 2.57 g/mL at –20°C; solidifies at –49°C; soluble in water, alcohol and alkalies; pKa 2.6 (for first dissociation constant at 18°C) and 11.0 (the dissociation constant at 25°C) for the second replaceable hydrogen.

Thermochemical Properties

$\Delta H_f°$	23.80 kcal/mol
ΔH_{vap}	4.59 kcal/mol

Preparation

Hydrogen telluride is prepared by the reaction of aluminum telluride, Al_2Te_3 with hydrochloric acid:

$$Al_2Te_3 + 6HCl \rightarrow 3H_2Te + 2AlCl_3$$

It also may be prepared by electrolysis of a 50% sulfuric acid solution using a tellurium cathode.

Analysis

Elemental composition H 1.56%, Te 98.44%. The gas is identified by its physical properties and measured by chemical analysis. Two most confirmatory methods recommended here are (1) GC/MS, the characteristic mass ions should be in the range 126 to 132, and (2) furnace-AA or ICP emission spectroscopic analysis for metalic tellurium. For the AA analysis, hydrogen telluride gas should be passed through water and the solution acidified and analyzed for tellurim. Hydrogen may be measured by the classical combustion method involving oxidation to form water, followed by gravimetry.

Toxicity

Hydrogen telluride is a highly toxic gas and a strong irritant to eyes, nose and upper respiratory tract. Toxic properties are similar to hydrogen selenide. Inhalation can cause damage to lungs, liver and spleen. Short exposure to a high concentration can be lethal.

HYDROXYLAMINE

[7803-49-8]
Formula: H_2NOH; MW 33.03
Synonym: oxammonium

Uses

Hydroxylamine is used as a reducing agent in many inorganic and organic synthetic reactions. Other applications of this compound include purification of aldehydes and ketones; dehairing of hides; as an antioxidant for fatty acids; to stabilize lower oxidation states of metal ions for analysis; and in photography.

Physical Properties

White crystalline solid; orthogonal plates or needles; unstable; density 1.21 g/cm^3 at 20°C; melts at 33°C; vaporizes at 58°C; very soluble in water, liquid ammonia and lower alcohols; sparingly soluble in most other organic solvents; decomposes in hot water; pK_a 5.94 at 25°C.

Thermochemical Properties

$\Delta H_f°$ –27.29 kcal/mol

Preparation

Hydroxylamine is unstable as a free base. It is prepared from hydroxylamine hydrochloride, $NH_2OH \cdot HCl$, which is obtained by electrolytic reduction of ammonium chloride solution. The hydrochloride undergoes alkaline decomposition to hydroxylamine, which is collected by vacuum distillation.

Analysis

Elemental composition: H 9.15%, N 42.41%, O 48.44%. Hydroxylamine may be measured by coulometric titration to a potentiometric end point using a coulometric titration cell. A standard solution of bromine may be used as oxidizer in the redox reaction. (Skoog, D. A., D. M. West, and F. J. Holler. 1992. *Fundamentals of Analytical Chemistry*, 6th ed. pp. 467, Orlando: Saunders College Publishing)

Hazard

Hydroxylamine is a poison by oral, subcutaneous, and intraperitoneal routes, the systemic effect being methemoglobinemia. It also is corrosive to skin and an irritant to eyes and respiratory tract.

Hydroxylamine also is a fire hazard. It may ignite spontaneously when placed on paper, and it explodes when heated in air above 70°C. It ignites or explodes when combined with oxidizing agents or alkali metals.

HYDROXYLAMINE HYDROCHLORIDE

[5470-11-1]
Formula: $H_2NOH \cdot HCl$; MW 69.491
Synonym: oxammonium hydrochloride

Uses

Hydroxylamine hydrochloride is used for controlled reduction reactions. It is used in organic synthesis; as an antioxidant for fatty acids; and in photographic developer solutions.

Physical Properties

Colorless monoclinic crystals; hygroscopic; decomposes slowly in moist air; density 1.67 g/cm^3 at 17°C; melts at 151°C (decomposes); highly soluble in water (84g/100g at 20°C); soluble in lower alcohols and glycols; pH of 0.1 molar solution 3.4.

Preparation

Hydroxylamine hydrochloride is prepared by electrolytic reduction of ammonium chloride.

Analysis

Elemental composition: H 5.80%, N 20.16%, Cl 51.02%, 23.02. The aqueous solution may be measured by coulometric titration (See Hydroxylamine).

Toxicity

Hydroxylamine hydrochloride is moderately toxic by ingestion and subcutaneous and intraperitoneal administration. The oral LD_{50} in mice is in the range 400 to 450 mg/kg.

HYDROXYLAMINE SULFATE

[10039-54-0]
Formula: $(H_2NOH)_2 \cdot H_2SO_4$; MW 164.14
Synonym: oxammonium sulfate

Uses

Most applications of this compound are similar to those of the hydrochloride. It is primarily used as a reducing agent for organic synthesis and chemical analysis. Other uses are to purify aldehydes and ketones; to inhibit oxidation of fatty acids; in dehairing hides; in synthesis of oximes for paints and varnishes; in photographic developer solutions; in rust proofing; and as a catalyst.

Physical Properties

Colorless, crystalline solid; melts at 177°C (decomposes); very soluble in water; slightly soluble in alcohol.

Preparation

Hydroxylamine sulfate may be prepared by mixing stoichiometric amounts of hydroxylamine and sulfuric acid. It also may be prepared by electrolytically reducing an aqueous solution of ammonium sulfate.

Analysis

Elemental composition: H 4.92%, N 17.06%, O 58.49%, S 19.59%. The concentration of hydroxylamine sulfate in aqueous solution may be measured by coulometric titration against a standard solution of oxidizing agent, such as bromine (See Hydroxylamine). Sulfate anion may be measured by ion chromatography.

HYPOCHLOROUS ACID

[7790-92-3]
Formula: $HOCl$; MW 52.460
Hypochlorous acid exists only in dilute aqueous solution. It is found in many wastewaters that have been subjected to chlorination.

Uses

Hypochlorous acid is used in bleaching fibers and textiles; as an antiseptic; and as a disinfectant for purification. It also is used as a chlorinating agent for aliphatic and aromatic hydrocarbons.

Physical Properties

Greenish-yellow aqueous solution; unstable; weak acid, pK_a 7.40 at 25°C; soluble in water.

Thermochemical Properties

$\Delta H_f°$ (gas)	–18.81 kcal/mol
$\Delta G_f°$ (gas)	–15.80 kcal/mol
S° (gas)	56.57 cal/degree mol
C_ρ (gas)	8.89 cal/degree mol

Preparation

Hypochlorous acid is obtained by dissolving chlorine in water, or by adding bleaching powder or sodium hypochlorite to water. A better method of production is passing chlorine gas into a well-agitated suspension of mercuric oxide:

$$2Cl_2 + 2HgO + H_2O \rightarrow HgO \cdot HgCl_2 + 2HOCl$$

or by distilling chlorine hexahydrate and mercuric oxide at low pressure:

$$2Cl_2 \cdot 6H_2O + HgO \rightarrow 2HOCl + HgCl_2 + 5H_2O$$

The latter process can yield a 25% acid solution.

Hypochlorous acid also may be obtained by hydrolysis of chlorine monofluoride:

$$ClF + H_2O \rightarrow H^+ + F^- + HOCl$$

The above reaction may be explosive and is not recommended for preparing hypochlorous acid.

Reactions

Chlorine gas is slightly soluble in water (~6.45 g/L or 0.091 mol/L at 25°C). A disproportion reaction occurs rapidly in water forming hypochlorous acid:

$$Cl_2\,(aq) \rightarrow H^+ + Cl^- + HOCl$$

The equilibrium constant, K, for this reaction at 25°C is $4.2 \times 10^{-4.}$ The standard redox potentials for the following two reactions:

$$H^+ + HOCl + e^- \rightarrow \tfrac{1}{2}Cl_2\,(g) + H_2O$$

$$2H^+ + 2Cl^- + \tfrac{1}{2}O_2 \rightarrow Cl_2 + H_2O$$

are 1.63V and –0.13V, respectively. A saturated solution of chlorine at 25°C consists of about 33% hypochlorous acid.

The acid is unstable in water. It reacts with hypochlorite ion forming chlorate:

$$2HOCl + OCl^- \rightarrow ClO_3^- + 2H^+ + 2Cl^-\text{, dissociation constant } 3.4 \times 10^{-8.}$$

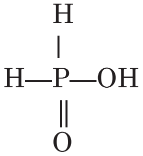
Hypochlorous acid is a strong oxidizing agent which can oxidize many reducing agents, particluarly in acid solution. The reaction can be vigorous to violent, depending on reaction temperature and nature of the oxidants.

Analysis

The total free chlorine in wastewaters as measured by colorimetric techniques constitutes both the dissolved molecular chlorine, hypochlorite ion, OCl^-, and hypochlorous acid. An equilibrium exists between these species, the concentrations of which depend on the temperature and pH of the wastewater. Concentration of the hypochlorous acid may be estimated from the K value or from the ratio (33% of the measured concentration of "free" chlorine). The "free" chlorine may be measured by amperometric titration after the addition of a phosphate buffer solution to produce a pH between 6.5 and 7.5. The sample is titrated against a standard solution of phenylarsine oxide. Alternatively, the syringaldazine (3,5-dimethoxy-4-hydroxybenzaldazine) colorimetric test may be performed. This color-forming reagent in 2-propanol yields a colored product with "free" chlorine, the absorbance of which may be measured by a spectrophotometer at 530nm (APHA, AWWA, WEF, 1999. *Standard methods for the Examination of Water and Wastewaters*, Washington DC: American Public Health Association).

HYPOPHOSPHOROUS ACID

[6303-21-5]
Formula: H_3PO_2; MW 65.997
Structure:



$$\mathrm{H{-}\overset{\displaystyle H \atop |}{\underset{\displaystyle \| \atop O}{P}}{-}OH}$$

Synonym: phosphinic acid

Uses

Hypophosphorous acid is used to prepare hypophosphite salts and in electroplating baths.

Physical Properties

Colorless deliquescent crystals or oily liquid; sour odor; density 1.493 g/cm^3; melts at 26.5°C; boils at 130°C; very soluble in water, alcohol and ether; density of a 50% aqueous solution is 1.13 g/mL.

Thermochemical Properties

$\Delta H_f°$ (cry)	–144,50 kcal/mol
$\Delta H_f°$ (liq)	–142.30 kcal/mol
ΔH_{fus}	2.32 kcal/mol

Preparation

Hypophosphorous acid may be prepared by various methods:

1. Boiling white phosphorus with calcium hydroxide:

$$P_4 + 4Ca(OH)_2 + 8H_2O \rightarrow 4Ca(H_2PO_2)_2 + 4H_2$$

The calcium salt is soluble in water. Treatment with sulfuric acid yields the hypophosphorous acid:

$$(H_2PO_2)_2Ca + H_2SO_4 \rightarrow 2H_3PO_2 + CaSO_4$$

The product mixture is filtered to remove insoluble $CaSO_4$. The aqueous solution of hypophosphorous acid is concentrated under reduced pressure. Concentrated baryta water may be used instead of calcium hydroxide.

2. By treating sodium hypophosphite, NaH_2PO_2 with an ion-exchange resin. The sodium salt may be produced by boiling white phosphorus with a solution of sodium hydroxide, a reaction similar to (1) above.

3. By oxidation of phosphine with an aqueous iodine solution:

$$PH_3 + 2I_2 + 2H_2O \rightarrow H_3PO_2 + 4HI$$

The above method may be considered safer than that involving heating white phosphorus with an alkali.

Hypophosphorous acid must be stored below 50°C. It is sold commercially as an aqueous solution at various concentrations.

Reactions

Pure hypophosphorous acid is a monobasic acid, pKa=1.2. It reacts with bases forming the corresponding salts:

$$H_3PO_2 + NaOH \rightarrow NaH_2PO_2 + H_2O$$

It decomposes rapidly on heating above 100°C to orthophosphoric acid and phosphine:

$$2H_3PO_2 \xrightarrow{100^\circ C} H_3PO_4 + PH_3$$

The phosphorus atom in hypophosphorus acid is in the lowest oxidation state, +1. The compound is, therefore, a powerful reducing agent. It combines readily and often explosively with oxidizing agents. For example, the acid reduces mercury(II) nitrate or mercury(II) oxide into mercury metal violently.

Analysis

Elemental composition: H 4.58%, P 46.94%, O 48.49%. The hypophosphite ion may be oxidized to orthophosphate by careful oxidation. The orthophophate, PO_4^{3-} ion, may be measured by colorimetry either by using ammonium molybdate and vanadium (yellow color), ammonium molybdate and stannous chloride (blue color), or ammonium molybdate, potassium antimonyl tartrate and asorbic acid (an intense blue color). Absorbances of the solution are read at 400 (or 470), 650 (or 690) and 880 nm, respectively. Hypophosphite ion alternatively may be identified by ion chromatography.

Hazard

The compound is a very powerful reducing agent. Reactions with oxidizing agents may progress to explosive violence (See Reactions). Also, heating this compound above 100°C can produce toxic phosphine, which also may explode in air.

INDIUM

[7440–74–6]

Symbol In; atomic number 49; atomic weight 114.82; a Group IIIA (Group 13) metallic element; electron configuration $[Kr]4d^{10}5s^25p^1$; most common valence state: +3; also exhibits valence +2 and +1; two stable isotopes, In-113 (4.23%), In-115 (95.77%)

History, Occurrence, and Uses

Indium was discovered by Reich and Richter in 1863 in Germany during spectroscopic observations of local zinc ores. The new element was named indium after its characteristic indigo blue spectral lines. Although widely distributed in nature, its concentration is very low, estimated to be about 0.1 mg/kg in the earth's crust. It is found mostly in zinc sulfide ores and to a lesser extent in sulfide ores of iron and copper. The metal does not occur in free elemental form in nature.

A major use of indium metal is in production of bearings for automobile and aircraft engines. Addition of indium improves strength and hardness of bearings and their resistance to corrosion and fatigue. Electroplated coatings of indium are applied onto aluminum for electrical wiring and as indium oxide coatings in sodium-vapor lamps. In the semiconductor industry, In is used as a doping agent to obtain ρ-type germanium. Other applications are in glass-to-metal seals; in electro luminescent panels; as conductive coatings on glasses and ceramics; and in nuclear reactor control rods.

Physical Properties

Silver-white lustrous soft metal; highly malleable and ductile; face-centered tetragonal crystalline structure (a=4.583Å, c=4.936Å); diamagnetic metal; density 7.31 g/cm^3 at 20°C; melts at 156.6°C; vaporizes at 2,072°C; electrical resistivity 8.4 x 10^{-6} ohm-cm; superconducting at 3.38°K (–269.8°C); hardness 0.9 (Brinnel); tensile strength 26.19 atm; modulus of elasticity 10.8 GPa; thermal neutron absorption cross-section 190±10 barns; soluble in acids.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	58.15 kcal/mol
$\Delta G_f°$ (gas)	49.88 kcal/mol
S° (gas)	41.54 cal/degree mol
C_ρ (gas)	4.97 cal/degree mol
ΔH_{fus}	0.784 kcal/mol
ΔH_{vap}	13.28 kcal/mol
Coeff. linear expansion (at 0 to 100°C)	25 x 10^{-6}/°C
Thermal conductivity	71.1 W/m.K

Production

Indium may be recovered from zinc ores by several patented processes. Usually it is recovered from residues obtained from zinc extraction. The residues, slags, fume, or dusts from zinc smelting or lead-zinc smelting are treated with a mineral acid. Other steps involved in recovery often vary, but mostly use solvent extraction and precipitation steps. In some processes, treatment with caustic soda yields indium hydroxide. The hydroxide is calcined to obtain oxide, which then is reduced with hydrogen at elevated temperatures to obtain the metal. Distillation or electrolysis are the final steps to high purity metal.

Reactions

Indium is stable in air at ambient temperature. At red heat, it oxidizes to indium trioxide, In_2O_3. Three other oxides of indium are known: the suboxide, In_2O [12030-22], monoxide, InO [12136-26-4] and the sesquioxide, In_3O_4 [66525-54-0], which is a mixture of the trioxide and monoxide.

The most common valence state of indium is +3. However, +2 and +1 valence states also exist. Chemical properties of indium are similar to aluminum. Its redox potential is –0.34V. When heated with chlorine at 200°C, indium becomes a dichloride:

$$In + Cl_2 \rightarrow InCl_2$$

However, in the presence of excess chlorine, indium trichloride, $InCl_3$ is formed:

$$2In + 3Cl_2 \rightarrow 2InCl_3$$

Similar reactions occur with other halogens. Monohalides of indium include chloride, bromide and iodide. Monohalides are obtained by passing indium trihalides over heated indium:

$$In + InCl_3 \rightarrow InCl + InCl_2$$

Indium dissolves in mineral acids. Concentration or evaporation of the solution produces corresponding salts. With sulfuric acid, it forms indium trisulfate, $In_2(SO_4)_3$ and indium hydrogen sulfate, $In(HSO_4)_2$. The latter salt is obtained upon concentration of trisulfate solution. With nitric acid, the salt is indium nitrate trihydrate, $In(NO_3)_3 \cdot 3H_2O$ [13770-61-1] which on dehydration yields monohydrate, $In(NO_3)_3 \cdot H_2O$.

The metal combines with sulfur and phosphorous on heating, forming the sulfide and phosphide salts, respectively. Metalloid elements, such as arsenic, antimony, selenium and tellurium also combine with indium at elevated temperatures, forming their respective binary salts.

Indium combines with several metals, such as sodium, potassium, magnesium, iron, palladium, platinum, lanthanium and cerium, forming semiconductor-type intermetallic compounds.

Indium reacts with Grignard reagent, forming indium trialkyls which are highly flammable and less stable than the corresponding aluminum trialkyls:

$$2In + 6CH_3MgBr \rightarrow 2In(CH_3)_3 + 3MgBr_2$$

The trialkyls also may be obtained by reaction of mercury dialkyls with indium:

$$2In + 3Hg(C_2H_5)_2 \rightarrow 2In(C_2H_5)_3 + 6Hg$$

Analysis

Indium produces characteristic lines in the indigo-blue region and may be detected by spectroscopic analysis. At trace concentrations In may be determined by flame-AA, furnace-AA, ICP-AES, x-ray fluorescence, or neutron activation analysis.

INDIUM ANTIMONIDE

[1312-41-0]
Formula: InSb; MW 236.58

Uses

Indium antimonide is used in semiconductor and Hall effect devices, and infrared detectors.

Physical Properties

Black cubic crystal; zincblende structure; density 5.775 g/cm^3; melts at 525°C; density of melt 6.48 g/mL; dielectric constant 15.9; insoluble in water.

Thermochemical Properties

$\Delta H_f°$	–7.30 kcal/mol
$\Delta G_f°$	–6.10 kcal/mol
S°	20.6 cal/degree mol
C_ρ	11.82 cal/degree mol

Preparation

Indium antimonide may be synthesized from its elements by fusion of stoichiometric amounts of indium and antimony at elevated temperatures in an evacuated, sealed ampule.

Analysis

Elemental composition: In 48.53%; Sb 51.47%. The compound may be analysed by x-ray analysis. Also, both indium and antimony may be measured by AA or ICP spectrophotometry after digestion with aqua regia. The metals may be measured nondestructively by x-ray fluorescence technique.

INDIUM TRIOXIDE

[1312-43-2]
Formula: In_2O_3; MW 277.63
Synonym: indium(III) oxide

Uses

Indium trioxide is used to make special glasses and to impart yellow color to glass.

Physical Properties

Light-yellow powder; cubic crystal; occurs in both amorphous and crystalline forms; pale-yellow amorphous form converts to crystalline form on heating at higher temperatures; isomorphous with hematite, Fe_2O_3; density 7.18 g/cm^3; melts around 2,000°C; insoluble in water; amorphous form dissolves readily in mineral acids; crystalline form has low solubility in acids.

Thermochemical Properties

$\Delta H_f°$	–221.27 kcal/mol
$\Delta G_f°$	–198.54 kcal/mol
S°	24.90 cal/degree mol
C_ρ	21.99 cal/degree mol

Preparation

Indium trioxide may be obtained by heating indium in air or oxygen:

$$4In + 3O_2 \rightarrow 2In_2O_3$$

or by calcination of indium hydroxide, nitrate, or carbonate at elevated temperatures:

$$2In(OH)_3 \rightarrow In_2O_3 + 3H_2O$$

$$In_2(CO_3)_3 \rightarrow In_2O_3 + 3CO_2$$

Reactions

When heated with excess hydrogen at 450°C to 500°C, indium trioxide is reduced to indium metal:

$$In_2O_3 + 3H_2 \rightarrow 2In + 3H_2O$$

At lower temperatures or stoichiometrically lower amounts of hydrogen, lower oxides of indium are obtained:

$$In_2O_3 + 2H_2 \rightarrow In_2O + 2H_2O$$

Similar reactions occur with carbon monoxide and other reducing gases:

$$In_2O_3 + 3CO \rightarrow 2In + 3CO_2$$

$$In_2O_3 + 2CO \rightarrow In_2O + 2CO_2$$

Indium trioxide dissolves in sulfuric acid, forming indium trisulfate:

$$In_2O_3 + 2H_2SO_4 \rightarrow In_2(SO_4)_3 + 3H_2O$$

The oxide dissolves in acetic acid, forming indium triacetate:

$$In_2O_3 + 3CH_3COOH \rightarrow (CH_3COO)_3In + 3H_2O$$

Analysis

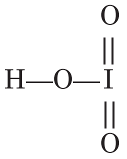
Elemental composition: In 82.71%, O 17.29%. Indium trioxide may be digested with nitric acid, diluted appropriately and analyzed for indium by AA or ICP. It may be identified by x-ray diffraction. The oxide may be heated with excess hydrogen and water formed may be analyzed quantitatively by gravimetry or the Karl-Fisher method.

IODIC ACID

[7782-68-5]

Formula: HIO_3; MW175.93; iodine in +5 oxidation state; solid acid contains $(HO)IO_2$ molecules joined by hydrogen bonding; a monoprotic acid

Structure:



$$\mathrm{H{-}O{-}}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{\mathrm{I}}}$$

A pyro- form of the acid also is known. That has the formula HI_3O_8.

Uses

Aqueous solutions of iodic acid serve as strong oxidizing agents. The acid also is used in redox titrations.

Physical Properties

White stable crystalline solid; rhombohedral crystals; occurs in two forms: the normal HIO_3, and pyroiodic acid HI_3O_8.

Preparation

Iodic acid may be prepared by the reaction of sulfuric acid with barium iodate. The solution is filtered to remove barium sulfate and then crystallized to obtain iodic acid:

$$Ba(IO_3)_2 + H_2SO_4 \rightarrow BaSO_4 + 2HIO_3$$

It also may be produced by oxidation of iodine with concentrated nitric acid:

$$3I_2 + 10HNO_3 \rightarrow 6HIO_3 + 10NO + 2H_2O$$

Also, iodic acid may be obtained by oxidation of iodine with chlorine in dilute acidic solutions:

$$I_2 + 5Cl_2 + 6H_2O \rightarrow 2HIO_3 + 10HCl$$

Another method of preparation involves oxidation of iodine with hydrogen peroxide:

$$I_2 + 5H_2O_2 \rightarrow 2HIO_3 + 4H_2O$$

It also may be prepared by treating hypoiodous acid with a base:

$$3HIO + 2OH^- \rightarrow HIO_3 + 2H_2O + I^-$$

Hypoiodous acid may be obtained by alkaline hydrolysis of iodine at pH 12:

$$I_2 + H_2O \rightarrow HIO + H^+ + I^-$$

Iodic acid dehydrates to iodine pentaoxide when heated at 180°C:

$$2HIO_3 \rightarrow I_2H_5 + H_2O$$

Iodic acid is a relatively weak monoprotic acid, the Ka value at 25°C is 1.6×10^{-1}. Several species have been detected in concentrated aqueous solutions, which include IO_3^-, H^+, HIO_3, $(HIO_3)_2$ and $(HIO_3)_3$. Its solution turns blue litmus red and then bleaches the litmus paper because of its strong oxidizing properties.

When heated with potassium iodate, potassium hydrogen iodate is formed:

$$HIO_3 + KIO_3 \rightarrow KH(IO_3)_2$$

An aqueous solution of iodic acid is a strong oxidizing agent. It liberates iodine from iodides:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \quad \text{or,}$$

$$HIO_3 + 5HI \rightarrow 3I_2 + 3H_2O$$

In an aqueous solution, iodic acid oxidizes hydrogen sulfide to sulfur:

$$2HIO_3 + 5H_2S \rightarrow I_2 + 6H_2O + 5S$$

The solid iodic acid reacts vigorously with sulfur, phosphorus and other nonmetals.

Analysis

Iodic acid can be analyzed by iodometric titration. Its acidic aqueous solution reacts with potassium iodide to liberate iodine (as shown above). Liberated iodine may be titrated against a standard solution of sodium thiosulfate using starch indicator. At the end point, the blue color of the solution decolorizes.

IODINE

[7553-56-2]

Symbol I: atomic number 53; atomic weight 126.905; a nonmetallic halogen element of Group VII A (Group 17); occurs as a diatomic molecule; atomic radius 1.33Å; ionic (I^-) radius 2.20Å; the I—I bond length is 2.66Å and bond energy is 36.1 kcal/mol; electron configuration $[Kr]4d^{10}5s^25p^5$; electronegativity 2.2; common valence –1; also exhibits valence states +1, +3, +5 and +7; natural isotope I-127; several radioisotopes are known that range in mass numbers from 117 to 139.

History, Occurrence, and Uses

Iodine was discovered in 1811 by French chemist, Bernard Courtois during the production of potassium nitrate for Napoleon's armies. It was recognized as a new element by Gay-Lussac who named it iodine.

Iodine is widely distributed in nature, found in rocks, soils and underground brines. An important mineral is lautarite, which is anhydrous calcium iodate found in nitrate deposits in Chile. The element also occurs in brown seaweeds, in seawater, and in many natural gas wells. Its concentration in the earth's crust is an estimated 0.5 mg/kg; and in seawater 0.06 mg/L.

Iodine is used in many dyes and as a colorant for foods and cosmetics. Its silver salt is used in photographic negative emulsions. Other industrial applications include dehydrogenation of butane and butylenes to 1,3-butadiene; as a catalyst in many organic reactions; in treatment of naphtha to yield high octane motor fuel; and in preparation of many metals in high purity grade, such as titanium, zirconium and hafnium.

Iodine is an essential nutrient element required for thyroid gland. It is added to salt and to animal feeds for the prevention of goiter. In medicine it is used as a therapeutic reagent for the treatment of various thyroid-related diseases. It also is used as an antiseptic. Radioactive isotopes of iodine are used for treating thyroid cancer, heart diseases including tachycardia, and as a tracer for diagnosing certain diseases.

An important application of iodine is in water purification and sanitation. It is used as a disinfectant in food-processing plants, dairies and restaurants. It is applied to disinfect municipal and other water supplies and swimming pools.

Physical Properties

Bluish-black orthorhombic crystals; refractive index 3.34; density of solid 4.933 g/cm^3 at 20°C; density of the element in liquid form at 120°C 3.96 g/cm^3; melts at 113.6°C to a black mobile liquid; the solid can be sublimed to vapor below its melting point; vapor pressure of solid at 25°C 0.3075 torr; vapor pressure at 113.6°C 90.5 torr; the liquid boils at 184.3°C giving violet vapors; vapor density 6.75 g/L; critical temperature 545.8°C; critical pressure 48.9 atm; critical volume 155 cm^3/mol; dielectric constant of solid 10.3 at 23°C and liquid 11.08 at 118°C; resistivity 5.85 x 10^6 ohm-cm at 25°C, and 1.10 x 10^5 ohm-cm at 140°C; slightly soluble in water, 0.33 g/L at 25°C; soluble in ethanol, carbon disulfide, benzene and chloroform, forming brown solutions; sulfur, selenium, metal iodides and many organic compounds dissolve in liquid iodine.

Thermochemical Properties

$\Delta H_f°$ (I_2 crystal)	0.0
$\Delta H_f°$ (I_2 gas)	14.91 kcal/mol
$\Delta H_f°$ (I gas)	25.53 kcal/mol
$\Delta G_f°$ (I_2 gas)	4.61 kcal/mol
$\Delta G_f°$ (I gas)	16.78 kcal/mol
S° (I_2 crystal)	27.75 cal/degree mol
S° (I_2 gas)	62.31 cal/degree mol
S° (I gas)	43.21 cal/degree mol
C_ρ (I_2 crystal)	13.00 cal/degree mol
C_ρ (I_2 gas)	8.82 cal/degree mol
C_ρ (I gas)	4.97 cal/degree mol
ΔH_{fus} (I_2 crystal)	3.71 kcal/mol
ΔH_{vap} (I_2 liquid)	9.94 kcal/mol
ΔH_{sublim} (I_2 crystal, at 113.6°C)	14.46 kcal/mol
Thermal conductivity (at 24.4°C)	0.421 W/(m.K)

Production

Iodine is produced in large scale from Chilean nitrate. Iodine occurs in this mineral as sodium iodate, $NaIO_3$. The iodate extract of the mineral becomes more concentrated in iodate after sodium nitrate crystallizes out. The mother liquor is then treated with sodium bisulfite solution to give sodium iodide:

$$2NaIO_3 + 6NaHSO_3 \rightarrow 2NaI + 3Na_2SO_4 + 3H_2SO_4$$

The solution becomes acidic due to the formation of sulfuric acid. This solution is treated with an equivalent amount of fresh iodate mother liquor. Iodide-iodate reaction in acid medium yields iodine:

$$5NaI + NaIO_3 + 3H_2SO_4 \rightarrow 3I_2 + 2Na_2SO_4 + 3H_2O$$

Iodine is separated by filtration or centrifugation, washed with water, dried and purified by sublimation.

In the United States and most parts of the world, iodine is obtained commercially from brine wells. Many subsurface brines have iodine concentrations in the range of 10 to 100 mg/L. Various extraction processes are known including: (i) precipitation with silver nitrate, (ii) oxidation with chlorine, and (iii) ion exchange. In the chlorine oxidation process, natural subsurface brine first is acidified with sulfuric acid and then treated with chlorine. Chlorine liberates iodine from the brine solution. Iodine is blown out into a countercurrent stream of air. It is dissolved in a solution of hydriodic acid and sulfuric acid by passing the iodine-enriched air through the solution. Treatment with sulfur dioxide reduces iodine to iodide. Iodine is finally recovered from the iodide solution in acid by oxidation with chlorine.

In the silver nitrate precipitation process, iodide in the brine is precipitated as silver iodide. The iodide is treated with iron to yield ferrous iodide. Passing chlorine through the ferrous iodide solution liberates iodine.

In the ion-exchange method, brine solution is passed through an anion-exchange resin. Iodide (and polyiodide) anions from the solution adsorb onto the resin from which they are desorbed by treatment with caustic soda solution. The resin is treated with sodium chloride solution to regenerate its activity for reuse. The iodide solution (also rich in iodate, IO_3^- ions) is acidified with sulfuric acid. The acid solution is oxidized to precipitate out iodine. Iodine is purified by sublimation.

Iodine is packed and supplied in polyethylene-lined fiber drums or high silicon iron, Hastelloy B, or lead coated steel containers. Glass, graphite and acid-proof bricks are very suitable for storing iodine and its solutions.

Reactions

Chemical properties of iodine are quite similar to those of other halogens, especially chlorine and bromine. However, being less electronegative than chlorine and bromine, its reactivity towards most metals, nonmetals, and their compounds may differ vastly. All iodine reactions occur in vapor phase or aqueous media. Vapor phase reactions require elevated temperatures.

Iodine vapors combine with metals forming their iodides. The rates of such reactions vary with metals, their states, and temperatures. The reaction is very rapid when the metal is in finely divided state, and slow when the metal is in massive form.

$$2Al + 3I_2 \rightarrow 2AlI_3$$

Heating with hydrogen at high temperatures gives hydrogen iodide:

$$H_2 + I_2 \rightarrow 2HI$$

In aqueous solutions, iodine hydrolyzes to hypoiodous acid, hydrogen ion and iodide anion:

$$I_2 + 2H_2O \rightarrow HIO + H^+ + I^-$$

The equilibrium constant for the above reaction is 5.0×10^{-15} at 25°C.

In acid solution, iodine is a weak oxidizing agent. The redox potential is –0.534 V at 25°C. It readily oxidizes thiosulfate to tetrathionate ion:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Similarly, it oxidizes SO_3^{2-}, Sn^{2+}, and Ti^{2+} ions in acid solution to SO_4^{2-}, Sn^{4+}, and Ti^{4+}, respectively:

$$Sn^{2+} + I_2 \rightarrow Sn^{4+} + 2I^-$$

In dilute aqueous solutions, iodine oxidizes sulfur dioxide to sulfuric acid:

$$I_2 + SO_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$$

In acid solutions, iodine reduces powerful oxidizing agents and is oxidized itself. For example, it reduces chlorate and bromate to chlorine and bromine, respectively, and nitric acid to nitric oxide. In all these reactions, iodine is oxidized to iodate:

$$I_2 + 2ClO_3^- \rightarrow 2IO_3^- + Cl_2$$

$$I_2 + 2BrO_3^- \rightarrow 2IO_3^- + Br_2$$

$$3I_2 + 10HNO_3 \rightarrow 6HIO_3 + 10NO + 2H_2O$$

Iodine behaves as a powerful oxidizing agent in strong alkaline solution due to the formation of hypoiodite ion:

$$I_2 + 2OH^- \rightarrow IO^- + I^- + H_2O$$

The hypoiodite ion, however, is unstable, decomposing to iodate and iodide ions:

$$3IO^- \rightarrow 2I^- + IO_3^-$$

Thus, when the overall reaction in aqueous base goes to completion at higher temperatures, the reaction may be written as:

$$3I_2 + 6OH^- \rightarrow IO_3^- + 5I^- + 3H_2O$$

When chlorine is passed through an alkaline solution of iodine, the latter is oxidized to periodate:

$$I_2 + 8OH^- + 4Cl_2 \rightarrow 2IO_4^- + 8HCl$$

Reaction with iodic acid and hydrochloric acid produces iodine monochloride:

$$2I_2 + HIO_3 + 5HCl \rightarrow 5ICl + 3H_2O$$

Iodine combines with fluorine, chlorine and bromine, forming interhalogen compounds such as ICl, IBr_5, IF_7. Fluorine successively adds on to iodine forming mono-, tri-, penta-, and heptafluorides of iodine:

$$I_2 + F_2 \rightarrow 2IF$$

$$IF + F_2 \rightarrow IF_3$$

$$IF_3 + F_2 \rightarrow IF_5$$

$$IF_5 + F_2 \rightarrow IF_7$$

The oxidation state of iodine in iodine heptafluoride is +7.

Iodine partially dimerizes in organic solvents, forming tetraatomic I_4 species.

Among organic compounds, alkenes readily react with iodine, giving addition products. For example, iodine adds to ethylene, forming ethylene diiodide:

$$CH_2{=}CH_2 + I_2 \rightarrow C_2H_4I_2$$

Such reactions are reversible and the presence of free iodine decomposes the products back to alkenes.

Substitution reactions occur at high temperatures:

$$C_2H_6 + I_2 \rightarrow C_2H_5I + HI$$

The yield is higher in basic solution in the presence of an oxidizing agent. Iodine forms a blue complex with β-amylose in starch. A linear array of I_5^- species consisting of $I_2 - I^- - I_2$ units bound to the amylose helix causes blue color formation.

Analysis

Free iodine may be determined from its color and physical properties.

Iodine in aqueous solution may be measured quantitatively by acidifying the solution, diluting it, and titrating against a standard solution of sodium thiosulfate, sodium arsenite or phenyl arsine oxide using starch indicator. The blue color of the starch decolorizes at the end point. The indicator must be added towards the end of titration when the color of the solution turns pale yellow. Prior to titration, iodine in the dilute acidic solution is oxidized to iodate by adding bromine water or potassium permanganate solution. Excess potassium iodide is then added. The liberated iodine is then titrated as above.

Iodine in water also may be determined by the Leucocrystal violet colorimetric method. An aqueous sample is treated with mercuric chloride followed by Leucocrystal violet reagent [4,4',4"—methylidynetris(N,N-dimethylaniline)] in the pH range 3.5 to 4.0. A violet color is produced. The absorbance or transmittance is measured at 592 nm by a spectrophotometer or filter photometer. Iodine concentration is calculated from a standard calibration curve.

All forms of iodine including the elemental iodine, hypoiodous acid (HOI), hypoiodite anion (OI^-), free iodide anion (I^-) , and triiodide anion (I_3^-) in water also may be measured by the Leuco crystal violet method. The sample is treated with potassium peroxymonosulfate to oxidize all iodide species in the sample. It then is treated with leukocrystal violet reagent for color development. Interference from free chlorine may be eliminated by addition of an ammonium salt.

Iodide ion may be measured by amperometric titration and, more accurately, by ion chromatography.

Toxicity

Iodine vapors are an irritant to eyes, nose and mucous membranes. Inhalation can cause headache, irritation, and congestion of lungs. Oral intake can produce burning of the mouth, vomiting, diarrhea, and abdominal cramps. Skin contact can cause rashes.

IODINE HEPTAFLUORIDE

[16921-96-3]
Formula: IF_7; MW 221.90; pentagonal bipyramidal structure.
Synonym: heptafluoroiodine

Uses

Iodine heptafluoride is used as a fluorinating agent.

Physical Properties

Colorless gas; mold-like pungent odor; melting point 6.45°C; sublimes at 4.77°C; supercools to a colorless liquid that boils at 4.5°C; liquid density 2.8g/mL at 6°C; soluble in water.

Preparation

Iodine heptafluoride may be prepared by the reaction of fluorine with potassium iodide:

$$KI + 4F_2 \rightarrow IF_7 + KF$$

Dried KI should be used to minimize the formation of IOF_5.

Also, IF_7 can be prepared by passing fluorine gas through liquid iodine pentafluoride at high temperature (90°C) and then heating the vapors to 270°C to complete the reaction:

$$IF_5 + F_2 \rightarrow IF_7$$

Reactions

Most reactions of iodine heptafluoride are similar to those of iodine pentafluoride, except that it does not undergo any further fluorine addition reactions (See Iodine Pentafluoride). The compound reacts with a number of inorganic substances, forming their fluorides, and forms fluoro-derivatives with organics when in diluted form.

Toxicity

The compound is corrosive. Vapors are highly irritating to eyes and mucous membranes.

IODINE MONOCHLORIDE

[7790-99-0]
Formula: ICl; MW 162.357
Synonyms: Wijs' chloride; iodine chloride

Uses

Iodine monochloride is used as an analytical reagent to determine iodine values of oils and fats. It is dissolved in glacial acetic acid (Wijs' solution) for the analysis. ICl is used in organic synthesis. It also is used as a topical antiseptic.

Physical Properties

Black crystalline solid; exists in two modifications: stable black needles known as alpha form that produces ruby-red color in transmitted light, and a labile, metastable beta modification consisting of black platelets which appear brownish-red in transmitted light; density of alpha form 3.86 g/cm^3 at 0°C; density of beta form 3.66 g/cm^3 at 0°C; alpha form melts at 27.3°C, vapor pressure being 28 torr at 25°C; beta form melts at 13.9°C; liquid iodine monochloride has bromine-like reddish-brown color; liquid density 3.10 g/mL at 29°C; viscosity 1.21 centipoise at 35°C; decomposes around 100°C; supercools below its melting point; polar solvent; as a liquid it dissolves iodine, ammonium chloride and alkali metal chlorides; liquid ICl also miscible with carbon tetrachloride, acetic acid and bromine; the solid crystals dissolve in ethanol, ether, acetic acid and carbon disulfide; solid ICl also dissolves in conc. HCl but decomposes in water or dilute HCl.

Thermochemical Properties

$\Delta H_f°$ (liq)	–5.712 kcal/mol
$\Delta H_f°$ (gas)	4.254 kcal/mol
$\Delta G_f°$(liq)	–3.250 kcal/mol
$\Delta G_f°$ (gas)	–1.315 kcal/mol
S° (liq)	32.29 cal/degree mol
S° (gas)	59.18 cal/degree mol
C_ρ (liq)	0.0257 cal/degree mol
C_ρ (gas)	8.51 cal/degree mol
ΔH_{fus}	2.77 kcal/mol
ΔH_{vap}	9.95 kcal/mol

Preparation

Iodine monochloride is prepared by the action of liquid or dry chlorine on a stoichiometric quantity of solid iodine. Aqueous solutions of ICl are prepared by passing chlorine gas into a suspension of iodine in moderately strong hydrochloric acid:

$$5I_2 + 4HCl + 3Cl_2 \rightarrow 10ICl + 2H_2$$

Alternatively, iodine monochloride may be made by oxidation of iodine with iodic acid in strong hydrochloric acid solution:

$$2I_2 + HIO_3 + 2HCl \rightarrow 2ICl + 3HIO$$

Reactions

When vaporized at 100°C iodine monochloride decomposes to chlorine and iodine:

$$2ICl \rightarrow I_2 + Cl_2$$

Heating with hydrogen at elevated temperatures yields hydrogen chloride and hydrogen iodide:

$$ICl + H_2 \rightarrow HCl + HI$$

Reactions with metals in a finely-divided state or at elevated temperatures, produce metal chlorides and metal iodides:

$$3Al + 3ICl \rightarrow AlCl_3 + AlI_3$$

It hydrolizes in water, decomposing to iodine, hydrochloric acid and iodic acid:

$$5ICl + 3H_2O \rightarrow 2I_2 + 5HCl + HIO_3$$

Under milder conditions and in equimolar ratio, hypoiodous acid forms:

$$ICl + H_2O \rightarrow HIO + HCl$$

Similar hydrolysis occurs in dilute HCl.

Reactions with alkanes produce iodo derivatives and hydrogen chloride:

$$C_4H_{10} + ICl \rightarrow C_4H_9I + HCl$$

Iodine monochloride adds to unsaturated compounds. Some examples are:

$$CH_2{=}CH_2 + ICl \rightarrow ICH_2CH_2Cl$$

$$CH_3CH{=}CH_2 + ICl \rightarrow CH_3CHClCH_2I$$

$$CH{\equiv}CH + ICl \rightarrow ClCH{=}CHI$$

Analysis

Elemental composition: Cl 21.84%, I 78.16%. The compound is hydrolyzed in water and the product chloride and iodate ions are analyzed by ion chromatography. Iodine is separated by filtration and measured by gravimetry or by the Leuco Crystal violet colorimetric method (See Iodine). Alternatively, the liquid or solid compound is dissolved in organic solvent, diluted appropriately, and analyzed by GC/MS.

IODINE PENTAFLUORIDE

[7783-66-6]
Formula: IF_5; MW 221.90; square pyramidal structure.

Uses

Iodine pentafluoride is a fluorinating agent. It also is used in incendiaries.

Physical Properties

Colorless to yellowish liquid; fumes in air; density 3.19 g/mL; freezes at 9.43°C; boils at 100.5°C; reacts with water.

Thermochemical Properties

$\Delta H_f°$ (l)	–206.7 kcal/mol
$\Delta H_f°$ (g)	–196.6 kcal/mol
$\Delta G_f°$ (g)	–179.7 kcal/mol
S° (g)	78.3 cal/degree mol
C_ρ	23.7 cal/degree mol
ΔH_{vap}	9.87 kcal/mol

Preparation

Iodine pentafluoride is best obtained by passing fluorine gas over iodine under cooling conditions:

$$I_2 + 5F_2 \rightarrow 2IF_5$$

Also, it may be prepared by the reaction of fluorine with iodine trifluoride; or heating potassium iodide with a stoichiometric amount of fluorine:

$$IF_3 + F_2 \rightarrow IF_5$$

$$KI + 3F_2 \rightarrow KF + IF_5$$

Reactions

Thermal dissociation of iodine pentafluoride yields iodine trifluoride and fluorine:

$$IF_5 \rightarrow IF_3 + F_2$$

It combines with fluorine, forming iodine heptafluoride:

$$IF_5 + F_2 \rightarrow IF_7$$

Iodine pentafluoride similar to other halogen fluorides exhibits amphoteric behavior; i.e., with strong Lewis acids, such as SbF_5, it can form cation, IF_4^+:

$$IF_5 + SbF_5 \rightarrow IF_4^+SbF_6^-$$

Similarly, with strong bases like potassium fluoride, it forms the anion IF_6^-:

$$IF_5 + KF \rightarrow K^+IF_6^-$$

Iodine pentafluoride reacts with many inorganic substances, forming their fluorides. Such inorganic substances include metals, metal oxides and several nonmetals. Some examples are:

$$Zn + IF_5 \rightarrow ZnF_2 + IF_3$$

$$2Al_2O_3 + 3IF_5 \rightarrow 4AlF_3 + 3IF + 3O_2$$

$$2P_4 + 2IF_5 \rightarrow 8PF_5 + I_2$$

It reacts violently with water, forming hydrogen fluoride and iodic acid:

$$IF_5 + 3H_2O \rightarrow 5HF + HIO_3$$

Iodine pentafluoride reacts with organic substances, forming their fluoroderivatives only when it is diluted with nitrogen. The pure compound may otherwise carbonize organics on contact, sometimes violently.

Analysis

Elemental composition: I 57.19%, F 42.81%. The compound may be hydrolyzed with water slowly and cautiously (a violent reaction occurs). Iodate anion may be measured by redox titration and the fluoride ion by using a fluoride ion-selective electrode. Alternatively, these anions in their aqueous solution may be determined by ion chromatography after appropriate dilution.

Hazard

Most reactions are violent. Accidental contact with a number of organics and inorganic substances may present a fire or explosion hazard. Rapid mixing with water can be explosive. The compound is highly corrosive. Skin contact can cause a severe burn. Vapors are highly irritating to eyes, nose and mucous membranes. (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd. Ed. New York: John Wiley & Sons.)

IODINE PENTOXIDE

[12029-98-0]
Formula: I_2O_5; MW 333.81

Uses

Iodine pentoxide is used for analysis of carbon monoxide and for CO removal from air. It also is used as an oxidizing agent in other oxidation reactions.

Physical Properties

White crystals; hygroscopic; density 4.98 g/cm^3; decomposes around 300°C; highly soluble in water; soluble in nitric acid; insoluble in ethanol, ether and carbon disulfide.

Preparation

Iodine pentoxide is prepared by dehydration of iodic acid at 240°C.

$$2HIO_3 \rightarrow I_2O_5 + H_2O$$

Reactions

Iodine pentoxide is a strong oxidizing agent and reacts with various oxidizable substances. It oxidizes carbon monoxide to carbon dioxide. The reaction is quantitative and used to measure carbon monoxide in the air:

$$I_2O_5 + 5CO \rightarrow I_2 + 5CO_2$$

It reacts with hydrogen sulfide, forming sulfur dioxide:

$$3I_2O_5 + 5H_2S \rightarrow 3I_2 + 5SO_2 + 5H_2O$$

Oxidation reaction also occurs with hydrogen chloride, metal hydrides and a number of metal salts. It dissolves in water reacting to form iodic acid:

$$I_2O_5 + H_2O \rightarrow 2HIO_3$$

Dissociation into iodine and oxygen commences when heated above 270°C.

IODINE TRICHLORIDE

[865-44-1]
Formula: ICl_3; MW 233.262

Uses

Iodine trichloride is used in organic synthesis as a chlorinating and iodinating agent to introduce chlorine and iodine into organic compounds producing their halogen derivatives. It also is used as a topical antiseptic.

Physical Properties

Orange yellow triclinic crystals or fluffy powder; hygroscopic; density 3.111 g/cm^3 at 15°C; sublimes at 64°C with decomposition; melts at 101°C at 16 atm; hydrolyzes in water; soluble in ethanol, carbon tetrachloride and benzene; soluble in concentrated hydrochloric acid but hydrolyzes in dilute acid.

Preparation

Iodine trichloride is prepared by adding iodine to liquid chlorine in a stoichiometric amount:

$$3Cl_2 + I_2 \rightarrow 2ICl_3$$

Reactions

Iodine trichloride decomposes on heating at 77°C, forming iodine monochloride and chlorine:

$$ICl_3 \rightarrow ICl + Cl_2$$

It dissolves in concentrated hydrochloric acid , forming $HICl_4 \cdot 4H_2O$:

$$ICl_3 + HCl + 4H_2O \rightarrow HICl_4 \cdot 4H_2O$$

Iodine trichloride hydrolyzes in water or dilute acids, the products depending upon reaction conditions. This reaction usually is similar to iodine monochloride:

$$4ICl_3 + 6H_2O \rightarrow I_2 + 6HCl + 2HIO_3 + 3Cl_2$$

It combines with potassium chloride, forming a complex salt, $KICl_4$:

$$ICl_3 + KCl \rightarrow KICl_4$$

Reaction with acetylene produces chlorovinyl iododichloride, containing two active chlorine atoms attached to the iodine atom:

$$ICl_3 + HC{\equiv}CH \rightarrow ClCH{=}CHICl_2$$

The above product has many applications in chemical synthesis..

Toxicity

Iodine trichloride is highly corrosive. Contact with skin can cause a burn. Vapors are highly irritating to eyes and respiratory tract.

IRIDIUM

[7439-88-5]
Symbol: Ir; atomic number 77: atomic weight 192.22; a Group VIII (Group 8) transition metal; electron configuration $[Xe]4f^{14}5d^{7}6s^{2}$; common valence states +3 and +4; valence states 0, +1, +2, +5 and +6 are known; two natural isotopes, Ir-191 (37.30%) and Ir-193 (62.70%) The element has 28 radioisotopes, ranging in masses from 170 to 198.

History, Occurrence, and Uses

Iridium metal was detected in the black residue of aqua regia extract of platinum and identified as an element by British chemist Smithson Tennant in 1803. Around the same time, existence of this new metal was proposed by Vauquelin and deFourcroy in France in the course of their extraction of platinum by aqua regia. Tennant named this element Iridium after the Greek word, Iris, meaning rainbow.

Iridium occurs in small amounts in native platinum or platinum metal alloys. Iridium and osmium together constitute “osmiridium,” which is resistant to chemical attack and is a byproduct of platinum extraction.

The most important use of iridium is as an alloying metal for platinum and palladium. Such alloys are used for jewelry, decorative purposes, electrical contacts, thermocouples, crucibles, electrodes, hypodermic needles, and medical accessories. Iridium enhances resistance of platinum to chemical attack and corrosion. It also enhances hardness and tensile strength. The radioisotope Ir-192 is used in examination of ferrous welds and in other radiographic applications.

Physical Properties

Silvery-white metal; close-packed cubic crystals; lattice constant 3.8394Å at 20°C; density 22.42 g/cm^3 (highest among metals); melts at 2410°C; vaporizes at 4,130°C; hardness 6–6.5 Mohs; electrical resistivity 4.71 μohm-cm; Young’s modulus 3.75 x 10^4 tons/in^2; magnetic susceptibility 0.133 x 10^{-6} cm^3/g; thermal neutron absorption cross section 440 barns.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	159.0 kcal/mol
ΔG_f° (gas)	147.87 kcal/mol
S° (cry)	8.48 cal/degree mol
S° (gas)	46.24 cal/degree mol
C_ρ (cry)	6.00 cal/degree mol
C_r (gas)	4.97 cal/degree mol
Thermal conductivity (0-100°C)	1.48 watts/cm/°C
Coeff. linear expansion (20 to 100°C)	6.8 x 10^{-6}/°C

Reactions

At ordinary temperatures iridium exhibits strong resistance to chemical attack. At elevated temperatures of about 600°C, iridium metal combines with oxygen to form a coating of iridium dioxide, IrO_2. Similarly, the metal reacts with halogens only at elevated temperatures. It reacts with fluorine at 250°C, forming iridium hexafluoride, IrF_6, and, to a lesser extent, iridium tetrachloride $IrCl_4$. Heating with chlorine at 600°C produces iridium trichloride, $IrCl_3$. Iridium forms alloys with several metals—mostly platinum group metals.

Iridium does not react with concentrated acids or with molten alkalies.

Analysis

Iridium may be analyzed by x-ray. Also, AA or ICP measurements may be performed after digestion in hot acid mixture. The metal is practically insoluble in all mineral acids and aquaregia, even on heating. A 20:1 mixture of $HCl:HNO_3$ may be used to dissolve it with strong heating.

IRON

[7439-89-6]
Symbol: Fe; atomic number 26; atomic weight 55.847; a Group VIII (Group 8) metallic element; transition metal; atomic radius 1.24Å; electron configuration $[Ar]3d^64s^{2;}$ most common valence states +2 and +3; other oxidization states –1, 0, +1, +4 and +6 are known but rare; most abundant isotope Fe-56; natural isotopes and their abundances: Fe-54 (5.90%), Fe-56 (91.52%), Fe-57 (2.245%), Fe-58 (0.33%).

History, Occurrence, and Uses

Iron has been known to mankind from early civilization. In fact, a period of history, the "iron age," is named for the widespread use of this metal. For almost a thousand years, it remained as the single most-used metal, and its use in mechanization made the industrial revolution possible.

Iron, after oxygen, silicon and aluminum, is the fourth most abundant element in the earth's crust. It is the prime constituent of earth's core along with nickel. Its abundance in the crust is 5.63%. Its concentration in the seawater is about 0.002mg/L. The principal ores of iron are hematite, Fe_2O_3; pyrite, Fe_2S_2; ilmenite, $FeTiO_3$; magnetite, Fe_3O_4; siderite, Fe_2CO_3; and limonite [FeO(OH)]. It also is found in a number of minerals, such as corundum, as an impurity. It also is found in meteorites.

Iron occurs in every mammalian cell and is vital for life processes. It is bound to various proteins and found in blood and tissues. The iron-porphyrin or heme proteins include hemoglobin, myoglobin and various heme enzymes, such as cytochromes and peroxidases. Also, it occurs in non heme compounds, such as ferritin, siderophilin, and hemosiderin. Hemoglobin, found in the red blood cells, is responsible for transport of oxygen to the tissue cells and constitutes about two-thirds (mass) of all iron present in the human body. An adult human may contain about 4 to 6 grams of iron.

Industrial uses of iron as carbon steels are numerous and surpass any other alloys. Carbon steels are alloys of iron containing carbon in varying proportions, usually up to 1.7% carbon. Other metals also are incorporated into carbon steels to produce low-alloy steels. Such metals are usually nickel and chromium and are classified as stainless steel, tool steels, and heat-resistant steels. Non-steel iron alloys such as cast iron, wrought iron, nickel iron and silicon iron also have many important applications.

Another important application of iron is as an industrial catalyst. It is used in catalyst compositions in the Haber process for synthesis of ammonia, and in Fischer-Tropsch process for producing synthetic gasoline.

Physical Properties

Soft white, ductile metal; high-purity metal is very ductile at ordinary temperatures; occurs in three allotropic forms: (i) body-centered cubic form, alpha iron stable up to 910°C, (ii) face-centered cubic form, gamma iron occurring between 910 to 1,390°C, and (iii) body-centered delta iron allotrope forming above 1,390°C. Density 7.873 g/cm^3 at 20°C; melting point 1,538°C; vaporizes at 2,861°C; hardness (Brinell) 60; electrical resistivity 4.71 microhm-cm at 0°C; tensile strength 30,000 psi; Poisson's ratio 0.29; modulus of elasticity 28.5 x 10^6 psi; thermal neutron absorption cross-section 2.62 barns; velocity of sound 5,130 m/s at 20°C.

Molten iron: Density 7.00 g/cm^3 at 1,564°C; vapor pressure 0.06 torr at 1,600° C, and 1 torr at 1,850°C, respectively; viscosity 4.45 centipoise at 1,743°C; surface tension 1,835-1,965 dynes/cm; electrical resistivity 139 microhm-cm at the melting point. Magnetic properties: attracted by magnets; rapidly loses its magnetism; ferromagnetic at ordinary temperature; becomes paramagnetic when heated to its Curie point, 768°C.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	99.5 kcal/mol
$\Delta G_f°$ (gas)	88.6 kcal/mol
S° (cry)	6.52 cal/degree mol
S° (gas)	43.1 cal/degree mol
C_ρ (cry)	6.00 cal/degree mol
C_ρ (gas)	6.14 cal/degree mol
ΔH_{fus}	3.30 kcal/mol
Latent heat of fusion	65.5 cal/g
Latent heat of vaporization	1,598 cal/g
Coeff. linear expansion:	
Alpha form (20-100°C)	23.04 x 10^{-6}/°C
Gamma form (916-1388°C)	23.6 x 10^{-6}/°C
Delta form (1388-1502°C)	9.7 x 10^{-6}/°C
Thermal conductivity (at 0°C)	0.2 cal/cm/sec/°C

Production

Most iron produced today is from its oxide minerals, hematite and magnetite. The process involves reducing mineral iron with carbon in a blast furnace. There are several types of blast furnaces which vary in design and dimensions. The overall processes, however, are more or less the same. One such process is outlined below:

The mixture of ore, coke and limestone is fed into the blast furnace from the top. The materials are preheated to about 200°C in the top most zone. Hematite is partially reduced to magnetite and then to FeO by the ascending stream of carbon monoxide formed at the bottom and mid zones of the furnace resulting from high temperature oxidation of carbon. The ferrous oxide FeO formed at the top zone is reduced to metallic iron at about 700°C in the mid zone by carbon monoxide. A hot air blast at 900°C passes through the entire furnace for a very short time (usually for a few seconds). This prevents any gas-solid reaction product from reaching equilibrium. In the temperature zone 700 to 1,200°C ferrous oxide is completely reduced to iron metal by carbon monoxide. Also, more CO is formed by oxidation of carbon by carbon dioxide. Further down the furnace at higher temperatures, around 1,500°C, iron melts, dripping down into the bottom. Also, in this temperature zone acidic silica particles react with basic calcium oxide produced from the decomposition of limestone, producing calcium silicate. The molten waste calcium silicate also drips down into the bottom. In the hottest zone of the blast furnace, between 1,500 to 2,000°C, some carbon dissolves into the molten iron. Also at these temperatures any remaining silicates and phosphates are reduced to silicon and phosphorus, and dissolve into the molten iron. Additionally, other tract metals such as manganese dissolve into the molten iron. The impure iron melt containing about 3 to 4% carbon is called "pig iron". At the bottom, the molten waste slag floats over the impure pig iron melt that is heavier than the slag melt and immiscible with it. Pig iron is separated from the slag and purified for making different types of steel. Chemical reactions and processes occurring in various temperature zones of blast furnace are summarized below:

Top preheating zone:	
200°C	$3Fe_2O_3(s) + CO(g) \xrightarrow{reduction} 2Fe_3O_4(s) + CO_2(g)$ $Fe_2O_4(s) + CO(g) \xrightarrow{reduction} 2FeO(s) + CO_2(g)$ $CaCO_3(s) + CO(g) \xrightarrow{decomposition} CaO(s) + CO_2(g)$
Mid zone:	
700°	$FeO(s) + CO(g) \xrightarrow{reduction} Fe(s) + CO_2(g)$ $C(s) + CO_2(g) \xrightarrow{\text{carbon oxidation}} 2CO(g)$
1,200-1,500°C	$Fe(s) \xrightarrow{melting} Fe\ (l)$ $CaO(s) + SiO_2(s) \xrightarrow{\text{slag formation}} CaSiO_3(l)$
Bottom zone:	
1,500-2,000°C	$\text{phosphates} \xrightarrow{reduction} P + O_2$ $\text{silicates} \xrightarrow{reduction} Si + O_2$ $C,P,Si,Mn,\ldots(s) + Fe(l) \xrightarrow{dissolution} \text{pig iron (l)}$
2,000°C	$2C(s) + O_2(g) \xrightarrow{oxidation} 2CO(g) + \text{heat}$

Pig iron produced in the blast furnace is purified and converted to steel in a separate furnace, known as a basic-oxygen furnace. Jets of pure oxygen gas at high pressure are blown over and through the pig iron melt. Metal impurities are converted into oxides. Part of the dissolved carbon in the impure iron melt is converted into carbon dioxide gas. Formation of SiO_2, CO_2, and other metal oxides are exothermic reactions that raise the temperature to sustain the melt. A lime flux (CaO) also is added into the melt, which converts silica into calcium silicate, $CaSiO_3$, and phosphorus into calcium phosphate, $Ca_3(PO_4)_2$, forming a molten slag immiscible with molten steel. The lighter molten slag is decanted from the heavier molten steel.

Reactions

The most common oxidation states of iron are +2 (ferrous) and +3 (ferric). The standard electrode potential for $Fe \rightarrow Fe^{2+} + 2e^-$ is –0.440 volts. Thus, the metal can replace hydrogen from water at ordinary temperatures:

$$Fe + H_2O \rightarrow FeO + H_2$$

The reaction, however, is slow at room temperature, but rapid above 500°C. Decomposition of steam when passed over hot iron filings was discovered by Lavoisier:

$$3Fe(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 4H_2(g)$$

Iron also exhibits single replacement reactions, precipitating less electropositive metals out of their salt solutions. Thus, solid iron can reduce many metals, such as copper, silver, gold, mercury, tin and nickel:

$$Fe(s) + Sn^{2+}(aq) \rightarrow Fe^{2+}(aq) + Sn(s)$$
$$Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)$$

Solid iron undergoes rusting by reacting with oxygen in the presence of water (or water vapor). Thus, in moist air, it rapidly converts to rust, which is hydrous iron(III) oxide. The reaction occurs at ordinary temperatures, catalyzed by acid. The overall reaction is:

$$4Fe(s) + 3O_2(s) + nH_2O(l) \rightarrow Fe_2O_3 \cdot nH_2O$$

Iron dissolves in mineral acids. In nonoxidizing acids, such as HCl or H_2SO_4, and in the absence of air or oxidizing agents, the metal is oxidized to ferrous state (Fe^{2+}) liberating hydrogen:

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

In air, Fe^{2+} is partially oxidized to (ferric) ion. With warm dilute nitric acid, the product mixture contains both Fe^{2+} and Fe^{3+} ions.

Hot dilute nitric acid reacts with iron, forming ferric nitrate, $Fe(NO_3)_3$. Also, nitrogen oxides evolve in the reaction, probably from decomposition of nitric acid catalyzed by iron.

No reaction occurs with concentrated nitric acid nor with a strong oxidizing agent such as $Cr_2O_7^{2-}$ ion. Iron also does not precipitate out other metals in such concentrated nitric acid or other strong oxidizing medium. Such "passivating effect" of concentrated nitric acid on iron is attributed to formation of an oxide film on the metal surface. The passivating oxide film can be removed by treatment with reducing agents or by scratching the metal surface.

Iron reacts with nonmetals forming their binary compounds. It combines readily with halogens. Reaction is vigorous with chlorine at moderate temperature. With oxygen, it readily forms iron oxides at moderate temperatures. In a finely divided state, the metal is pyrophoric. Iron combines partially with nitrogen only at elevated temperatures. It reacts with carbon, sulfur, phosphorus, arsenic, and silicon at elevated temperatures in the absence of air, forming their binary compounds.

When heated with iodide of potassium, rubidium, or cesium and iodine at 300°C in a sealed quartz tube, iron forms tetraiodide complex anion, FeI_4^-:

$$Fe + KI + {}^3/_2\, I_2 \rightarrow KFeI_4$$

Analysis

Iron metal can be analyzed by x-ray spectroscopy, flame- and furnace atomic absorption, and ICP atomic emission spectroscopy at trace concentration levels. Other instrumental techniques include ICP-mass spectrometry for extreme low detection level and neutron activation analysis.

Several colorimetric methods also are known in which various organic complexing agents are used. One such method involves complexing iron with 1,10-phenanthroline. The metal is dissolved and reduced to Fe^{2+} state by boiling in an acid with excess hydroxylamine. The solution then is treated with 1,10-phenanthroline. An orange-red color develops rapidly in the pH range of 3.2 to 3.3. The concentration of iron in the solution is proportional to the absorbance or transmittance measured at 510nm. This analytical method may be applied to distinguish ferrous iron from the ferric form. X-ray methods may be applied on solid samples without dissolving the metal samples.

IRON(II) AMMONIUM SULFATE

[10045-89-3]

Formula: $(NH_4)_2Fe(SO_4)_s \cdot 6H_2O$ or $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$; MW 392.14; occurs as hexahydrate

Synonyms: ferrous ammonium sulfate; ammonium ferrous sulfate; Mohr's salt.

Uses

Iron ammonium sulfate is an analytical reagent in titrations and colorimetric measurements to measure oxidizing substances, such as chlorine, or to measure the chemical oxygen demand in waste water. The compound is used to prepare Fe(II) standard solution for these analyses. It also is a calibration standard in magnetic measurements; a reducing agent; a catalyst for polymerization; and is used in photographic chemistry.

Physical Properties

Bluish-green monoclinic crystal; density 1.86 g/cm^3; deomposes at 100°C; soluble in water; insoluble in alcohol.

Preparation

Ferrous ammonium sulfate may be prepared by mixing an equimolar solution of ferrous sulfate and ammonium sulfate, followed by evaporation and crystallization.

Analysis

Elemental composition: Fe 19.66%, H 2.84%, N 9.86%, O 45.06%, S 22.57%. It may be analyzed by titrating against a standard solution of an oxidizing agent. Also, iron content of the compound can be determined by AA, ICP or x-ray analysis.

IRON(III) AMMONIUM SULFATE

[10138-04-2]
Formula: $NH_4Fe(SO_4)_2 \cdot 12H_2O$; MW 482.19
The compound occurs as dodecahydrate containing 12 molecules of water of crystallization.
Synonyms: ferric ammonium sulfate; ammonium ferric sulfate; iron alum; ferric alum; ferric ammonium alum

Uses

Iron(III) ammonium sulfate is a mordant in dyeing and printing of fabrics and textiles. The compound also is an analytical reagent; and is used in medicine.

Physical Properties

The dodecahydrate is lilac to violet crystal (anhydrous compound is colorless); density 1.71 g/cm^3; melts around 37°C; hydrated crystals lose all water molecules at 230°C; readily dissolves in water; insoluble in alcohol; aqueous solution is acidic.

Preparation

Ferric ammonium sulfate is prepared by mixing an equimolar solution of ferric sulfate, $Fe_2(SO_4)_3$, and ammonium sulfate, $(NH_4)_2SO_4$. Hydrated crystals are obtained following evaporation and cooling of the solution.

Analysis

Elemental composition: Fe 21.00%, H 1.52%, N 5.27%, O 48.12%, S 24.10%. Iron content in the compound may be measured by various instrumental techniques (See Iron).

IRON(III) BROMIDE

[10031-26-2]
Formula: $FeBr_3$; MW 295.56
Synonym: ferric bromide; iron tribromide

Uses

Iron(III) bromide is a catalyst in bromination of aromatic compounds.

Physical Properties

Dark red hexagonal crystal; hygroscopic; partially decomposes to $FeBr_2$, losing some bromine on exposure to air or light; density 4.50 g/cm^3; decomposes on heating; soluble in water, ethanol, and ether.

Thermochemical Properties

$\Delta H_f°$	–61.10 kcal/mol

Preparation

Iron(III) bromide is prepared by the action of bromine with iron filings:

$$2Fe + 3Br_2 \rightarrow 2FeBr_3$$

The compound should be stored in dark bottles protected from air or light.

It also may be obtained by double decompostion reactions between a ferric salt and a bromide (alkali metal bromide) in aqueous solution followed by evaporation and crystallization:

$$Fe_2(SO_4)_3 + LiBr \rightarrow 2FeBr_3 + 3Li_2SO_4$$

It also may be prepared in high yield by photochemical reaction of dibromoirontetracarbonyl with bromine in hexane (Yoon, K.B. and J.K. Kochi. 1990. *Inorg. Chem.* 29, pp. 869):

$$(CO)_4FeBr_2 + \tfrac{1}{2}\, Br_2 \rightarrow FeBr_3 + 4CO$$

Reactions

The aqueous solution of iron(III) bromide decomposes to iron(II) bromide and bromine on boiling:

$$2FeBr_3(aq) \rightarrow 2FeBr_2\,(aq) + Br_2(g)$$

It is reduced by iron in tetrahydrofuran forming iron(II) bromide:

$$2FeBr_3 + 3Fe \rightarrow 3FeBr_2$$

Iron(III) bromide forms several adduct with donor molecules in solutions. For example, with triphenylphosphine, ($P(C_6H_5)_3$), it forms trigonal bipyramidal complex, $FeBr_3[P(C_6H_5)_3]_2$.

Analysis

Elemental composition: Fe 18.89%, Br 81.11%. The solid material may be analyzed nondestructively by x-ray techniques. The aqueous solution may be acidified with nitric acid (to prevent reduction) and analyzed for iron without further hot digestion by AA or ICP techniques. The bromide ion may be best determined by ion chromatography following appropriate dilution.

IRON CARBONYLS

Iron forms a few carbonyl compounds in all of which the valence state of iron is zero. The names, CAS numbers, formulas and molecular weights of known iron carbonyls are:

Iron pentacarbonyl	[13463-40-6]	$Fe(CO)_5$	195.90
Iron nonacarbonyl	[15321-51-4]	$Fe_2(CO)_9$	363.78
Iron dodecacarbonyl	[12088-65-2]	$Fe_3(CO)_{12}$	503.66
Iron hydrocarbonyl	[17440-90-3]	$H_2Fe(CO)_4$	169.90

Uses

Iron pentacarbonyl is the most important carbonyl compound of iron. It is used primarily to produce finely divided iron metal. Other applications are in catalysis of organic reactions; in ceramics; as an anti-knock in gasoline; and in production of red iron oxide pigment. Other carbonyls of iron have very few commercial applications.

Physical Properties

Iron pentacarbonyl is a yellow oily liquid; flammable; density 1.490 g/mL; freezes at –20°C; boils at 103°C; vapor pressure 40 torr at 30°C; insoluble in water; slightly soluble in ethanol; soluble in acetone, ether, and benzene.

The nonacarbonyl is an orange-yellow crystalline solid at ambient temperatures; density 2.85 g/cm^3; decomposes at 100°C. Iron dodecacarbonyl is a black crystalline solid; density 2.0g/cm^3; decomposes at 140°C. Iron hydrocarbonyl is an unstable colorless liquid; solidifies at –70°C; decomposes on heating; insoluble in water, soluble in alkalis.

Thermochemical Properties

Iron pentacarbonyl

$\Delta H_f°$	–185.0 kcal/mol
$\Delta G_f°$	–168.6 kcal/mol
$S°$	80.8 cal/degree mol
C_ρ	57.5 cal/degree mol

Preparation

Iron pentacarbonyl may be prepared by heating iron powder at 200°C with carbon monoxide at a pressure of 200 atm.

$$Fe + 5CO \rightarrow Fe(CO)_5$$

Other carbonyls are prepared from iron pentacarbonyl. For example, iron nonacarbonyl is formed by decomposition of the pentacarbonyl when exposed to light. When nonacarbonyl in ether, benzene, or toluene is heated at 60°C, it produces dodecacarbonyl and pentacarbonyl:

$$2Fe_2(CO)_9 \rightarrow Fe(CO)_5 + Fe_3(CO)_{12} + CO$$

Reactions

Iron pentacarbonyl is stable in the dark but decomposes on exposure to light or on heating. In an alcoholic solution, the carbonyl is decomposed by acids also.

In acetic acid solution iron pentacarbonyl forms iron nonacarbonyl:

$$2Fe(CO)_5 \rightarrow Fe_2(CO)_9 + CO$$

When heated in air pentacarbonyl converts to iron(III) oxide:

$$4Fe(CO)_5 + 13O_2 \rightarrow 2Fe_2O_3 + 20CO_2$$

Reaction with an alkali produces iron hydrocarbonyl:

$$Fe(CO)_5 + 2OH^- \rightarrow H_2Fe(CO)_4 + CO_3^{2-}$$

Iron hydrocarbonyl reacts with halogens forming halogen substituted carbonyl derivatives:

$$H_2Fe(CO)_4 + Cl_2 \rightarrow Cl_2Fe(CO)_4 + H_2$$

Also, iron hydrocarbonyl can combine with several metals forming metallic derivatives in which hydrogen is replaced by the metal ions:

$$H_2Fe(CO)_4 + Hg \rightarrow HgFe(CO)_4$$

The same product is obtained by reaction of diethylmercury with iron hydrocarbonyl:

$$H_2Fe(CO)_4 + (C_2H_5)_2Hg \rightarrow HgFe(CO)_4 + 2C_2H_6$$

Iron carbonyls form complexes with many donor molecules, such as pyridine, ammonia, ethylenediamine, and o-phenanthroline. In such complexes, carbonyl groups are partially replaced by the ligands. Some examples are:

$$\mathrm{Fe(CO)_5} \xrightarrow{pyridine} \mathrm{Fe(CO)_3(py)} \xrightarrow{pyridine} \mathrm{Fe(CO)_4(py)_3}$$

$$\mathrm{Fe(CO)_5} \xrightarrow{ethylenediamine(en)} \mathrm{Fe(CO)_3(en)} \xrightarrow{en} \mathrm{Fe(CO)_5(en)_2}$$

$$\mathrm{Fe(CO)_5} \xrightarrow{NH_3} \mathrm{Fe(CO)_3(NH_3)_2}$$

Thermal decomposition of vapors yields finely divided iron powder and carbon monoxide.

Analysis

Iron carbonyls may be identified by electron diffraction and x-ray analysis. Also, its solutions in appropriate organic solvents, such as ether, methanol, or acetone may be analyzed by GC/MS. The characteristic mass spectra should indicate the molecular ions corresponding to the carbonyl as well as the mass spectra of CO and $Fe(CO)_n$, where n is the number of CO units in the fragmented mass ions. Flame- or furnace-AA or ICP/AES analysis may be applied on the nitric acid extract of the compound(s) after appropriate dilution to determine the concentration of iron (See Iron).

Hazard

Iron pentacarbonyl is moderately toxic by ingestion or inhalation of its vapors. LD_{50} oral (rats): 40 mg/kg

Exposure to light evolves toxic carbon monoxide gas. The liquid is highly flammable; flash point (cc) 5°F.

IRON(II) CHLORIDE

[7758-94-3]
Formula: $FeCl_2$; MW 126.75; also forms a dihydrate, $FeCl_2 \cdot 2H_2O$ [16399-77-2] and a tetrahydrate, $FeCl_2 \cdot 4H_2O$ [13478-10-9].
Synonyms: ferrous chloride; iron dichloride

Occurrence and Uses

Iron(II) chloride occurs in nature as the mineral lawrencite. Iron dichloride is used as a mordant for dyeing; and as a reducing agent. It also is used in pharmaceutical preparation; in sewage treatment; and in metallurgy.

Physical Properties

White hexagonal crystal; hygroscopic; density 3.16g/cm^3; melts at 677°C; vaporizes at 1,023°C; vapor pressure 20 torr at 737°C and 200 torr at 897°C; highly soluble in water, ethanol and acetone; slightly soluble in benzene. The dihydrate and tetrahydrate are greenish monoclinic crystals; densities 2.39 and 1.39 g/cm^3, respectively; decomposing at 120 and 105°C, respectively; both the hydrates soluble in water.

Thermochemical Properties

$\Delta H_f°$	–81.69 kcal/mol
$\Delta G_f°$	–72.25 kcal/mol
S°	28.20 cal/degree mol
C_ρ	18.33 cal/degree mol
ΔH_{fus}	10.28 kcal/mol

Preparation

Iron(II) chloride is prepared by passing chlorine or hydrogen chloride gas over iron at red heat or 700°C:

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$
$$Fe + Cl_2 \rightarrow FeCl_2$$

It also may be produced by the reduction of iron(III) chloride with hydrogen or other reducing agents at elevated temperatures:

$$2FeCl_3 + H_2 \rightarrow 2FeCl_2 + 2HCl$$

The tetrahydrate is obtained by dissolving the metal in hydrochloric acid followed by crystallization at room temperature.

$$Fe + 2HCl + 4H_2O \rightarrow FeCl_2{\cdot}4H_2O + H_2$$

The tetrahydrate gradually loses water when heated above 105°C forming dihydrate, monohydrate and the anhydrous salt. At 220°C it loses all its water of crystallization.

Analysis

Elemental composition: Fe 44.06%, Cl 55.94%. The water of crystallization in hydrate salt can be determined by gravimetry. Iron can be analyzed in the aqueous solution of the salt by AA or ICP/AES techniques (See Iron). Chloride ion can be determined by titration with silver nitrate or mercuric nitrate or by ion chromatography.

IRON(III) CHLORIDE

[7705-08-0]
Formula: $FeCl_3$; MW 162.21; occurs as a dimer Fe_2Cl_6 in vapor phase.
Synonym: ferric chloride

Occurrence and Uses

Iron(III) chloride occurs naturally as the mineral molysite. The compound is widely used to prepare a number of iron(III) salts. Also, it is applied in sewage and industrial waste treatment processes. It also is used in the manufacture of dyes, pigments and inks; as a chlorinating agent; and as a catalyst in chlorination reactions of aromatics.

Physical Properties

Dark brown hexagonal crystals; hygroscopic; density 2.898g/cm^3; melts at 306°C; decomposes at 315°C; highly soluble in water (74.4g/100g water at 0°C); very soluble in alcohol, ether and acetone.

The hexahydrate is brownish-yellow crystalline mass; deliquesces; melts at 37°C; vaporizes around 280°C; highly soluble in water (92g/100g water at 20°C); very soluble in organic solvents such as ethanol, ether and acetone.

Thermochemical Properties

$\Delta H_f°$ (cry)	–95.48 kcal/mol
$\Delta H_f°$ (aq)	–131.5 kcal/mol
$\Delta H_f°$ (hexahydrate, cry)	–531.5 kcal/mol
$\Delta G_f°$ (cry)	–79.84 kcal/mol
$\Delta G_f°$ (aq)	–95.20 kcal/mol
S° (cry)	34.0 cal/degree mol
C_ρ (cry)	23.1 cal/degree mol

Preparation

Iron(III) chloride forms passing chlorine gas over iron filings at 350°C:

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

It also forms heating iron(III) oxide with HCl at elevated temperatures:

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$$

The product may be sublimed in a stream of chlorine to give high purity grade iron(III) chloride.

The anhydrous chloride also may be made by heating the hexahydrate, $FeCl_3 \cdot 6H_2O$, with thionyl chloride:

$$FeCl_3 \cdot 6H_2O + 6SOCl_2 \rightarrow FeCl_3 + 12HCl + SO_2$$

Analysis

Elemental composition: Fe34.43%, Cl 65.57%. The compound may be identified by x-ray methods. Iron may be analyzed by various instrumental techniques (See Iron). Chloride in the aqueous solution of the compound may be measured by titrating with a standard solution of silver nitrate or mercuric nitrate or by ion chromatography.

IRON-CYANIDE COMPLEXES

Iron in both the +2 and +3 valence states forms several stable hexacoordinated octahedral complexes with cyanide (CN^-) ion, known as ferrocyanide or hexakiscyanoferrate(4–), $[Fe(CN)_6]^{4-}$; and ferricyanide or hexakiscyanoferrate(3–), $[Fe(CN)_6]^{3-}$, respectively. The simple iron(II) cyanide, $Fe(CN)_2$ is unstable and all iron cyanide compounds known are coordination complexes.

Such cyanide complexes are also known for several other metals. All the ferrocyanide complexes may be considered as the salts of ferrocyanic acid $H_4Fe(CN)_6$; and ferricyanide complexes are that of ferricyanic acid, $H_3Fe(CN)_6$. The iron-cyanide complexes of alkali and alkaline-earth metals are water soluble. These metals form yellow and ruby-red salts with ferrocyanide and ferricyanide complex anions, respectively. A few of the hexacyanoferrate salts have found major commercial applications. Probably, the most important among them is ferric ferrocyanide, $FeFe(CN)_6$, also known as Prussian blue. The names, formulas and the CAS registry numbers of some hexacyanoferrate complexes are given below. Prussian blue and a few other important complexes of this broad class of substances are noted briefly in the following sections:

Complex/Synonyms	**Formula**	**CAS No.**
Potassium ferrocyanide [dipotassium hexakiscyanoferrate(4$^-$)]	$K_4Fe(CN)_6$	[14459-95-1]
Potassium ferricyanide [tripotassium hexakiscyanoferrate(3$^-$)]	$K_3Fe(CN)_6$	[13736-66-2]
Ferric ferrocyanide[tetrairon(III) tris(hexakiscyanoferrate)(Prussian blue)	$Fe^{III}_4[Fe(CN)_6]_3$	[14038-43-8]
Barium ferricyanide [tribarium bis(hexakiscyanoferrate(3–)]	$Ba_3[Fe(CN)_6]_2$	[21729-04-4]
Dipotassium sodium ferricyanide [dipotassium sodium hexacyanoferrate(3–)]	$K_2Na[Fe(CN)_6]$	[31940-93-9]
Potassium cupric ferricyanide [potassium copper(II)hexakis (cyanoferrate(3–))]	$KCu^{II}[Fe(CN)_6]$	[53295-15-1]
Potassium nickel ferricyanide [potassium nickel hexakis(cyanoferrate(3–))]	$KNi[Fe(CN)_6]$	[53295-14-0]
Potassium cobalt(II) ferricyanide [potassium cobalt(II) hexakis(cyanoferrate(3–))]	$KCo^{II}[Fe(CN)_6]$	[14874-73-8]
Ammonium ferrocyanide [tetraammonium hexakis-(cyanoferrate(4–)]	$(NH_4)_4[Fe(CN)_6]$	[14481-29-9]
Ferrocyanic acid [tetrahydrogen hexakis(cyanoferrate(4–)]	$H_4Fe(CN)_6$	[17126-47-5]

Prussian blue

Prussian blue or ferric ferrocyanide or iron(III) hexakis(cyanoferrate(3–)) has the formula $Fe_4[Fe(CN)_6]_3$. There are several commercial applications. It is used as pigment for paints, inks, typewriter ribbons, alkyd resins, enamels, plastics, and rubbers.

Physical properties:

Dark-blue powder or lumps; density 1.80 g/cm^3; dehydrates and partially decomposes around 250°C; insoluble in water, dilute acids and most organic solvents.

Prussian blue is obtained as a dark blue precipitate by the addition of an iron(III) salt to potassium ferrocyanide solution:

$$Fe^{3+} + [Fe(CN)_6]^{4-} \rightarrow Fe^{3+}[Fe^{2+}(CN)_6]^{-} \text{ (Prussian blue)}$$

A similar substance, known as Turnbull's blue, is obtained as a blue precipitate by adding an iron(II) salt to a solution of potassium ferricyanide. Iron(II) is oxidized to iron(III) by ferricyanide ion, the latter is reduced to ferrocyanide:

$$\underset{\text{}}{Fe^{2+}} + \underset{\text{(ferricyanide)}}{[Fe(CN)_6]^{3-}} \rightarrow Fe^{3+} + \underset{\text{(ferrocyanide)}}{[Fe(CN)_6]^{4-}}$$

The ferrocyanide ion formed reacts with iron(III) obtained to produce Prussian blue as shown above in the reaction. Thus, Turnbull's blue is chemically the same as the Prussian blue except that it is less intense in color, probably due to the presence of a white salt of composition $Ke_2Fe^{II}[Fe^{II}(CN)_6]$.

Potassium ferrocyanide

Potassium ferrocyanide, $K_4[Fe(CN)_6]\cdot 3H_2O$ occurs as a trihydrate. The compound is a spin-paired diamagnetic complex in which the ferrocyanide anion constitutes the Fe^{2+} ion, octahedrally coordinated with six CN^{-} ions. It is a yellow monoclinic crystalline solid; density 1.85 g/cm^3; decomposes at 60°C; and soluble in water but insoluble in alcohol and ether.

The compound is obtained from the 'spent oxide' of coal gas purifiers. In the laboratory it may be prepared by treating ferrous sulfate solution with a solution of potassium cyanide:

$$Fe^{2+} + 6CN^{-} \rightarrow [Fe(CN)_6]^{4-}$$

Although ferrocyanide anion is stable at ordinary temperatures, at high temperatures it oxidizes to ferricyanide. That is, when the aqueous solution of the complex is evaporated, red crystals of ferricyanide are obtained. Similar oxidation can also occur at ambient temperatures in the presence of oxidizing agents:

$$2Fe(CN)_6^{4-} + Br_2 \rightarrow 2Fe(CN)_6^{4-} + 2Br^{-}$$

Reactions with dilute acids give hydrogen cyanide:

$$Fe(CN)_6^{4-} + 12H^+ + 6H_2O \rightarrow Fe^{2+} + 6NH_4^+ + 6CO$$

As mentioned earlier, potassium ferrocyanide reacts with Fe^{3+} to produce Prussian blue. On the other hand, reaction with Fe^{2+} first gives a white precipitate of $K_2Fe^{II}[Fe^{II}(CN)_6]$, which can readily oxidize in the air forming Prussian blue.

Hexacyanoferric(II) acid [$H_4Fe(CN)_6$]

Hexacyanoferric(II) acid, ferrocyanic acid or tetrahydrogen hexakis(cyanate-(4–)) [17126-47-5] is used to prepare many adducts with oxygen-containing organics. Also addition compounds with inorganic salts are known. This acid may be obtained as a white precipitate upon addition of potassium ferrocyanide to concentrated hydrochloric acid:

$$K_4Fe(CN)_6 + HCl \rightarrow H_4Fe(CN)_6 + 4KCl$$

Cupric ferrocyanide

Cupric ferrocyanide, also known as copper(II) hexacyanoferrate(II) or copper(II) hexakis(cyanoferrate(3–)) $Cu_2Fe(CN)_6$, is obtained as a chocolate-brown precipitate by the addition of a copper(II) salt solution to ferrocyanide:

$$[Fe(CN)_6]^{4-} + 2Cu^{2+} \rightarrow Cu_2Fe(CN)_6$$

The above reaction also serves to determine the presence of Cu(II) ion in the solution.

Uses

The applications of cupric ferrocyanide are very limited. It is used as a chemical membrane for osmosis.

IRON DICYCLOPENTADIENYL

[102-54-5]
Formula: $(C_5H_5)_2Fe$ or $(\eta\text{-}C_5H_5)_2Fe$; MW 186.04; a metal π "sandwich" complex in which the six π electron system of the cyclopentadienidide ion $C_5H_5^-$ is bound to Fe^{2+} ion; Fe—C distance 2.045 Å and C—C bond distance 1.4 Å.
Synonyms: bis(cyclopentadienyl)iron; ferrocene; dicyclopentadienyliron

Uses

Dicyclopentadienyliron finds limited application as a catalyst. It was used earlier as an antiknock additive for gasoline. The complex also is used to synthesize other metal π–complexes and their derivatives.

Physical Properties

Orange crystals; camphor-like odor; melts at 172.5°C; vaporizes at 249°C; sublimes above 100°C; thermally stable above 500°C; insoluble in water; soluble in alcohol, ether and benzene; also soluble in dilute nitric acid and concentrated sulfuric acid forming a deep red solution that fluoresces.

Preparation

Dicyclopentadienyliron may be obtained in a single-step synthetic route by heating cyclopentadiene with iron or iron pentacarbonyl at 300°C:

$$2C_5H_5 + Fe \rightarrow (C_5H_5)_2Fe$$

Also, it can be prepared by the reaction of iron(II) chloride with cyclopentadiene in the presence of an alkyl amine or a similar base.

Another convenient method of preparing this π–complex of iron is a two-step process in which the first step involves preparation of cyclopentadienyl Grignard reagent, such as 2,4-cyclopentadienylmagnesium bromide C_5H_5MgBr which may then be combined with ferric chloride to yield dicyclopentadienyl iron:

$$3C_5H_5MgBr + FeCl_3 \rightarrow (C_5H_5)_2Fe + 3MgBrCl$$

Another general method of preparation involves the reaction of cyclopentadiene with sodium metal or sodium hydride in tetrahydrofuran (THF). Addition of iron(II) chloride to this solution forms the complex dicyclopentadienyliron:

$$2C_5H_6 + 2Na \xrightarrow{THF} 2C_5H_5^{-} + 2Na^{+} + H_2$$

In 3:2 molar ratio of cyclopentadiene to sodium cyclopentene is obtained along with cyclopentadienidide ($C_5H_5^{-}$) anion:

$$3C_5H_6 + 2Na \xrightarrow{THF} 2C_5H_5^{-} + 2Na^{+} + C_5H_8$$

$$FeCl_2 + 2C_5H_6Na \xrightarrow{THF} (C_5H_5)_2Fe + 2NaCl$$

Reactions

The most important reactions of dicyclopentadienyliron may be attributed to the aromatic behavior of cyclopentadienyl ring in the complex. Thus, the ring can undergo electrophilic substitution reactions with electrophiles to form various mono-, and disubstituted products. For example, with an equimolar of acetyl chloride and in the presence of aluminum chloride, the product is essentially monoacetylferrocene; while in the presence of an excess of both of the reagents, the major product is 1,1-diacetylferrocene with a minor yield of 1,2-diacetylferrocene.

$$(C_5H_5)_2Fe + CH_3COCl \xrightarrow{AlCl_3} (CH_3COC_5H_4)(C_5H_5)$$

$$(C_5H_5)_2Fe + 2CH_3COCl \xrightarrow[(excess)]{AlCl_3}$$

$$\underset{\text{(major product)}}{(CH_3COC_5H_4)Fe(C_5H_4COCH_3)} + \underset{\text{(minor product)}}{((CH_3CO)_2C_5H_3)Fe(C_5H_5)}$$

The cyclopentadienyl ring in the complex may be partially reduced by sodium amalgam in ethanol.
Reaction with sulfuric acid or chlorosulfonic acid in acetic anhydride medium gives mono- and disubstituted ferrocenesulfonic acid.

$$(C_5H_5)_2Fe + H_2SO_4 \xrightarrow{\text{acetic anhydride}} (SO_3HC_5H_4)Fe(C_5H_5) + (SO_3HC_5H_4)Fe(C_5H_4SO_3H)$$

Reaction with formaldehyde in the presence of dimethylamine yields dimethylaminomethylferrocene:

$$(C_5H_5)_2Fe + HCHO + (CH_3)_2NH \rightarrow (C_5H_5)_2Fe(C_5H_4CH_2N(CH_3)_2)$$

The above product is an important intermediate in the synthesis of several ferrocene derivatives.

Analysis

Elemental composition: Fe 30.02%, C 64.56%, H 5.42%. An alcoholic or benzene solution of the compound may be analyzed by GC/MS. Additionally, the cyclopentadienyl ligand may be identified from the IR (303 cm^{-1}) and nmr spectra and x-ray crystallographic analysis. Furthermore, the compound may be derivatized with an electrophile (See Reactions) and the derivative formed may be identified by its physical and chemical properties and elemental composition.

IRON DISULFIDE

[1317-66-4]
Formula: FeS_2; MW 119.98; composed of Fe^{2+} and S_2^{2-} ions in the cubic crystals
Synonyms: ferrous disulfide; iron pyrites; marcasite.

Occurrence and Uses

Iron disulfide is found in nature in two different crystal forms, as the minerals iron pyrite and marcasite. The mineral pyrite is mostly used for the production of iron and sulfur. Iron disulfide also is used to produce sulfuric acid, although the latter is commercially made by other processes that are more economical.

Physical Properties

The natural pyrite consists of yellow cubic crystals; density 5.02g/cm^3; hardness 6.3 Mohs; melts at 1,171°C; soluble in dilute acids.

The mineral marcasite constitutes yellow rhombic crystals; density 4.87g/cm^3; transforms to more stable pyrite form when heated at 480°C; insoluble in dilute acids. Both forms dissolve in concentrated nitric acid and are insoluble in water (4.9 mg/L at 20°C).

Thermochemical Properties

$\Delta H_f°$ (pyrite)	–42.6 kcal/mol
$\Delta H_f°$ (marcasite)	–37.0 kcal/mol
$\Delta G_f°$ (pyrite)	–39.9 kcal/mol
S° (pyrite)	12.65 cal/degree mol
C_ρ (pyrite)	14.86 cal/degree mol

Production

Iron disulfide is obtained from its naturally occurring minerals, pyrite and marcasite. In the laboratory it may be prepared along with iron(II) sulfide by passing dry hydrogen sulfide through a suspension of hydrated iron(III) oxide or iron(III) hydroxide in alkaline medium. The unstable product formed decomposes to FeS_2 and FeS.

Reactions

Both forms of iron disulfide are very stable at ordinary temperatures and also inert towards most chemicals. Heating at elevated temperatures gives iron(III) oxide and sulfur dioxide. This process for producing sulfur dioxide is also applied to manufacture sulfuric acid:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

When the disulfide is heated at 600°C in a vacuum, it decomposes to iron(II) sulfide and sulfur:

$$FeS_2 \rightarrow FeS + S$$

Analysis

Elemental composition: Fe 46.55%, S 53.45%. The mineral may be characterized nondestructively by x-ray techniques. The compound may be analyzed for iron by AA or ICP/AES methods following digestion with nitric acid and appropriate dilution.

IRON(II) FLUORIDE

[7789-28-8]
Formula: FeF_2; MW 93.842; also, a tetrahydrate $FeF_2 \cdot 4H_2O$ (MW165.90) [13940-89-1] is known.
Synonym: ferrous fluoride

Uses

Iron(II) fluoride is used as a catalyst in organic fluorination reactions. Other applications are in ceramics; and in the preparation of fluoride salts of other metals.

Physical Properties

White tetragonal crystal; density 4.09g/cm³; melts at 1100°C; slightly soluble in water; insoluble in ethanol and ether; dissolves in dilute hydrofluoric acid. Tetrahydrate crystals are hexagonal shape; density 2.20g/cm³; decomposes at 100°C.

Thermochemical Properties

$\Delta H_f°$	–170.0 kcal/mol
$\Delta G_f°$	–159.8 kcal/mol
S°	20.8 cal/degree mol
C_ρ	16.3 cal/degree mol
ΔH_{fus}	12.43 kcal/mol

Preparation

Anhydrous iron(II) fluoride may be prepared by passing hydrogen fluoride gas over iron at a high temperature:

$$2HF + Fe \rightarrow FeF_2 + H_2$$

Alternative methods of preparation of anhydrous salt involve the reduction of iron(III) fluoride with hydrogen; or by passing fluorine gas over anhydrous iron(II) chloride in the cold:

$$2FeF_3 + H_2 \rightarrow 2FeF_2 + 2HF$$

$$FeCl_2 + F_2 \rightarrow FeF_2 + Cl_2$$

The tetrahydrate may be prepared by dissolving iron metal in aqueous hydrofluoric acid.

Reactions

Iron(II) fluoride is reduced to iron metal when heated with hydrogen or other reducing agents:

$$FeF_2 + H_2 \rightarrow Fe + 2HF$$

When heated with oxygen, it first forms iron(II) oxide which is converted into iron(III) oxide:

$$FeF_2 + O_2 \rightarrow FeO + 2F_2$$

$$4FeF_2 + 3O_2 \rightarrow 2Fe_2O_3 + 4F_2$$

Analysis

Elemental composition: Fe 59.51%, F 40.49%. The compound may be analyzed by x-ray techniques. Iron may be analyzed by AA or ICP/AES methods following digestion with dilute hydrofluoric acid and nitric acid and appropriate dilution.

IRON(II) HYDROXIDE

[18624-44-7]
Formula: $Fe(OH)_2$; MW 89.96
Synonym: ferrous hydroxide

Uses

The compound is used in abrasives; and in pharmaceutical applications.

Physical Properties

Pale green hexagonal crystals (in partially oxidized form) or white amorphous powder (when pure); density 3.4g/cm^3; decomposes on heating; insoluble in water (1.5 mg/L at 20°C), K_{SP} 8.0 x 10^{-16}; soluble in acids; moderately soluble in ammonium salt solutions; insoluble in alkalies.

Thermochemical Properties

$\Delta H_f°$	–136.0 kcal/mol
$\Delta G_f°$	–116.3 kcal/mol
S°	21.0 cal/degree mol

Preaparation

Iron(II) hydroxide may be prepared by precipitation of an iron(II) salt solution with caustic soda or caustic potash in the absence of air. Pure compound may be obtained by mixing solutions of caustic potash and iron(II) sulfate—both the solutions made in freshly boiled water—in a reducing atmosphere of hydrogen:

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2$$

Reactions

Iron(II) hydroxide dissolves in acids forming corresponding salts:

$$Fe(OH)_2 + HCl \rightarrow FeCl_2 + 2H_2O$$

$$Fe(OH)_2 + H_2SO_4 \rightarrow FeSO_4 + 2H_2O$$

It oxidizes slowly in the atmosphere, eventually forming the reddish-brown hydrated ferric oxide, $Fe_2O_3 \cdot nH_2O$.

Thermal decomposition in vacuum produces iron(II) oxide:

$$Fe(OH)_2 \rightarrow FeO + H_2O$$

Analysis

Elemental composition: Fe 62.15%, H 2.24%, O 35.61%. The compound may be characterized by x-ray techniques. It may be dissolved in HNO_3 or HCl, the solution diluted appropriately and analyzed for iron by various instrumental techniques (See Iron).

IRON(III) HYDROXIDE

[1309-33-7]
Formula: $Fe(OH)_3$; MW 106.87
Synonyms: ferric hydroxide; hydrated iron(III) oxide.

Uses

The compound is used in pigments and in water purifications.

Physical Properties

Red-brown amorphous powder; density 3.40g/cm^3; soluble in acids; insoluble in water and alcohol.

Preparation

Iron(III) hydroxide is obtained as a brown gelatinous precipitate by adding a strong base to a solution of iron(III) salt:

$$FeCl_3 + 3NaOH \rightarrow Fe(OH)_3 + 3NaCl$$

Analysis

Elemental composition: Fe 52.26%, O 44.91%, H 2.83%. The compound may be dissolved in dilute nitric acid and the acid extract analyzed for iron by various instrumental techniques (See Iron).

IRON(III) NITRATE

[10421-48-4]
Formula: $Fe(NO_3)_3$; MW 241.87; also exists as nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$, MW 404.00 [7782-61-8]

Uses

Iron(III) nitrate is used as a mordant for dyeing black and buff. Other applications are in tanning; weighting silks; and in preparation of analytical standards.

Physical Properties

The nonahydrate form occurs as grayish-violet crystal; density 1.68 g/cm^3; hygroscopic; decomposes at 47°C; very soluble in water, alcohol and acetone.

Preparation

Iron(III) nitrate is prepared by the action of nitric acid on iron filings or iron oxide followed by crystallization:

$$2Fe + 6HNO_3 \rightarrow 2Fe(NO_3)_3 + 3H_2$$
$$Fe_2O_3 + 6HNO_3 \rightarrow 2Fe(NO_3)_3 + 3H_2O$$

Analysis

Elemental composition: Fe 23.09%; N 17.37%, O 59.54%. The aqueous solution analyzed for iron by various instrumental methods (See Iron) and for nitrate by nitrate-ion selective electrode or ion chromatography following appropriate dilution.

IRON(II) OXIDE

[1345-25-1]
Formula: FeO; MW 71.844
Synonyms: ferrous oxide

Occurrence and Uses

Iron(II) oxide occurs in the mineral, wustite. It is used in the manufacture of heat-absorbing green glasses. It also is used in ceramic mixtures and enamels; and as a catalyst.

Physical Properties

Black cubic crystal; density 5.7g/cm^3; melts at 1,377°C; insoluble in water and alkalies; dissolves in acids.

Thermochemical Properties

$\Delta H_f°$	–65.04 kcal/mol
ΔH_{fus}	5.74 kcal/mol

Preparation

Iron(II) oxide may be prepared by thermal decomposition of iron(II) oxalate:

$$FeC_2O_4 \rightarrow FeO + CO + CO_2$$

The product obtained above is impure, that may contain small quantities of triiron tetroxide, Fe_3O_4 and carbon.

The oxide is stable above 575°C. Thus, it can be prepared by heating iron with oxygen under appropriate pressure at 575°C. Also, iron(II) oxide has been prepared by saturating the fused triiron tetroxide with iron, powdering the mixture, followed by magnetic separation of the oxide from excess iron (Sidgwick, N.V. 1950. *The Chemical Elements and Their Compounds*, Vol.2, pp 1328, Oxford: Clarendon Press).

Reactions

Iron(II) oxide readily oxidizes to iron(III) oxide. The oxide is stable at high temperatures. Upon cooling, it decomposes to triiron tetroxide and iron:

$$4FeO \rightarrow Fe_3O_4 + Fe$$

The oxide is basic in nature. It dissolves in acids forming the corresponding iron(II) salts of acids:

$$FeO + 2HCl \rightarrow FeCl_2 + H_2O$$

$$FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O$$

Analysis

Elemental composition: Fe 77.73%, O 22.27%. The oxide may be characterized by x-ray methods. The metal may be determined by dissolving the compound in dilute nitric acid, diluting the extract appropriately and analyzing by AA or ICP/AES techniques.

IRON(III) OXIDE

[1309-37-1]
Formula: Fe_2O_3; MW 159.70
Synonyms: ferric oxide, hematite, red iron oxide, ferric sesquioxide

Occurrence and Uses

Iron(III) oxide occurs in nature as the mineral hematite. It is the principal ore of iron from which the metal and its alloys are produced. Also, this oxide occurs in the mineral, limonite, $2Fe_2O_3 \cdot 3H_2O$. An important application of this compound involves producing red, orange, and yellow pigments. Other applications are in coatings for metals, steel and rubber; in ceramics; and as a catalyst for oxidation reactions.

Physical Properties

Reddish-brown hexagonal crystal; refractive index 2.91; density 5.25g/cm^3; Moh's hardness 6.0; melts at 1565°C; insoluble in water; dissolves in acids.

Thermochemical Properties

$\Delta H_f°$	–197.0 kcal/mol
$\Delta G_f°$	–177.8 kcal/mol
S°	20.9 cal/degree mol
C_ρ	24.8 cal/degree mol

Preparation

Iron(III) oxide is prepared as a reddish-brown hydrated precipitate by treating an aqueous solution of an iron(III) salt with caustic soda:

$$2FeCl_3 + 6NaOH \rightarrow Fe_2O_3 \cdot 3H_2O + 6NaCl$$

It also is obtained by thermal decomposition of iron(II) sulfate or the brown oxide hydroxide:

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3$$

$$2FeO(OH) \rightarrow Fe_2O_3 + H_2O$$

The oxide is prepared in industrial scale by first precipitating iron(II) hydroxide $Fe(OH)_2$ by treating aqueous solutions of iron(II) sulfate and caustic soda. The $Fe(OH)_2$ is then oxidized to iron(III) hydroxide by aeration. The latter is dehydrated by heating:

$$Fe^{2+} (aq) + OH^- (aq) \rightarrow Fe(OH)_2(s) \rightarrow 2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$$

It also is produced by ignition of iron(III) oxalate and iron carbonyls:

$$2Fe_2(C_2O_4)_3 + 3O_2 \rightarrow 2Fe_2O_3 + 12CO$$

Reactions

Iron(III) oxide decomposes to its elements when heated at elevated temperatures:

$$2Fe_2O_3 \rightarrow 4Fe + 3O_2$$

The oxide is reduced by most reducing agents. Reaction with carbon monoxide at elevated temperatures (that occurs in the blast furnace) gives metallic iron. The overall reaction is mildly exothermic (ΔH_{rxn} –113.4 kcal/mol):

$$2\ Fe_2O_3 + 6CO \rightarrow 4Fe + 6CO_2$$

It also is reduced by powdered aluminum at elevated temperatures, forming aluminum oxide and metallic iron:

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$$

The reaction is highly exothermic and becomes self-sustaining after ignition. When heated with sand in an electric furnace, iron(III) oxide forms ferrosilicon alloy. When heated in a vacuum at 1,000°C, it forms triiron tetroxide, Fe_3O_4.

Analysis

Elemental composition: Fe 69.94%, O 36.06%. The oxide may be characterized by physical and magnetic properties and by x-ray methods. Iron may be analyzed by various instrumental techniques following acid digestion and appropriate dilution (See Iron).

TRIIRON TETROXIDE

[1317-61-9]
Formula: Fe_3O_4; MW 231.53; exhibits a tendency to form nonstoichiometric structure.
Synonyms: iron(II,III) oxide; ferrosoferric oxide; magnetite; lodestone

Occurrence and Uses

Triiron tetroxide occurs in nature as the mineral magnetite, the magnetic oxide of iron. This mineral along with hematite is used as the starting material for producing iron, steel and other ferro-alloys.

Physical Properties

Black cubic crystal or amorphous powder; refractive index 2.42; density 5.17 g/cm^3; Moh’s hardness 6.0; melts at 1,597°C; insoluble in water, soluble in acids.

Thermochemical Properties

$\Delta H_f°$	–267.3 kcal/mol
$\Delta G_f°$	–242.7 kcal/mol
S°	35.0 cal/degree mol
C_ρ	34.3 cal/degree mol
ΔH_{fus}	33.0 kcal/mol

Preparation

Triiron tetroxide is obtained from its natural mineral magnetite. In the laboratory the compound may be prepared by adding sodium hydroxide solution to an aqueous solution of 1:2 molar mixture of ferrous and ferric salt. (i.e., 1 mol $FeCl_2$ + 2 mol $FeCl_3$). The resulting black precipitate of the hydroxide on heating dehydrates to gives triiron tetroxide:

$$Fe^{2+}(aq) + 2Fe^{3+}(aq) + 8OH^{-}(aq) \rightarrow Fe_3(OH)_8(s)$$

$$Fe_3(OH)_8(s) \rightarrow Fe_3O_4(s) + 4H_2O(g)$$

Also, the tetroxide may be produced by partial oxidation of iron or iron(II) sulfate by heating under limited amount of air. Another method of production involves heating iron metal with steam:

$$3Fe + \underset{\text{(steam)}}{4H_2O} \rightarrow Fe_3O_4 + 4H_2$$

Reactions

Triiron tetroxide, when heated at elevated temperatures with a reducing agent such as hydrogen or carbon monoxide in the absence of air, produces metallic iron:

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$$

Partial reduction gives iron(II) oxide. When treated with concentrated acids, the tetroxide dissolves in acids forming mixtures of iron(II) and iron(III) salts:

$$Fe_3O_4 + 8HCl \rightarrow FeCl_2 + 2FeCl_3 + 4H_2O$$

$$Fe_3O_4 + 4H_2SO_4 \rightarrow FeSO_4 + Fe_2(SO_4)_3 + 4H_2O$$

Analysis

The mineral magnetite may be characterized from its physical and magnetic properties and by x-ray methods. The iron content in the oxide may be determined by AA, ICP/AES, x-ray fluorescence and other instrumental techniques (See Iron).

IRON(II) SULFATE

[7720-78-7]
Formula: $FeSO_4$; MW 151.91
Synonyms: ferrous sulfate; green vitriol

Occurrences and Uses

Iron(II) sulfate is probably the most important salt of iron, as well as the longest-known iron(II) compound. The compound is used as a mordant in dyeing; as a component of writing ink; in electroplating baths; in radiation dosimeters; in lithography and engraving; as a weed-killer; and in water purification. A major application of this compound is in the manufacture of other iron(II) salts including Prussian blue or ferric ferrocyanide. Iron(II) sulfate also is used as a reducing agent and an analytical reagent (in brown ring test for nitrate).

Physical Properties

White orthorhombic crystal; hygroscopic; density 3.65 g/cm^3; soluble in water (26.6g/100g water at 20°C). The monohydrate is a yellowish-white monoclinic crystal; density 3.0 g/cm^3; decomposes at 300°C; soluble in water. Heptahydrate is bluish-green monoclinic crystal; refractive index 1.47; hardness 2 Mohs; density 1.89g/cm^3; decomposes at about 60°C; very soluble in water; soluble in absolute methanol; slightly soluble in ethanol.

Thermochemical Properties

$\Delta H_f°$	–221.9 kcal/mol
$\Delta G_f°$	–196.2 kcal/mol
S°	25.7 cal/degree mol
C_ρ	24.0 cal/degree mol

Production

Iron(II) sulfate in industrial scale is mostly produced in the pickling process as a by-product of the steel industry. It is obtained when the surface of steel is cleaned with dilute sulfuric acid to remove metal impurities. In the laboratory iron(II) sulfate heptahydrate may be prepared by dissolving iron in dilute sulfuric acid in a reducing atmosphere, followed by crystallization:

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

Alcohol may be added to the aqueous solution to speed up crystallization; iron(II) may otherwise oxidize to iron(III) during a slow crystallization process.

Iron(II) oxide or carbonate may be used instead of iron metal to prepare the heptahydrate.

Reactions

The heptahydrate loses three molecules of water on heating at 56°C, forming the tetrahydrate $FeSO_4 \cdot 4H_2O$. On further heating the tetrahydrate loses three more water molecules at 65°C, giving monohydrate, $FeSO_4 \cdot H_2O$. The latter is stable to 300°C. On further heating anhydrous $FeSO_4$ is obtained, which on strong heating decomposed to iron(III) oxide and sulfur oxides:

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3$$

Iron(II) sulfate reacts with concentrated sulfuric acid to form iron(III) sulfate and sulfur dioxide:

$$2FeSO_4 + 2H_2SO_4 \rightarrow Fe_2(SO_4)_3 + SO_2 + 2H_2O$$

Iron(II) sulfate is a reducing agent. In an aqueous solution, it reduces nitrate and nitrite ions forming a brown ring of $Fe(NO)SO_4$. This reaction is applied for qualitative detection of nitrate and nitrite ion in the solution.

The compound is oxidized by moist air forming basic iron(III) sulfate. Aqueous solutions exposed to air also undergo oxidation; the reaction, however, is very slow. The rate of oxidation increases with temperature and the pH. In alkaline medium, the oxidation is much faster. In solution, it also is oxidized to Fe^{3+} by radiations from radioactive substances. This reaction is utilized to measure the radiation dose in dosimeter solutions.

Iron(II) sulfate forms double salts with the sulfates of ammonium, alkali and alkaline-earth metals (K, Rb, Cs, Mg). Such double salts are obtained by mixing equimolar amounts of these salts followed by crystallization. Some examples are $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (Mohr's salt), $FeSO_4 \cdot K_2SO_4 \cdot 6H_2O$, and $FeSO_4 \cdot MgSO_4 \cdot 6H_2O$.

When sodium carbonate is added to an aqueous solution of iron(II) sulfate, a white precipitate of iron(II) carbonate is produced. The above reaction is manifested by all iron(II) salts in aqueous solution:

$$Fe^{2+}(aq) + CO_3^{2-}(aq) \rightarrow FeCO_3\ (s)$$

The white precipitate rapidly turns green and then oxidizes to brown FeO(OH):

$$4FeCO_3 + 2H_2O + O_2 \rightarrow 4FeO \cdot OH + 4CO_2$$

Analysis

Elemental composition: Fe 36.77%, S 21.10%, O 42.13%. The water of crystallization in the hydrate salt may be determined by gravimetry. Iron may be analyzed by various instrumental techniques (See Iron).

Sulfate may be analyzed in an aqueous solution of the salt either by ion chromatography or by gravimetry or colorimetry following treatment with barium chloride.

IRON(III) SULFATE

[10028-22-5]
Formula: $Fe_2(SO_4)_3$; MW 399.88. Several hydrates are known: monohydrate [43059-01-4]; hexahydrate [13761-89-2]; heptahydrate [35139-28-7]; nonahydrate [13520-56-4]
Synonyms: ferric sulfate; ferric persulfate; ferric sesquisulfate

Uses

Iron(III) sulfate is used as a pigment; as a mordant in calico printing and dyeing textiles; in sewage treatment; as a coagulant in water purification; in pickling stainless steel; in etching aluminum; and as a catalyst. An important application of this compound is for preparing other iron(III) salts and iron alums. It also is used in pharmaceutical preparations.

Physical Properties

The anhydrous salt constitutes grayish-white rhombic crystals; hygroscopic; density 3.10 g/cm^3; slightly soluble in cold water; decomposes in hot water. The nonahydrate is a yellow hexagonal crystalline substance; refractive index 1.54; density 2.10 g/cm^3; hardness 2.5 Mohs; decomposes at 400°C; very soluble in water.

Preparation

Iron(III) sulfate may be prepared by oxidation of iron(II) sulfate by hydrogen peroxide, nitric acid or any other suitable oxidizing agent. The reaction is carried out in sulfuric acid. Balanced molecular equations for the reactions with hydrogen peroxide and nitric acid are as follows:

$$2FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O$$

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

Even in the absence of an oxidizing agent, concentrated sulfuric acid alone can convert iron(II) sulfate to iron(III) sulfate:

$$2FeSO_4 + 2H_2SO_4 \rightarrow Fe_2(SO_4)_3 + SO_2 + 2H_2O$$

It also may be prepared by treating iron(III) oxide with sulfuric acid:

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O$$

Reactions

Thermal decomposition of iron(III) sulfate yields iron(III) oxide with evolution of sulfur trioxide:

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$$

Iron(III) sulfate readily forms alums with many isomorphous compounds by mixing equimolar amounts of both the salts in aqueous solutions followed by crystallization:

$$Fe_2(SO_4)_3\ (aq) + (NH_4)_3SO_4\ (aq) \rightarrow 2NH_4Fe(SO_4)_2 \cdot 12H_2O$$

$$Fe_2(SO_4)_3\ (aq) + Cr_2(SO_4)_3\ (aq) \rightarrow 2FeCr(SO_4)_3 \cdot 12H_2O$$

Iron(III) sulfate may be reduced to +2 oxidation state of the metal in solution in the presence of common reducing agents. For example, reaction with zinc in sulfuric acid can produce iron(II) sulfate. The molecular equation is as follows:

$$Fe_2(SO_4)_3 + Zn \rightarrow 2FeSO_4 + ZnSO_4$$

Analysis

Elemental composition: Fe 27.93%, S 24.06%, O 48.01%. The water of crystallization in the hydrate salt may be determined by gravimetry. Iron content of the salt may be determined by common instrumental techniques (See Iron). Sulfate can be analyzed in an aqueous solution of the salt by gravimetry or colorimetry after addition of barium chloride solution.

IRON(II) SULFIDE

[1317-37-9]

Formula: FeS; MW 87.911; the pure compound is nonstoichiometric, deficient in iron; the stoichiometric formula may be $Fe^{2+}_{0.86}S^{2-}$.

Uses

Iron(II) sulfide occurs in nature as the minerals magnetkies, troillite and pyrrhotine. The most important application of this compound is in Kipp's apparatus as a source for laboratory preparation of hydrogen sulfide. It also is used in paints, pigments, and ceramics and lubricant coatings.

Physical Properties

Colorless hexagonal or tetragonal crystals; density 4.7g/cm^3; melts at 1188°C; insoluble in water; soluble in acids (reacts)

Thermochemical Properties

$\Delta H_f°$	–23.9 kcal/mol
$\Delta G_f°$	–24.0 kcal/mol
$S°$	14.4 cal/degree mol
C_ρ	12.1 cal/degree mol
ΔH_{fus}	7.53 kcal/mol

Preparation

Iron(II) sulfide may be synthesized from the elements but the product is contaminated with iron. The reaction is exothermic and the heat of reaction melts iron. Pure sulfide may be obtained by using a slight excess of sulfur: the excess then is distilled off.

The compound also may be precipitated by treating an aqueous solution of an alkali metal sulfide with that of iron(II) chloride or any iron(II) salt solution:

$$S^{2-}(aq) + Fe^{2+}(aq) \rightarrow FeS(s)$$

Another method of preparation involves passing a mixture of hydrogen sulfide and hydrogen over iron(III) oxide at about 1,000°C:

$$Fe_2O_3 + 2H_2S + H_2 \rightarrow 2FeS + 3H_2O$$

Reactions

Iron(II) sulfide reacts with acids evolving hydrogen sulfide:

$$FeS + 2HCl \rightarrow H_2S + FeCl_2$$

The compound is readily oxidized under moist condition by action of air, forming triiron tetroxide and elemental sulfur:

$$3FeS + 2O_2 \rightarrow Fe_3O_4 + 3S$$

The above reaction is exothermic.

Iron(II) sulfide decomposes to its elements when heated above 1,100°C:

$$FeS \rightarrow Fe + S$$

When heated with boiled water, it generates sulfuric acid and hydrogen:

$$4FeS + 8H_2O + 7O_2 \rightarrow 4H_2SO_4 + 4H_2 + Fe_2O_3$$

Analysis

Iron(II) sulfide exhibits nonstoichiometric composition. It may be characterized by x-ray. Iron may be analyzed by various instrumental techniques. (See Iron).

IRON(II) THIOCYANATE

[6010-09-9]
Formula: $Fe(SCN)_2 \cdot 3H_2O$; MW 226.06; exists as a trihydrate.
Synonyms: ferrous thiocyanate; ferrous sulfocyanate; ferrous sulfocyanide

Uses

Iron(II) thiocyanate is used as an analytical reagent and as an indicator for detecting peroxides in organic solutions.

Physical Properties

Pale-green monoclinic prisms; unstable; readily oxidized on exposure to air; decomposes on heating; very soluble in water; also soluble in alcohol and ether.

Preparation

Iron(II) thiocyanate is obtained as a trihydrate by dissolving iron metal in thiocyanic acid in an inert atmosphere in the absence of air.

Analysis

Elemental composition: Fe 32.47%, S 37.28%, C 13.96%, N 16.29%. The compound may be analyzed by colorimetry following its ready oxidation to red iron(III) thiocyanate. The intense red color produced in acidic pH may be measured by a spectrophotometer or a filter photometer at 460 nm.

KRYPTON

[7439-90-9]
Symbol: Kr; atomic number 36; atomic weight 83.80; a Group 0 (Group 18) element; inert gas element; electron configuration $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$; valence state 0; an uncommon valence state +2 exists for its difluoride; first ionization potential 13.999 volt; six stable natural isotopes are known; most abundant isotope Kr-84. Natural isotopes and their abundances: Kr-78 (0.354%), Kr-80 (2.20%), Kr-82 (11.56%), Kr-83 (11.55%), Kr-84 (56.90%), Kr-86 (17.37%).

Seventeen radioisotopes have been synthesized in nuclear reactions. Among them Kr-85 and Kr-87 have the longest half-lives of 10 and 6 ½ years, respectively, both undergoing beta decay.

History, Occurrence, and Uses

Krypton was discovered by William Ramsay and M.W. Travers in 1898. The element was named krypton, after the Greek word kryptos which means hidden. Krypton in trace quantities is found in the earth's atmosphere at a concentration level of about 1.14 ppm. The gas also is found in the spent fuel from nuclear reactors, resulting from fission of uranium and plutonium nuclei. Krypton has been found in Mars' atmosphere in trace concentration.

The commercial applications of krypton are fewer than those of helium or argon. Its principal use is in fluorescent lights. It is mixed with argon as a filling gas to enhance brightness of fluorescent tubes. Other applications are in flash tubes for high-speed photography and incandescent bulbs. Radioactive Kr-85 is used as a tracer to monitor surface reactions. The unit of length, meter was previously defined in terms of the orange-red spectral line of Kr-86.

Physical Properties

Colorless, odorless, and tasteless gas; density 3.733 g/L at 0°C; liquefies at –153.22°C; solidifies at –157.36°C to a white crystalline substance that has a face-centered cubic structure; critical temperature –63.6°C; critical pressure

54.30 atm; critical density 0.908 g/L; triple point temperature –157.4°C; triple point pressure 0.722 atm; viscosity at 0°C 0.02327 centipoise; slightly soluble in water; solubility in water, 10.69 mL of the gas in 100mL water at 0°C and 1 atm; velocity of sound 213 m/s at 0°C and 1 atm.

Thermochemical Properties

$\Delta H_f°$	0.0
S°	39.2 cal/degree mol
C_ρ	4.97 cal/degree mol
ΔH_{vap}	2.17 kcal/mol
ΔH_{fus}	0.327 kcal/mol

Production

Most krypton produced in commercial scale comes from air. Krypton and other inert gases are obtained from air by a distillation-liquefaction process. Different types of air-separation plants varying in design are known for commercial production of nitrogen, oxygen, and inert gases (See Helium).

Krypton also may be recovered from spent fuel rods of nuclear power plants. It is produced, along with xenon, in fission of uranium and plutonium. This process, however, is not a major source of krypton, and the recovered gas also contains radioactive Kr-85 isotope.

Reactions

Krypton is an inert gas element. Its closed-shell, stable octet electron configuration allows zero reactivity with practically any substance. Only a few types of compounds, complexes, and clathrates have been synthesized, mostly with fluorine, the most electronegative element. The most notable is krypton difluoride, KrF_2 [13773-81-4], which also forms complex salts such as $Kr_2F_3^+AsF_6^-$ [52721-23-0] and $KrF^+PtF_6^-$ [52707-25-2]. These compounds are unstable at ambient conditions. Krypton also forms clathrates with phenol and hydroquinone. Such interstitial substances are thermodynamically unstable and have irregular stoichiometric compositions (See Argon clathrates).

Analysis

Krypton may be analysed most conveniently by GC/MS. The characteristic masses for its mass spectroscopic identification are 84, 86, and 83, the most abundant natural isotopes of the element. It also may be analyzed by gas-solid chromatography by its retention times.

KRYPTON DIFLUORIDE

[13773-81-4]

Formula: KrF_2; MW 121.80; The molecule exhibits linear geometry in gas phase.

Uses

Krypton difluoride is used as a powerful oxidizing agent to oxidize halogen fluorides and gold.

Physical Properties

White tetragonal crystal; sublimes under vacuum at 0°C; decomposes slowly at 25°C; density 3.24 g/cm^3; reacts with water; vapor pressure 30 torr at 0°C; slightly soluble in liquid fluorine.

Preparation

Krypton difluoride may be prepared by the reaction of krypton with fluorine in an electric discharge at low pressure and liquid oxygen temperature. Also it may be made by irradiating krypton with ultraviolet rays in a fluorine—argon gas mixture at liquid helium temperature (–196°F).

$$Kr + F_2 \rightarrow KrF_2$$

The product can be stored at –78°C without decomposition.

Reactions

Krypton difluoride forms complexes with fluorides of many metals, such as arsenic, antimony, tantalum, niobium, gold, and platinum.

$$KrF_2 + SbF_5 \rightarrow KrF^+SbF_6^-$$

$$KrF_2 + TaF_5 \rightarrow KrF^+TaF_6^-$$

Krypton difluoride is a powerful oxidizing and fluorinating agent. For example, it fluorinates ruthenium tetroxide, RuO_4, to ruthenium oxytetrafluoride, $RuOF_4$, in liquid HF.

Krypton difluoride decomposes into its elements at ambient temperatures.

Analysis

Elemental composition: Kr 68.80%, F 31.20%. Krypton difluoride may be analyzed by GC/MS under cryogenic conditions following its decomposition into its gaseous elements.

LANTHANUM

[7439-91-0]
Symbol: La; atomic number 57; atomic weight 138.91; a rare-earth transition metal, precursor to a series of 14 inner-transition elements known as the lanthanide series; electron configuration [Xe]5d^{1}6s^2; oxidation state +3; atomic radius 1.879Å; ionic radius (La^{3+}) 1.061Å; electronegativity 1.17; two natural isotopes are La-139 (99.911%) and La-138 (0.089%).

History, Occurrence, and Uses

Lanthanum was isolated from cerium nitrate in 1839 by Mosander. The element in its oxide form was called “lanthana” meaning “hidden”. Although the electron configuration of the element shows a vacant 4*f* orbital and, therefore, does not belong to the “true rare-earth elements,” the metal exhibits striking similarities to other rare-earths. In nature, lanthanum never occurs in free state and is always found associated with other rare-earth metals. The principal minerals are monazite and bastnasite. Its concentration in the earth’s crust is estimated to be 30 mg/kg. Lanthanum as a pure metal has limited applications. However, in the form of alloys, the metal has several metallurgical applications. When alloyed with iron, chromium, nickel, and molybdenum, it improves resistance of these metals to oxidation. It also improves the impact strength, fluidity, ductility and other mechanical properties of the alloys. The pure metal is used only for research.

Physical Properties

Silvery white metal; soft and malleable; hexagonal closed pack crystal system; transforms to face-centered cubic crystals at 310°C which further transforms to a body-centered cubic allotropic modification at 868°C; density 6.166 g/cm^3; Brinnel hardness (as cast) 37; melts at 918°C; vaporizes at 3,464°C; vapor pressure 1 torr at 2,192°C; electrical resistivity 56.8 x 10^6 ohm-cm at 25°C; Young’s modulus 3.84 x 10^{-11} dynes/cm^2; Poisson’s ratio 0.288; thermal neutron cross section 8.9 barns.

Thermochemical Properties

ΔH_f° (cry)	0.0
S° (cry)	13.6 cal/degree mol
C_ρ (cry)	6.48 cal/degree mol
ΔH_f° (g)	103.0 kcal/mol
ΔG_f° (g)	94.1 kcal/mol
S°(g)	43.56 cal/degree mol
C_ρ (g)	5.44 cal/degree mol
ΔH_{fus}	2.75 kcal/mol
ΔH_{vap}	100.8 kcal/mol
$\Delta H_{transformation}$ (alpha-beta)	0.095 kcal/mol
Thermal conductivity (at 28°C)	0.033 cal/cm^2/cm/sec/°C
Coeff. thermal expansion (at 400°C)	7.9 x 10^{-6}/°C

Production

Lanthanum is most commonly obtained from the two naturally occurring rate-earth minerals, monazite and bastnasite. Monazite is a rare earth-thorium phosphate that typically contains lanthanum between 15 to 25%. Bastnasite is a rare earth-fluocarbonate-type mineral in which lanthanum content may vary, usually between 8 to 38%. The recovery of the metal from either of its ores involves three major steps: (i) extraction of all rare-earths combined together from the non-rare-earth components of the mineral, (ii) separation or isolation of lanthanum from other lanthanide elements present in the mineral extract, and (iii) preparation of high-purity grade lanthanum from its isolated product.

Industrial production processes also may vary depending on the nature and availability of mineral, manufacturing cost, demand for other byproducts, purity level of the metal desired, and its end use. Recovery processes are quite similar to other rare-earth metals and chemistry of the processes does not differ noticeably from one metal to another.

Extraction of lanthanum from monazite is discussed below first, followed by that from bastnasite.

The mineral mixtures are crushed and ground. Monazite, because of its magnetic properties, may be separated from other minerals that may be either magnetic or nonmagnetic by repeated electromagnetic separation using electromagnets of varying intensities. After its separation the mineral is treated with hot concentrated sulfuric acid, which converts thorium, lanthanum, and rare-earth metals present into their sulfates. These sulfates are soluble in water. The soluble products are leached into water. The insoluble residues and impurities are filtered out. Then the acidic filtrate is partially neutralized with caustic soda to pH 3 to 4. Thorium precipitates out of solution as hydroxide. Alternatively, thorium may be precipitated as pyrophosphate by adding sodium pyrophosphate to the acid solution. The solution after removal of thorium is treated with ammonium oxalate. This converts all lanthanide elements in the ore into their insoluble oxalate salts. The oxalates decompose into oxides when calcined in air. Cerium is the major component of this mixture of rare-earth oxides. Also, it is the only lanthanide element oxidized to its tetravalent state, Ce^{4+}. The tetravalent cerium(IV) oxide is insoluble in dilute nitric acid. The oxide mixture is, therefore, treated with dilute nitric acid to dissolve lanthanum oxide and other rare-earth oxides to separate them from cerium. Lanthanum is separated from this cerium-free rare-earth mixture as a double salt with ammonium nitrate by crystallization. The lanthanum-ammonium double salt is relatively less soluble than other rare-earth double salts and stays in the most insoluble fraction.

The most efficient method of separating lanthanum from rare-earth salts solution involves ion exchange. In this process, lanthanum and other tripositive rare-earth metal ions are sorbed onto suitable cation-exchange resin beds by exchange with hydrogen, ammonium, or cupric ions incorporated into the resins. The rare-earth ions are then selectively removed in successive steps by eluting with solutions of suitable complexing agents. Several complexing agents have been used successfully. These include ammonium citrate (a buffered solution, pH 2-4); buffered nitrilotriacetate; buffered ethylenediamine tetraacetic acid (EDTA); and ammonium or metal salts of EDTA. Buffered solution of ammonium-EDTA (pH ~8.4) has been found to be highly effective in such ion-exchange separation, yielding high purity products. EDTA complexes of lanthanide elements have high formation constants in a significantly wide range, between 10^{14} and 10^{19}.

Lanthanum also may be separated from aqueous solutions of rare-earth nitrates by liquid-liquid extraction using a suitable water-immiscible organic liquid such as tributyl phosphate or another complexing agent dissolved in it.

The method, however, is not as efficient as the ion-exchange technique discussed above.

Lanthanum in purified metallic state may be obtained from its purified oxide or other salts. One such process involves heating the oxide with ammonium chloride or ammonium fluoride and hydrofluoric acid at 300° to 400°C in a tantalum or tungsten crucible. This is followed by reduction with alkali or alkaline earth metals at 1,000°C under argon or in vacuum.

A typical reaction is:

$$La_2O_3 + 6NH_4Cl \rightarrow 2LaCl_3 + 6NH_3 + 3H_2O$$

$$LaCl_3 + 3Li \rightarrow La + 3LiCl$$

Also high purity lanthanum may be produced by electrolysis of a molten mixture of anhydrous lanthanum chloride and sodium chloride or potassium chloride at elevated temperatures.

When lanthanum is produced from the mineral bastnasite, all processes except ore extraction discussed above are the same. The mineral is crushed and concentrated by flotation process. This is followed by treatment with dilute HCl, which converts lanthanum and the rare-earths contained in the mineral into their chlorides. Calcination in air results in rare-earth oxides.

Reactions

Lanthanum metal forms salts in +3 oxidation state, the only stable valence state of this element. The redox potential for the reaction $La \rightarrow La^{3+} + 3e^-$ in aqueous phase is 2.522 V. The La^{3+} ion is colorless.

Combustion in air or oxygen produces lanthanum sesquioxide. However, at ambient temperatures, when exposed to moist air, the metal forms a hydrated oxide with a large volume increase.

Lanthanum reacts with water forming its hydroxide, $La(OH)_3$. The reaction is slow in cold water but faster in hot water.

Lanthanum reacts vigorously when heated with halogens above 200°C, forming lanthanum halides:

$$2La + 3Cl_2 \rightarrow 2LaCl_3$$

With hydrogen, interstitial hydrides are formed, the compositions of which may vary from LaH_2 to LaH_3.

Lanthanum combines with nitrogen, carbon, sulfur and phosphorus at elevated temperatures, forming binary salts. Also, with metalloid elements such as boron, silicon, selenium, and arsenic, similar reactions occur at high temperatures forming similar binary compounds.

Analysis

The element may be analyzed by several instrumental techniques including atomic absorption and emission spectrophotometry, ICP-MS, x-ray fluorescence, and neutron activation analysis.

LANTHANUM CHLORIDE

[10099-58-8]
Formula: $LaCl_3$; MW 245.26; forms a stable heptahydrate, $LaCl_3 \cdot 7H_2O$, [20211-76-1], MW 371.37.

Uses

Lanthanum chloride is used to prepare other lanthanum salts. The anhydrous chloride is employed to produce lanthanum metal.

Physical Properties

The anhydrous chloride is a white hexagonal crystal; hygroscopic; density 3.84 g/cm^3; melts at 850°C; soluble in water. The heptahydrate is a white triclinic crystal; decomposes at 91°C; soluble in water and ethanol.

Thermochemical Properties

$\Delta H_f°$	–255.6 kcal/mol
C_ρ	26.0 kcal/ mol

Preparation

The heptahydrate is formed by dissolving the oxide, hydroxide or carbonate in hydrochloric acid, followed by crystallization. The anhydrous chloride is obtained by heating oxide, hydroxide, or carbonate in an atmosphere of dry hydrogen chloride.

$$La_2(CO_3)_3 + 6HCl \rightarrow 2LnCl_3 + 3CO_2 + 3H_2O$$

Another method involves heating lanthanum oxide with excess ammonium chloride at 300°C:

Reactions

When heated in the presence of water vapor, lanthanum oxochloride is formed:

$$LaCl_3 + H_2O \xrightarrow[\text{temperature}]{\text{high}} LaOCl + 2HCl$$

Heating with glass at elevated temperatures also forms oxochloride:

$$LaCl_3 + SiO_2 \xrightarrow[\text{temperature}]{\text{elevated}} 2LaOCl + SiCl_4$$

Lanthanum chloride reacts with hydrogen sulfide when heated at 1100°C, forming lanthanum sulfide:

$$2LaCl_3 + 3H_2S \xrightarrow{1100^\circ C} La_2S_3 + 3H_2S$$

Reactions with ammonia and phosphine at elevated temperatures yield lanthanum nitride and phosphide, respectively:

$$LaCl_3 + PH_3 \xrightarrow{\substack{elevated\\temperature}} LaP + 3HCl$$

The addition of hydrofluoric acid to an aqueous solution of lanthanum chloride precipitates out lanthanum fluoride, LaF_3:

$$LaCl_2 + 3HF \rightarrow LaF_3 + 3HCl$$

Lanthanum chloride is reduced to lanthanum metal when heated with an alkali or alkaline earth metal at temperatures above 1000°C:

$$LaCl_3 + 3Li \xrightarrow{>1000^\circ C} La + 3LiCl$$

Analysis

Elemental composition: La 56.63%, Cl 43.36%. The salt and its hydrate may be characterized by x-ray methods. Water of crystallization may be determined by gravimetry. Lanthanum may be analyzed by flame or furnace AA or by ICP-AES methods (See Lanthanum). Chloride ion in an aqueous solution of the salt may be measured by titration with a standard solution of silver nitrate or mercuric nitrate or by ion chromatography following appropriate dilution.

LANTHANUM FLUORIDE

[13709-38-1]
Formula: LaF_3; MW 195.90

Uses

Lanthanum fluoride is used in phosphor lamp coating. Mixed with other rare earths, it is used in carbon arc electrodes and lasers. Also, the fluoride is used in the production of lanthanum metal, an intermediate step in the manufacture of high purity metal.

Physical Properties

White hexagonal crystal; hygroscopic; density 5.9 g/cm^3; melts at 1,493°C; insoluble in water and acids.

Preparation

Lanthanum fluoride may be precipitated by adding hydrofluoric acid to an aqueous solution of lanthanum nitrate or chloride:

$$La(NO_3)_3 + 3HF \rightarrow LaF_3 + 3HNO_3$$

The compound also can be made by heating lanthanum oxide with ammonium fluoride in hydrofluoric acid at 300 to 400°C. Ammonium fluoride released in the reaction sublimes at this temperature:

$$La_2O_3 + 6NH_4F \cdot 6HF \xrightarrow{300-400^\circ C} 2LaF_3 + 6NH_4F\uparrow + 3H_2O\uparrow$$

Anhydrous lanthanum fluoride also may be made by passing dry hydrogen fluoride over lanthanum oxide. This process, however, produces trace amounts of lanthanum oxyfluoride, LaOF. Highly purified material may be obtained by passing dry purified HF over molten fluoride in a platinum crucible.

Analysis

Elemental composition: La 70.91%, F 29.01%. The compound may be characterized by x-ray methods. Lanthanum may be analyzed by AA or ICP technique following digestion in nitric acid and appropriate dilution of acid extract.

LANTHANUM HYDROXIDE

[14507-19-8]
Formula: $La(OH)_3$; MW 189.93

Uses

Lanthanum hydroxide is used to prepare other lanthanum salts.

Physical Properties

White amorphous solid; decomposes on heating; insoluble in water.

Preparation

Lanthanum hydroxide is precipitated by adding excess of caustic soda, caustic potash or ammonia to an aqueous solution of a La^{3+} salt, such as $LaCl_3$, $La(NO_3)_3$ or $La(SO_4)_3$:

$$La^{3+} + 3OH^- \rightarrow La(OH)_3$$

Reactions

The hydroxide is strongly basic. It reacts with acids undergoing neutralization reactions; i.e., reaction with HCl or HNO_3 yields hydrated salt of lanthanum chloride or nitrate on evaporation and crystallization of the solution.

It reacts with ammonium salts displacing ammonia:

$$La(OH)_3 + 3NH_4Cl \rightarrow LaCl_3 + 3NH_3 + 3H_2O$$

The hydroxide absorbs CO_2 from air forming lanthanum carbonate:

$$2La(OH)_3 + 3CO_2 \rightarrow La_2(CO_3)_3 + 3H_2O$$

Lanthinum hydroxide on dehydration produces lanthanum oxide monohydrate, $La_2O_3 \cdot H_2O$:

$$2La(OH)_3 \xrightarrow{heat} La_2O_3 \cdot H_2O + H_2O$$

.

Analysis

Elemental composition: La 73.13%; O 25.27%, H 1.59%. Lanthanum may be analyzed in the acidified extract of the compound by AA or ICP technique (See Lanthanum). Dehydration at 100°C produces $La_2O_3 \cdot H_2O$, releasing one mole of water of crystallization per mole of hydroxide (9.5%) loss, which may be measured by gravimetry.

LANTHANUM NITRATE

[10277-43-7]
Formula: $La(NO_3)_3 \cdot 6H_2O$; MW 433.01; stable as hexahydrate
Synonym: lanthanum nitrate hexahydrate

Uses

The nitrate is used as an analytical standard; as a matrix modifier in furnace AA analysis; and for preparing other lanthanum salts.

Physical Properties

White crystalline solid; hygroscopic; decomposes around 40°C; very soluble in water and alcohol.

Preparation

The salt is prepared by dissolution of lanthanum oxide, hydroxide or carbonate in nitric acid, followed by crystallization, and obtained as a hexahydrate. The general reactions are as follows:

$$La_2O_3 + 6HNO_3 \rightarrow 2La(NO_3)_3 + 3H_2O$$

$$La(OH)_3 + 3HNO_3 \rightarrow La(NO_3)_3 + 3H_2O$$

$$La_2(CO_3)_3 + 6HNO_3 \rightarrow 2La(NO_3)_3 + 3CO_2 + 3H_2O$$

Reactions

Thermal dissociation yields lanthanum oxide, La_2O_3. Its reactions in aqueous solutions are those of La^{3+} ion. It forms double salts with magnesium, calcium and ammonium nitrates and many other salts when mixed in stoichiometic amounts. Such double salts are obtained from solution mixtures on crystallization and may vary in their compositions.

Analysis

Elemental composition (for hexahydrate): La 32.08%, N 9.70%, H 2.79%, O

55.43%. The water of crystallization may be determined by heating a weighted quantity of the salt and measuring the loss in weight by gravimetry. Lanthanum may be analyzed in a dilute aqueous solution by AA or ICP spectrophotometry. N, H and O may be determined by elemental analysis.

LANTHANUM OXIDE

[1312-81-8]
Formula: La_2O_3; MW 325.81
Synonyms: lanthanum trioxide; lanthanum sesquioxide; lanthana

Uses

Highly pure lanthanum oxide is used to make optical glass of high refractive index for camera lenses. It also is used to make glass fibers. The oxide also is used to improve thermal and electrical properties of barium and strontium titanates. Other applications are in glass polishes; carbon arc electrodes; fluorescent type phosphors; and as a diluent for nuclear fuels. In such applications, lanthinum oxide is usually combined with other rare earth oxides.

Physical Properties

White amorphous powder; density 6.51 g/cm^3; melts at 2,305°C; vaporizes at 4,200°C; insoluble in water; dissolves in dilute mineral acids.

Thermochemical Properties

$\Delta H_f°$	–428.7 kcal/mol
$\Delta G_f°$	–407.7 kcal/mol
S°	30.43 cal/degree mol
C_ρ	26.00 cal/degree mol

Preparation

Lanthanum oxide can be produced by direct combustion of lanthanum in oxygen or air. The oxide also may be prepared by decomposition of an oxo salt of lanthanum, such as nitrate, sulfate, carbonate, hydroxide or oxalate.

$$La(CO_3)_3 \cdot 8H_2O \xrightarrow{\text{elevated temperature}} La_2O_3 + 3CO_2 + 8H_2O$$

$$2La_2(C_2O_4)_3 \cdot 9H_2O + 3O_2 \xrightarrow{\text{elevated temperature}} 2La_2O_3 + 12CO_2 + 18H_2O$$

Reactions

The oxide reacts with acids forming their salts:

$$La_2O_3 + 6HCl + 7H_2O \rightarrow LaCl_3 \cdot 7H_2O + 3H_2O$$

$$La_2O_3 + 6HNO_3 + 6H_2O \rightarrow La(NO_3)_3 \cdot 6H_2O + 3H_2O$$

The hydrated salts contain the ions $[La(H_2O)_n]^{3+}$.

Heating the oxide with an excess of ammonium chloride yields lanthanum chloride:

$$La_2O_3 + 6NH_4Cl \xrightarrow{300^\circ C} 2LaCl_3 + 3H_2O + 6NH_3$$

Reaction with strong alkalies at high temperature and pressure slowly forms crystals of lanthanum hydroxide, $La(OH)_3$.

Analysis

Elemental composition: La 85.27%, O 14.73%. The compound may be characterized by x-ray. Lanthanum may be analyzed by various instrumental techniques (See Lanthanum).

LANTHANUM SULFATE

[10294-62-9]
Formula: $La_2(SO_4)_3 \cdot 9H_2O$; MW 728.14; stable as nonahydrate
Synonym: lanthanum sulfate nonhydrate

Uses

Lanthanum sulfate is used to prepare many lanthanum compounds.

Physical Properties

White hexagonal crystals; density 2.82 g/cm^3; slightly soluble in cold water, solubility decreasing with temperature; insoluble in ethanol; dehydrates in the air at 400°C.

Preparation

Lanthanum sulfate is prepared by dissolving lanthanum oxide, hydroxide or carbonate in sulfuric acid, followed by crystallization.

$$La_2O_3 + 3H_2SO_4 \rightarrow La_2(SO_4)_3 + H_2O$$

$$La_2(CO_3)_3 + 3H_2SO_4 \rightarrow La_2(SO_4)_3 + 3CO_2 + 3H_2O$$

Analysis

Elemental composition (for nonahydrate, $La_2(SO_4)_3 \cdot 9H_2O$): La 38.15%, S 13.21%; H 2.49%, O 46.14%. Water of crystallization 22.27%. The compound is digested in nitric acid, the acid extract diluted and analyzed for lanthanum by AA or ICP (See Lanthanum). The water of crystallization may be determined by measuring loss of water by gravimetry following dehydrating a weighted amount of substance at 400°C. Also, the solid crystals may be characterized by x-ray.

LAWRENCIUM

[22537-19-5]
Symbol: Lr; atomic number 103; atomic weight 262; a transuranium inner-transition actinide series element; a synthetic radioactive element; electron configuration [Rn]$7s^25f^{14}6d^1$; valence +3; six isotopes of masses 255 to 260 have been synthesized; longest-lived known isotope Lr-260 has half-life of ~3 minutes.

History

Lawrencium was synthesized by Ghiorso, Sikkeland, Larsh and Latimer in 1961 in Lawrence Radiation Laboratory, Berkeley, California. The new element was named after Ernest O. Lawrence. The element has no practical application.

Synthesis

Lawrencium has been synthesized only in very minute quantities. It was first synthesized by irradiating a mixture of californium isotopes with boron ions:

$$^{250-252}_{\ \ \ \ 98}Cf + ^{11}_{5}B \rightarrow ^{258}_{103}Lr + 3-5\,^{1}_{0}n$$

The isotope obtained this way has a half-life of about 4.2 seconds and is an alpha emitter.

Lawrencium-256 (~35 seconds) is prepared by bombarding americium-243 with oxygen-18:

$$^{243}_{95}Am + ^{18}_{8}O \rightarrow ^{256}_{103}Lr + 5\,^{1}_{0}n$$

All lawrencium isotopes of masses 255 to 260 have been synthesized by bombardment of transuranium elements with heavy ions.

LEAD

[7439-92-1]
Symbol Pb; atomic number 82; atomic weight 207.20; a Group IV A (Group 14) metallic element; metallic radius 1.75 Å; covalent radius (sp^3) 1.44 Å; ionic radius Pb^{2+} 1.18 Å; Pb^{4+} 0.70 Å; electron configuration [Xe]$4f^{14}5d^{10}6s^26\rho^2$; valence +2 and +4. Four stable isotopes are known: Pb-204 (1.48%), Pb-206 (23.6%), Pb-207 (22.6%) and Pb-208(52.3%); three of these (Pb-206, Pb-207 and Pb-208) are the end products of uranium, actinium and thorium series, respectively. Twenty-seven (27) radioisotopes are known.

History, Occurrence, and Uses

Lead is one of the oldest metals known to civilization. The uses of some of its alloys and salts have been documented early in history. The element derived its symbol Pb from the Latin word plumbium. The metal is rarely found in nature in its native form; however, it is found in several minerals, such as galena (PbS), anglesite ($PbSO_4$), minium (Pb_3O_4) and cerussite ($PbCO_3$). Its concentration in the earth's crust is 12.5 mg/kg and in sea water 0.03mg/L.

Lead has numerous applications as metal, alloys and compounds. The major applications of the metal and its alloys such as solder are as materials of construction for pipe lines, plumbing fixtures, wires, ammunition, containers for corrosive acids and shield against short-wavelength radiation. Another major application is in storage batteries in which both the metal and its dioxide are used. Several lead compounds, such as lead chromate (chrome yellow), lead sulfate (white lead), lead tetroxide (red lead), and the basic carbonate are used in paints.

Physical Properties

Silvery grey metal with bright luster; face-centered cubic crystals; very soft, malleable and ductile; easily cast, rolled and extruded; density 11.3 g/cm^3; Moh's hardness 1, Brinell hardness 4.0 (high purity metal); easily melted, melts at 327.46°C; vaporizes at 1,749°C; vapor pressure 1 torr at 970°C and 10 torr at 1160°C; poor conductor of electricity; electrical resistivity 20.65 microhm–cm at 20°C and of liquid melt 94.6 microhm–cm at its melting point; viscosity of molten metal 3.2 centipoise at its melting point and 2.32 centipoise at 400°C; surface tension 442 dynes/cm at 350°C; tensile strength 2,000 psi; thermal neutron absorption cross section 0.17 barn; standard electrode potential, $Pb^{2+} + 2e^- \leftrightarrows Pb$ –0.13V; very resistant to corrosion.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	46.65 kcal/mol
$\Delta G_f°$ (gas)	38.77 kcal/mol
S° (cry)	15.49 cal/degree mol
S° (gas)	41.92 cal/degree mol
C_ρ (cry)	6.31 cal/degree mol
C_ρ (gas)	4.97 cal/degree mol
ΔH_{fus}	1.14 kcal/mol
ΔH_{vap}	49.9 kcal/mol
Thermal conductivity	
at 18°C	0.083 cal/cm^2/sec/cm/°C
at 330°C	0.039 cal/cm^2/sec/cm/°C
Coefficient of linear expansion	2.9×10^{-6}/°C

Production

Lead is produced commercially from its principal ore, galena (PbS). The ore is associated with sulfides of several metals including iron, copper, zinc, silver, bismuth, arsenic, antimony and tin. The ore is crushed and ground. It then is selectively separated from gangue and other valuable minerals by one or more processes that include gravity separation and flotation. Selective flotation processes are most commonly employed to remove significant quantities of most metal sulfides, silica, and other impurities. This yields relatively pure galena concentrate containing 50 to 80% lead.

The lead concentrate must be roasted for effective removal of sulfur and then smelted in a blast furnace. Sulfur is mostly removed by a sinter process. The galena concentrate or the ore itself, if its impurity content is low, is mixed with silica and other slag-forming reagents and roasted in sinter machines to produce lead oxide, lead silicate, and some metallic lead. The principal reactions are:

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$

$$2PbO + SiO_2 \rightarrow Pb_2SiO_4$$

$$PbS + 2PbO \rightarrow 3Pb + SO_2$$

Lead oxide, silicate, and the gangue material consisting of silica, lime, iron oxide, zinc oxide and alumina, react in a blast furnace at 1,000°C, producing lead (lead bullion) along with matte and speiss that result from reactions of residual sulfur with copper and arsenic. Slag, dust, and gases (CO and CO_2) are the other products generated in the blast furnace. The principal reactions in the furnace are:

$$2PbO + C \rightarrow 2Pb + CO_2$$

$$CO_2 + C \rightarrow 2CO$$

$$PbO + CO \rightarrow Pb + CO_2$$

$$Pb_2SiO_4 + CaO + FeO \rightarrow 2PbO + \text{slag } (CaO \cdot FeO, SiO_2)$$

Lead bullion obtained from the blast furnace contains copper and other metals which may be removed either by pyrometallurgical methods or by electrolysis. Copper mostly is removed by cooling the bullion from the furnace to 350°C at which temperature it becomes insoluble and separates out. Trace copper left in the lead eutectic mixture is removed by addition of elemental sulfur to form copper sulfide. Arsenic, antimony, and tin may be removed either by Harris process, involving pumping the lead bullion through molten sodium hydrate, or by a “softening” process that involves blowing air over molten bullion at 750°C, whereby these metals are converted into their oxides and form slags. Silver and gold may be removed either by Parkes process or the old Pattinson process. In the Parkes process, molten zinc is added to the molten lead bullion. Zinc forms alloys with silver and gold and rises to the top as a crust that also contains some lead. The crust is distilled in a retort to free zinc metal for reuse. Trace zinc is removed from the lead bullion either as zinc chloride, by treatment with chlorine gas, or by vacuum distillation. The last remaining bismuth metal is separated by Kroll-Betterton process. In this process, calcium and magnesium are added into the lead bullion. They form calcium and magnesium bismuthides, Ca_3Bi_2 and Mg_3Bi_2, respectively, which are removed as dross. Refined bismuth may be obtained from this dross.

Electrolytic refining of lead bullion is commonly employed in many modern plants to obtain high purity grade metal. Various separation processes for removal of individual metals are not required. In such refining (Betts process), a solution of lead fluosilicate is used as an electrolyte, while the anode consists of impure lead bullion and the cathode constitutes a thin sheet of pure lead. Lead deposits on to the cathode during electrolysis. Impurity metals remain undissolved and attached to the anode, forming a slime which may be removed after electrolysis and treated for recovery of these metals.

Reactions

Lead forms amphoteric compounds in +2 and +4 valence states, forming plumbous and plumbic salts, such as $PbCl_2$ and $PbCl_4$, as well as plumbites and plumbates, such as Na_4PbO_3 and Ca_2PbO_4,. Over a thousand compounds of lead are known which include divalent and tetravalent salts, complexes, and organometallics. Divalent compounds of lead are far more numerous than the tetravalent compounds. Most compounds, however, result from the reactions involving other lead compounds, rather than elemental lead. Only the reactions involving elemental lead are outlined briefly below.

In very finely divided form, lead is pyrophoric. When heated in oxygen or air, the metal forms lead monoxide, PbO, which is oxidized further in the presence of excess oxygen or air to lead tetroxide, Pb_3O_4. The finely divided metal dissolves in a solution of sodium in liquid ammonia, forming a green solution of Na_4Pb_9.

The metal is not attacked by hot water. But in the presence of free oxygen, lead(II) hydroxide is formed. The overall reaction is:

$$2Pb + 2H_2O + O_2 \rightarrow 2Pb(OH)_2$$

In hard water, however, the presence of small amounts of carbonate, sulfate, or silicate ions form a protective film on the metal surface, and prevent the occurrence of the above reaction and thus, corrosion of the metal.

Lead does not evolve hydrogen readily with acids. Nitric acid attacks the metal readily, forming lead nitrate and oxides of nitrogen:

$$3Pb + 8HNO_3 \rightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

This reaction is faster in dilute nitric acid than strong acid. Hydrochloric acid has little effect on the metal. At ordinary temperatures, lead dissolves slowly in hydrochloric acid, forming a coating of lead(II) chloride, $PbCl_2$ over the metal, which prevents further attack.

At ordinary temperatures, lead is not readily attacked by sulfuric acid. A coating of insoluble lead sulfate formed on the metal surface prevents any further reaction of the metal with the acid. The acid is, therefore, stored in specially designed lead containers. Also, the action of hot concentrated sulfuric acid is very low up to about 200°C. However, at temperatures near 260°C, both the concentrated sulfuric and hydrochloric acids dissolve lead completely.

At ordinary temperatures, hydrofluoric acid also has little action on the metal. Formation of insoluble PbF_2 prevents dissolution of lead in the acid.

Organic acids in the presence of oxygen react slowly with lead, forming their soluble salts. Thus, acetic acid in the presence of oxygen forms lead(II) acetate:

$$2Pb + 4CH_3COOH + O_2 \rightarrow 2Pb(CH_3COO)_2 + 2H_2O$$

Lead dissolves in alkalies forming plumbite ion, $Pb(OH)_4^{2-}$ with the evolution of hydrogen:

$$Pb + 2OH^- + 2H_2O \rightarrow Pb(OH)_4^{2-} + H_2$$

Lead combines with fluorine, chlorine, and bromine, forming bivalent lead halides:

$$Pb + Cl_2 \rightarrow PbCl_2$$

Fusion with sulfur at elevated temperatures yields lead sulfide, PbS.

The metal is oxidized to PbO when heated with sodium nitrate at elevated temperatures.

$$Pb + NaNO_3 \rightarrow PbO + NaNO_2$$

Lead is widely used in storage batteries. Each cell consists of a spongy lead plate as cathode and lead dioxide as anode immersed in the electrolyte sulfuric acid. The overall chemical reaction in the cell during discharge is as follows:

$$PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$$

Analysis

A number of methods have been described in old literature based on colorimetry and gravimetry. Such methods apply to measuring soluble lead(II) salts in water. One method involves precipitating Pb^{2+} using chromic acid to obtain yellow lead chromate. Dithizone colorimetric method is very sensitive in measuring lead in water. The method involves acidifying the sample, mixing with ammoniacal citrate-cyanide reducing solution, and extracting with dithizone in chloroform to a cherry-red derivative and measuring absorbance at 510 nm using a spectrophotometer. The most sensitive and accurate measurements, however, involve instrumental techniques. Lead may be analyzed in aqueous matrices or the nitric acid extracts of its salts by flame and furnace

AA, ICP-AES, and ICP/MS techniques. The measurements are done at the wavelengths 283.3 and 217.0 nm for flame and furnace AA and 220.35 and 217.00 nm for ICP-AES analyses. The instrument detection levels are high ppb range for flame AA and low ppb by furnace AA and ICP-AES, and much lower for ICP-MS.

Lead may be analyzed both in aqueous and nonaqueous matrices by x-ray techniques. High concentration of the metal in paint chips can be measured rapidly and nondestructively by x-ray fluorescence.

Lead in water may be analyzed very precisely at low concentrations by anodic stripping voltametry using an electrochemical analyzer; static or controlled growth mercury drop electrodes, reference calomel or silver-silver chloride electrodes; and silica or TFE cells. Copper, silver, gold, and certain organic compounds may interfere in the test. (APHA, AWWA and WEF. 1998. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington, D.C.: American Public Health Association.)

Lead also may be measured by neutron activation analysis.

Toxicity

Lead is an acute and a chronic toxicant. Acute effects are ataxia, headache, vomiting, stupor, hallucination, tremors and convulsions. Chronic symptoms from occupational exposure include weight loss, anemia, kidney damage and memory loss. (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons.) Permanent brain damage has been noted among children. Lead bioaccumulates in bones and teeth. The metal is classified as an environmental priority pollutant by the US EPA.

The action level for lead in drinking water is 15μg/L. Its content in food and house paints is regulated in the USA by the Food and Drug Administration.

LEAD ACETATE

[301-04-2]
Formula: $Pb(C_2H_3O_2)_2$; MW 325.29; also forms trihydrate $Pb[C_2H_3O_2]_2 \cdot 3H_2O$ and decahydrate $Pb[C_2H_3O_2] \cdot 10H_2O$
Synonyms: lead(II) acetate; plumbous acetate; normal lead acetate; neutral lead acetate; sugar of lead

Uses

Being the most soluble salt of lead, lead acetate is used extensively as starting material to prepare several other lead salts. It is used to produce basic lead acetates and basic lead carbonate for making pigments. The compound itself is used as a mordant for dyeing and printing cottons; in lead coating of metals; in the manufacture of lead driers for paints; as a sedative and astringent in medicine; in cosmetics, perfumes and toiletries; and in analytical chemistry for detection of sulfide.

Physical Properties

The anhydrous salt is a white crystalline solid; very sweet taste; density 3.25 g/cm^3 at 20°C; melts at 280°C; very soluble in cold water (44.39g/100g at 20°C); solubility is much greater in hot water (221g/100g at 50°C; also soluble in alcohols.

The trihydrate is a colorless monoclinic crystal or white granule or powder; refractive index 1.567 (along the beta axis); faint vinegar odor; intense sweet taste and then metallic after-taste; slowly effloresces; density 2.55 g/cm^3; melts at 75°C upon rapid heating; loses some of its water of crystallization on heating which dissolves in it; decomposes at 200°C; highly soluble in water (45.61g/100g at 15°C and 200g/100g at 100°C); insoluble in alcohol.

The decahydrate is white rhombic crystal; density 1.69 g/cm^3; melts at 22°C; soluble in water but insoluble in alcohol.

Preparation

Lead acetate is prepared by dissolving lead monoxide in strong acetic acid:

$$PbO + 2CH_3COOH \rightarrow Pb(C_2H_4O_2)_2 + H_2O$$

The trihydrate is obtained by dissolving lead monoxide in hot dilute acetic acid solution. Upon cooling, large crystals separate out.

Reactions

Exposure to carbon dioxide yields basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$, the composition of which may vary with reaction conditions.

Reactions with sulfuric acid, hydrochloric acid and hydriodic acid yield lead sulfate $PbSO_4$, lead chloride $PbCl_2$, and lead iodide PbI_2, respectively.

Reaction with hydrogen sulfide forms black precipitate of lead sulfide, PbS. A paper soaked with lead acetate solution turns black on exposure to H_2S, a test often used to detect sulfide.

Analysis

Elemental composition: Pb 63.70%, C 14.77%, H 1.86%, O 19.97%. The compound may be identified from its physical properaties and elemental analysis of C, H, O and Pb. Lead is analyzed by AA, ICP, x-ray fluorescence and other instrumental methods (See Lead).

Toxicity

Moderately toxic by intraperitoneal route and possibly by oral route.

LD_{50} intraperitoneal (mouse):400 mg/kg

LEAD ACETATES, BASIC

Several basic lead acetates are known with varying compositions of acetate, hydroxide ions, and/or water of crystallization. Some of them are:

$2Pb(OH)_2 \cdot Pb(C_2H_3O_2)_2$ [3335-32-6]
$Pb(OH)(C_2H_3O_2)_3$
$Pb(C_2H_3O_2)_2 \cdot 3PbO \cdot H_2O$
$Pb(C_2H_3O_2)_2 \cdot PbOH)_2 \cdot H_2O$

These basic acetates are used in the manufacture of pigments; in dyeing and printing fabrics, the aqueous solutions in medicine for washes and poultices; in sugar analysis; and as starting materials for preparing other lead salts.

The basic acetates are heavy white powders; decompose on heating; readily dissolve in water; and have low to moderately high solubility in ethanol.

Preparation

Basic lead acetates are prepared by dissolving lead monoxide in hot dilute acetic acid, or by dissolving the oxide in dilute acetic acid at alkaline pH. They may be made by dissolving lead monoxide in a solution of lead acetate. Crystalline products are obtained upon cooling the solutions.

Analysis

The composition of the salts is determined by elemental analysis including that of lead and x-ray methods. The water of crystallization may be measured by gravimetry.

LEAD AZIDE

[13424-46-9]
Formula: $Pb(N_3)_2$; MW 291.24

Uses

Lead azide is used in fuses and detonators as a primary explosive to initiate the booster. It also is used in shells and cartridges.

Physical Properties

Colorless needles or white powder; density ~4.0 g/cm^3; explodes on heating at 350°C; slightly soluble in water, 230 mg/L at 18°C and 900 mg/L at 70°C; very soluble in acetic acid; insoluble in ammonia solution.

Thermochemical Properties

$\Delta H_f°$ 110.5 kcal/mol

Preparation

Lead azide is prepared by the reaction of sodium azide with lead nitrate:

$$2NaN_3 + Pb(NO_3)_2 \rightarrow Pb(N_3)_2 + 2NaNO_3$$

Analysis

Elemental composition: Pb 71.14%, N 28.86%. Lead azide is digested cautiously in nitric acid under mild heating. The solution is diluted and analyzed for lead by various instrumental techniques (See Lead).

Hazard

Lead azide explodes on heating at 350°C or on percussion. Its detonation velocity is 5.1 km/sec (Meyer, E. 1989. *Chemistry of Hazardous Materials*, 2nd ed. Englewood Cliffs, N.J.: Prentice Hall). It undergoes violent explosive reaction with carbon disulfide and forms shock-sensitive copper and zinc azides when mixed with the solutions of copper and zinc salts (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley).

LEAD BROMIDE

[10031-22-8]
Formula: $PbBr_2$; MW 367.01
Synonym: lead dibromide; lead(II) bromide

Uses

Lead bromide is used for developing images in photography; as inorganic filler in fire-retardant plastics; as a photopolymerization catalyst for acrylamide monomer; and as a welding flux for welding aluminum or its alloys to other metals.

Physical Properties

White orthorhombic crystals; density 6.66 g/cm^3; melts at 373°C; forms a horn-like mass on solidification; vaporizes at 916°C; decomposes slowly on exposure to light; sparingly soluble in cold water (4.55 g/L at 0°C and 8.44 g/L at 20°C, respectively); moderately soluble in boiling water (44.1g/L at 100°C); K_{sp} 6.60×10^{-6} at 25°C; insoluble in alcohol; slightly soluble in ammonia; soluble in alkalies and also in sodium or potassium bromide solutions.

Thermochemical Properties

$\Delta H_f°$	–66.60 kcal/mol
$\Delta G_f°$	–62.60 kcal/mol
S°	38.60 cal/degree mol
C_ρ	19.15 cal/degree mol

Preparation

Lead bromide is prepared by treating an aqueous solution of lead nitrate with hydrobromic acid or with sodium or potassium bromide:

$$Pb^{2+} + 2Br^- \rightarrow PbBr_2$$

The solution is allowed to stand to let the precipitate settle.

The compound also may be obtained by adding lead carbonate or lead monoxide to hydrobromic acid.

Analysis

Elemental composition: Pb 56.45%, Br 43.55%. An aqueous solution may be analyzed for lead by AA or ICP spectroscopy and the bromide ion by ion chromatography, following appropriate dilution.

Toxicity

Moderately toxic by ingestion. The toxic effects are those of lead.

LEAD CARBONATE

[598-63-0]
Formula: $PbCO_3$; MW 267.21

Occurrence and Uses

Lead carbonate occurs in nature as the mineral cerussite. It has several applications. The compound is used in high pressure lubricating greases; as a coating on polyvinyl chloride to improve the dielectric properties of the polymers; in the PVC friction liners for pulleys; in corrosion-resistant grids in lead-storage batteries; in heat-sensitive sheets for thermographic copying; as a photoconductor in electrophotography; in thermistors; and in waxes for steel cables. Another major application of this compound is in catalysis—to catalyze polymerization of formaldehyde to high molecular weight polymeric products and to accelerate the process of curing of moldable thermosetting silicone resins.

Physical Properties

Colorless orthorhombic crystals; refractive index 1.804; Moh's hardness 3–3.5; density 6.60 g/cm^3; decomposes on heating at 315°C; practically insoluble in water (1.1 mg/L at 20°C); K_{SP} $1.46\text{x}10^{-13}$ at 25°C; also insoluble in alcohol and ammonia; soluble in acids and alkalies.

Thermochemical Properties

$\Delta H_f°$	–167.1kcal/mol
$\Delta G_f°$	–149.5 kcal/mol
S°	31.3 cal/degree mol
C_ρ	20.9 cal/degree mol

Preparation

Lead carbonate is prepared by passing carbon dioxide into a cold dilute solution of lead acetate:

$$Pb(C_2H_3O_2)_2 + CO_2 + H_2O \rightarrow PbCO_3 + CH_3COOH$$

The compound also is prepared in the laboratory by adding sodium bicarbonate to a cold dilute solution of a lead(II) salt, such as lead nitrate or acetate:

$$Pb^{2+} + 2HCO_3^{-} \rightarrow PbCO_3 + CO_2 + H_2O$$

Reactions

When heated at 315°C, lead carbonate decomposes to lead oxide and carbon dioxide:

$$PbCO_3 \xrightarrow{\rangle 300^{\circ} C} PbO + CO_2$$

When heated in water, it transforms to basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$

$$3PbCO_3 + H_2O \rightarrow 2PbCO_3 \cdot Pb(OH)_2 + CO_2$$

Lead carbonate dissolves in acids, forming the corresponding lead salt and evolving carbon dioxide:

$$PbCO_3 + 2HCl \rightarrow PbCl_2 + H_2O + CO_2$$

Reaction with concentrated acetic acid yields anhydrous lead(II) acetate.

Fusion with boric acid at high temperature forms lead metaborate that has an approximate composition $Pb(BO_2)_2 \cdot H_2O$. The product loses water of crystallization at 160°C.

Analysis

Elemental composition: Pb 77.54%, C 4.49%, O 17.96%. The compound is digested with nitric acid, diluted and analyzed for lead by various instrumental techniques (See Lead). Carbonate may be tested by treating the compound with dilute HCl. It will effervesce, the evolved CO_2 gas will turn limewater milky. Also, liberated CO_2 can be identified using a GC-equipped with a TCD or by GC/MS. The characteristic mass ion for GC/MS identification of CO_2 is 44.

Toxicity

Although an insoluble salt of lead, the compound exhibits low-to-moderate systemic effects from ingestion in humans. The effects are gastrointestinal contractions, jaundice, convulsions, nausea or vomiting, and degenerative changes in the brain (Lewis (Sr.), R. J. 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed. New York: Van Nostrand Reinhold).

LEAD CARBONATE, BASIC

[1319-46-6]
Formula: $Pb(OH)_2 \cdot 2PbCO_3$; MW 775.60; phase rule study indicates the existence of basic lead carbonates of other compositions: $3PbO \cdot 5PbCO_3$; $PbO \cdot PbCO_3$; $2PbO \cdot PbCO_3$
Synonyms: white lead; basic carbonate

Uses

White lead, in the basic carbonate form, was used extensively as white pigment in paint until its toxic properties became known. At present, most of its pigment applications are as red-reflecting pigment in plastic sheets; in UV light-reflecting paints; in ceramic glaze; and in many temperature-sensitive inks that cause color change. Other applications include use as a catalyst in terephthalic acid reactions with diols; as a heat-sensitive stabilizer for poly vinyl chloride polymers; in lubricating grease, and as a curing agent to improve polyethylene wire insulation.

Preparation

Many commercial processes have been developed for manufacturing basic lead carbonate. These include: Thomson-Stewart process, Carter process, and Dutch process. The method of preparation involves treating lead with acetic acid vapors in the presence of carbon dioxide at 60°C. In the Thomson-Stewart process, finely divided lead monoxide or lead metal is mixed with water to give aqueous slurry, which is then mixed with acetic acid in the presence of air and carbon dioxide. All these processes are slow, taking weeks to obtain products of desired composition.

Basic lead carbonate also is precipitated by dissolving lead monoxide in lead(II) acetate solution, and treating the solution with carbon dioxide. It also is produced by electrolysis of sodium nitrate or sodium acetate using lead anode and then precipitating out the product by adding sodium carbonate.

Analysis

The basic carbonates have varying compositions. They may be characterized by elemental analysis, x-ray methods and also by their physical properties.

LEAD CHROMATE

[7758-97-6]
Formula: $PbCrO_4$; MW 323.19
Synonyms: chrome yellow; crocoite

Occurrence and Uses

Lead chromate occurs in nature as the minerals, crocoite and phoenicochroite. It is an important pigment of lead used in oil paints and water colors. It is used for printing textiles and coloring porcelain.

Physical Properties

Yellow monoclinic crystals; refractive index 2.31; density 6.12 g/cm^3; melts at 844°C; decomposes on further heating; insoluble in water; also insoluble in ammonia and acetic acid; soluble in acids and alkalies.

Production

Lead chromate is found naturally in minerals crocoite and phoenicochroite. It also is readily prepared by adding a soluble chromate such as sodium or potassium chromate to a solution of lead nitrate, lead acetate or other soluble lead(II) salt in neutral or slightly acidic solution:

$$Pb^{2+} + CrO_4^{2-} \rightarrow PbCrO_4$$

The yellow precipitate is filtered, washed and dried.

Analysis

Elemental composition: Pb 64.11%, Cr 16.09%, O 19.80%. Lead chromate may be identified from its physical properties and x-ray crystallography. Lead and chromium can be measured in a nitric acid solution of the compound by AA, ICP, and other instrumental methods. (See Lead.)

Toxicity

Moderately toxic by intraperitoneal route. The effects, however, are mild from oral intake. Occupational exposure may cause cancer. There is sufficient evidence of carcinogenicity in animals and humans.

LEAD DICHLORIDE

[7758-95-4]
Formula: $PbCl_2$; MW 278.11
Synonyms: lead(II) chloride; lead chloride

Occurrence and Uses

Lead dichloride occurs in nature as the mineral cotunnite. The compound is used in making many basic chlorides, such as Pattison's lead white, Turner's Patent Yellow, and Verona Yellow, used as pigments. Also, it is used as a flux for galvanizing steel; as a flame retardant in nylon wire coatings; as a cathode for seawater batteries; to remove H_2S and ozone from effluent gases; as a sterilization indicator; as a polymerization catalyst for alpha-olefins; and as a co-catalyst in manufacturing acrylonitrile.

Physical Properties

White orthorhombic crystals; refractive index 2.199; density 5.85 g/cm^3; melts at 501°C; vaporizes at 950°C; partially soluble in cold water (6.73 g/L at

0°C and 9.9 g/L at 20°C); K_{SP} 1.17x10^{-5} at 25°C; moderately soluble in boiling water (33.4 g/L at 100°C); slightly soluble in dilute HCl and ammonia; insoluble in alcohol.

Thermochemical Properties

$\Delta H_f°$	–85.90 kcal/mol
$\Delta G_f°$	–75.98 kcal/mol
S°	32.50 cal/degree mol

Preparation

Lead dichloride is precipitated by adding hydrochloric acid or any chloride salt solution to a cold solution of lead nitrate or other lead(II) salt:

$$Pb^{2+} + 2Cl^{-} \rightarrow PbCl_2$$

Alternatively, it is prepared by treating lead monoxide or basic lead carbonate with hydrochloric acid and allowing the precipitate to settle.

Reactions

In dilute solutions of hydrochloric acid or halide ion, solubility of lead dichloride decreases; however, in concentrated solutions, solubility increases due to formation of the complex ion, tetrachloroplumbate(II), $[PbCl_4]^{2-}$:

$$PbCl_2 + 2Cl^{-} \rightarrow [PbCl_4]^{2-}$$

The latter also forms complex salts of alkali metals M_2PbCl_4 and MPb_2Cl_5.

Lead dichloride is hydrolyzed by steam to a basic chloride Pb(OH)Cl and hydrochloric acid:

$$PbCl_2 + H_2O \xrightarrow{110^\circ C} Pb(OH)Cl + HCl$$

$$PbCl_2 + H_2O \rightarrow Pb(OH)Cl + HCl$$

Aqueous solution of lead dichloride also undergoes double decomposition reactions with several metal salts, precipitating insoluble lead salts.

When an aqueous solution of lead dichloride is mixed with caustic soda or other alkalies, basic chlorides such as $PbCl_2 \cdot Pb(OH)_2$ are formed. They are used as pigments.

Analysis

Elemental composition: Pb 74.50%, Cl 25.49%. Lead chloride may be identified by its physical properties and using x-ray analysis. An aqueous solution may be analyzed for lead by AA, ICP and other instrumental techniques, and for chloride ion by ion chromatography, or by titration with a standard solution of silver nitrate or mercuric nitrate.

Toxicity

Toxic effects from ingestion may vary from low to moderate. The oral lethal dose in guinea pigs is documented as 1,500 mg/kg. (Lewis (Sr.), R. J. 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed. New York: Van Nostrand Reinhold).

LEAD DIFLUORIDE

[7783-46-2]
Formula: PbF_2; MW 245.20
Synonyms: lead fluoride; lead(II) fluoride; plumbous fluoride

Uses

Lead difluoride is used in low melting glasses; in glass coatings to reflect infrared rays; in phosphors for television-tube screens; for nickel plating on glass; and as a catalyst for the manufacture of picoline.

Physical Properties

Colorless orthorhombic crystals or white powder; converts to cubic form at 316°C; density 8.445 g/cm^3 (orthorhombic form) and 7.750 g/cm^3 (cubic form); melts at 855°C; vaporizes at 1,290°C; slightly soluble in water (640 mg/L at 20°C); K_{SP} 7.12×10^{-7} at 25°C; soluble in nitric acid; insoluble in acetone and ammonia.

Thermochemical Properties

$\Delta H_f°$	–158.7 kcal/mol
$\Delta G_f°$	–147.5 kcal/mol
$S°$	26.4 cal/degree mol

Preparation

Lead difluoride can be prepared by several methods. It is obtained by treating lead hydroxide or lead carbonate with hydrofluoric acid, followed by evaporation of the solution:

$$Pb(OH)_2 + 2HF \rightarrow PbF_2 + 2H_2O$$

Alternatively, it is precipitated by adding hydrofluoric acid to a lead(II) salt solution; or adding potassium fluoride to lead nitrate solution:

$$2KF + Pb(NO_3)_2 \rightarrow PbF_2 + 2KNO_3$$

Lead difluoride also can be directly synthesized from its elements, by the action of lead with fluorine.

Analysis

Elemental composition: Pb 84.50%, F 15.50%. The compound can be identified from its physical properties and x-ray measurement. Lead may be analyzed by various instrumental techniques (See Lead). Fluoride ion may be determined by dissolving a minute quantity of the compound in water (the compound is slightly soluble in water) and analyzing the solution by ion chromatography or by fluoride-ion selective electrode.

Toxicity

Slightly to moderately toxic by ingestion and subcutaneous routes. The oral LD_{50} in rats is around 3,000 mg/kg.

LEAD DIIODIDE

[10101-63-0]
Formula: PbI_2; MW 461.01
Synonyms: lead iodide; lead(II) iodide

Uses

Lead diiodide is used for recording optical images; for making gold spangles and mosaic gold for decorative purposes; in photographic emulsions; in mercury-vapor lamps; in asbestos brake linings; in far-infrared filters; in thermal batteries; in printing and recording papers; and in aerosols for cloud seeding.

Physical Properties

Yellow hexagonal crystals; density 6.16 g/cm^3; melts at 402°C; vaporizes at 954°C; decomposes at 180°C when exposed to green light; slightly soluble in water (0.44 g/L at 0°C and 0.63 g/L at 20°C); K_{sp} 8.49×10^{-9} at 25°C; partially soluble in boiling water (4.1 g/L at 100°C); insoluble in ethanol; soluble in alkalis and alkali metal iodide solutions.

Thermochemical Properties

$\Delta H_f°$	–41.94 kcal/mol
$\Delta G_f°$	–41.50 kcal/mol
S°	41.79 cal/degree mol
C_ρ	18.49 cal/degree mol

Preparation

Lead diiodide is prepared by mixing aqueous solutions of lead nitrate or lead acetate with an aqueous solution of potassium or sodium iodide or hydriodic acid, followed by crystallization. The product is purified by recrystallization.

$$Pb^{2+}(aq) + 2I^{-}(aq) \rightarrow PbI_2(s)$$

Analysis

Elemental composition: Pb 44.94%, I 55.06%. An accurately weighted amount of the salt may be digested with nitric acid and the acid extract analyzed for lead by AA, ICP or other instrumental techniques. (See Lead.) A few milligrams of salt is dissolved in water and analyzed for iodide anion by ion chromatography. The solutions must be appropriately diluted for these analyses.

Toxicity

Lead diiodide is toxic if ingested. The symptoms are those of lead poisoning.

LEAD DIOXIDE

[1309-60-0]
Formula: PbO_2; MW 239.20
Synonyms: lead(IV) oxide; lead peroxide; lead superoxide; brown lead oxide; plattnerite

Occurrence and Uses

Lead dioxide occurs in nature as the mineral plattnerite. It is used as an oxidizing agent in manufacturing dyes and intermediates. It also is used as a source of oxygen in matches, pyrotechnics, and explosives. In matches, the oxide is combined with amorphous phosphorus as an ignition surface. It also is used in making lead pigments, liquid polysulfide polymers and rubber substitutes. Lead dioxide electrodes are used in lead storage batteries in which lead dioxide accumulates on positive plates.

Physical Properties

Red tetragonal crystals or brown powder; density 9.64 g/cm^3; decomposes on heating at 290°C; practically insoluble in water; also insoluble in alkalis; moderately soluble in hydrochloric acid and also, in nitric acid-hydrogen peroxide mixture; slowly dissolves in acetic acid.

Thermochemical Properties

$\Delta H_f°$	–66.30 kcal/mol
$\Delta G_f°$	–51.94 kcal/mol
S°	16.40 cal/degree mol
C_ρ	15.44 cal/degree mol

Preparation

Lead dioxide is produced by oxidizing an alkaline slurry of lead monoxide with chlorine, sodium hypochlorite, or bleaching powder. Alternatively, it is obtained by passing chlorine into a hot aqueous suspension of lead sulfate and magnesium hydroxide. The ionic reaction is:

$$Pb(OH)_3^- + ClO^- \rightarrow PbO_2 + Cl^- + OH^- + H_2O$$

It also is produced by electrolysis of acidic solutions of lead salts using a lead or platinum electrode. In such electrolytic process, lead dioxide is deposited on the anode of the cell.

Insoluble powdered lead dioxide also may be obtained when lead tetroxide is heated with nitric acid:

$$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(N)_3)_2 + PbO_2 + 2H_2O$$

Lead dioxide also can be prepared by fusing lead monoxide with a mixture of sodium nitrate and sodium chlorate.

Reactions

Lead dioxide exhibits amphoteric properties, reacting with both acids and alkalies. With acids, it forms both divalent and tetravalent salts, depending on acid strength and reaction temperature. Thus, it dissolves in concentrated hydrochloric acid at ambient temperature, forming lead(II) chloride with evolution of chlorine:

$$PbO_2 + 4HCl \xrightarrow{25^\circ C} PbCl_2 + 2H_2O + Cl_2$$

However, at 0°C some lead(IV) chloride also forms:

$$PbO_2 + 4HCl \xrightarrow{0^\circ C} PbCl_4 + 2H_2O$$

The tetrachloride decomposes to dichloride on warming:

$$PbCl_4 \xrightarrow{\text{heat}} PbCl_2 + Cl_2$$

Lead dioxide reacts with alkalies forming various types of plumbates. Fusion with caustic soda or caustic potash yields orthoplumbates and metaplumbates, such as Na_4PbO_4 or Na_2PbO_3 (or the corresponding potassium salts). However, when dissolved in a concentrated aqueous solution of sodium or potassium hydroxide, the product is hydroxyplumbate:

$$PbO_2 + 2NaOH + 2H_2O \rightarrow Na_2Pb(OH)_6$$

The hydroxyplumbate decomposes to metaplumbate on gentle heating:

$$Na_2Pb(OH)_6 \xrightarrow{heat} Na_2PbO_3 + 3H_2O$$

When heated with quicklime in air, lead dioxide forms calcium plumbate:

$$2PbO + 4CaO + O_2 \xrightarrow{heat} 2Ca_2PbO_4$$

Lead dioxide is an oxidizing agent as well as a source of oxygen. It has many industrial applications. When heated with sulfur, the sulfur is oxidized to sulfur dioxide producing lead sulfate:

$$PbO_2 + S \rightarrow Pb + SO_2$$

$$PbO_2 + SO_2 \rightarrow PbSO_4$$

When heated with concentrated sulfuric acid, lead dioxide liberates oxygen, forming lead sulfate:

$$PbO_2 + H_2SO_4 \rightarrow PbSO_4 + O_2 + 2H_2O$$

It decomposes to lead monoxide and oxygen when heated above 290°C:

$$2PbO_2 \xrightarrow{>290^\circ C} 2PbO + O_2$$

Analysis

Elemental composition: Pb 86.62%, O 13.38%. The compound may be identified by its physical properties and characterized by x-ray crystallography. Lead may be analyzed in the acid extract of the oxide by AA or ICP spectroscopy. It also may be analyzed by its oxidative properties. It liberates iodine from an acidic solution of potassium iodide, and the liberated iodine may be titrated against a standard solution of sodium thiosulfate using starch indicator (blue color decolorizes at the end point).

LEAD HYDROXIDE

[19781-14-3]
Formula: $Pb(OH)_2$; MW 241.21
Synonym: plumbous hydroxide

Uses

Lead hydroxide is used in making porous glass; in electrical-insulating paper; in electrolytes in sealed nickel-cadmium batteries; in recovery of uranium from seawater; and as a catalyst for oxidation of cyclododecanol.

Physical Properties

White amorphous powder; density 7.41 g/cm^3; dehydrates above 130°C and decomposes at 145°C; slightly soluble in water, 155 mg/L at 20°C; K_{SP} 1.42×10^{-20} at 25°C; soluble in dilute acids and alkalies; insoluble in acetone and acetic acid.

Thermochemical Properties

$\Delta G_f°$	–108.1 kcal/mol

Preparation

Lead hydroxide is precipitated by adding sodium hydroxide or potassium hydroxide to a solution of lead nitrate:

$$Pb(NO_3)_2 + 2NaOH \rightarrow Pb(OH)_2 + 2NaNO_3$$

It also is produced by electrolysis of an alkali solution using lead anode. Lead hydroxide is formed on the anode.

Reactions

When heated at 145°C, lead hydroxide decomposes to lead monoxide:

$$Pb(OH)_2 \xrightarrow{145^\circ C} PbO + H_2O$$

It absorbs carbon dioxide forming lead carbonate:

$$Pb(OH)_2 + CO_2 \rightarrow PbCO_3 + H_2O$$

It reacts with acids forming their lead salts:

$$Pb(OH)_2 + H_2SO_4 \rightarrow PbSO_4 + 2H_2O$$

Analysis

Elemental composition: Pb 90.40%, H 0.29%, O 9.30%. The hydroxide is digested with nitric acid, diluted and analyzed for lead by AA, ICP or other instrumental technique (See Lead). A weighed amount of the salt is heated in an oven at 145°C and water lost is measured by gravimetry. The residue lead monoxide also may be analyzed by x-ray, or its lead content can be measured by various instrumental methods.

LEAD MONOXIDE

[1317-36-8]
Formula: PbO; MW 223.30
Synonyms: lead(II) oxide; yellow lead oxide; litharge (red alpha modification of the oxide); massicot (yellow beta form)

Uses

Lead monoxide has wide commercial applications. It is used in lead-sulfuric acid type storage battery plates; in optical and electrical glasses; in vitreous enamels, glazes, and fine tableware; in lead soaps for varnishes; as a vulcanizing agent for rubber and plastics; and as a lubricant at high temperatures. An important application of this oxide involves its use as the starting material for producing various lead pigments as well as other compounds of commercial interest such as lead arsenate, lead acetate, and sodium plumbite. Also, lead monoxide is used in certain organic syntheses as a neutralizing agent.

Physical Properties

The oxide exhibits two crystalline modifications, the reddish or orange-red alpha form, known as litharge, and the yellow beta form, massicot. The alpha form constitutes tetragonal crystals while the beta modification is a yellow amorphous powder of orthorhombic crystal structure. The alpha form is stable at ordinary temperatures, converting to the beta form when heated at 489°C; density 9.35 g/cm^3 (beta form); Moh's hardness 2 (alpha form); the oxide melts at 888°C; vaporizes at 1,472°C with decomposition; vapor pressure 1 torr at 943°C and 5 torr at 1,039°C; practically insoluble in water (the solubility of alpha form is 17 mg/L at 20°C and that of beta form 23 mg/L at 22°C); insoluble in ethanol; soluble in dilute nitric acid and alkalies.

Thermochemical Properties

$\Delta H_f°$	(alpha form)	–52.34 kcal/mol
$\Delta H_f°$	(beta form)	–51.94 kcal/mol
$\Delta G_f°$	(alpha form)	–45.15 kcal/mol
$\Delta G_f°$	(beta form)	–44.91 kcal/mol
$S°$	(alpha form)	15.89 cal/degree mol
$S°$	(beta form)	16.42 cal/degree mol
C_ρ	(both forms)	10.95 cal/degree mol

Production

Lead monoxide is obtained commercially by two processes, Barton process and the Ball Mill process. The Ball-Mill process involves reaction of molten lead with oxygen or air, and in the Barton process atomized molten lead is stirred in a mechanical furnace above 550°C. The molten metal splashed by the stirring paddle comes in contact with air fed into the cover of the furnace through a pipe, thus forming a mist of finely divided lead monoxide. The mist also contains a small amount of unreacted lead. The mist is passed through an upright shaft where a major portion of unreacted lead falls back into the furnace. It is then rapidly cooled and collected in condensing chambers. The crude product may contain 1 to 3% lead. It is finely ground and sold. The remaining lead in the crude product may be converted into the lead monoxide by stirring the molten mass in presence of air for several hours. The hot product is then cooled rapidly to a temperature below 300°C to prevent any formation of lead tetroxide, Pb_3O_4.

In an alternate process, a variation of the above method, molten lead is atomized in a shaft furnace. An air stream carries the very finely divided metal into the hot zone of the shaft furnace where the metal evaporates and oxidizes producing very finely divided lead monoxide. The product is passed through the cold zone of the furnace and cooled rapidly. The product obtained is a yellow powdery material, the beta form of lead oxide, massicot, consisting of orthorhombic crystals.

The red lead oxide (the tetragonal alpha modification) is obtained by slow cooling of the lead monoxide melt. The solidified mass may contain the red alpha form of the oxide resulting from slow cooling of the melt, under an outer layer of yellow beta form that may result from the rapid cooling of the outer portion.

Lead monoxide also is produced by a modified Ball Mill process in which high purity lead balls placed in the mill are partially oxidized to produce black or grey oxide. Both the red and yellow form of the oxide may be prepared by alkaline dehydration of lead hydroxide, $Pb(OH)_2$.

Reactions

Lead monoxide is amphoteric in nature; i.e., the oxide exhibits both the acid (weakly acidic) and base characteristics. It dissolves in acids forming their corresponding salts:

$$PbO + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O$$

Similarly, it combines with silica and chromium(VI) oxide at elevated temperatures, forming lead silicate and lead chromate, respectively:

$$PbO + SiO_2 \xrightarrow{\substack{\textit{elevated} \\ \textit{temperature}}} PbSiO_3$$

$$PbO + CrO_3 \xrightarrow{\substack{\textit{elevated} \\ \textit{temperature}}} PbCrO_4$$

It also reacts with alkalies, forming the plumbite ion, PbO_2^{2-}. In aqueous alkalies it dissolves slowly forming hydroxyplumbites; i.e., $Na_2Pb(OH)_4$, which decomposes to plumbite. The overall reaction is:

$$PbO + 2NaOH \rightarrow Na_2PbO_2 + H_2O$$

When heated at 450–500°C in air or oxygen in a reverberatory furnace, lead monoxide is oxidized to lead tetroxide. However, other oxides or their mixtures having varying compositions may also form. The reaction is slow and gradual above 430°C.

$$6PbO + O_2 \xrightarrow{>480^\circ C} 2Pb_3O_4$$

When heated with lead dioxide, at 250°C, the same product, lead tetroxide is obtained:

$$2PbO + PbO_2 \xrightarrow{250^\circ C} Pb_3O_4$$

The oxide can be reduced to metallic lead by hydrogen, carbon, carbon monoxide and other reducing agents when heated at elevated temperatures. Such reduction with carbon or carbon monoxide is carried out at about 1000°C in a blast furnace to produce lead metal:

$$2PbO + C \xrightarrow{\text{elevated temperature}} 2Pb + CO_2$$

$$PbO + CO \xrightarrow{\text{elevated temperature}} Pb + CO_2$$

Analysis

Elemental composition: Pb 92.83%, O 7.17%. The oxide may be characterized by x-ray crystallography, and physical properties. Lead may be analyzed in the acid extract by AA, ICP and other instrumental techniques (See Lead).

Toxicity

The monoxide is moderately toxic by ingestion and inhalation of dust. The symptoms are those of lead poisoning.

LEAD NITRATE

[10099-74-8]
Formula: $Pb(NO_3)_2$; MW 331.21

Uses

Lead nitrate is used as a mordant in dyeing and printing cotton; as a flotation agent to remove titanium from clays; to prepare several lead salts; in electrolytic refining for production of lead; in photothermography; as a heat stabilizer in nylon; as a catalyst for polyester synthesis; in delustering of rayon; in recovery of precious metals from cyanide solutions; in making electroluminescent mixtures; and as an analytical standard for lead. Lead nitrate also is used in matches, pyrotechnics and explosives, where it is a source of oxygen.

Physical Properties

Colorless cubic or monoclinic crystals; refractive index 1.782; density 4.53 g/cm^3 at 20°C; decomposes at 470°C; soluble in cold water; very soluble in boiling water 127 g/100 mL at 100°C; also soluble in caustic soda, caustic potash and ammonia solution, and moderately soluble in alcohol.

Preparation

Lead nitrate is prepared by dissolving lead metal, lead monoxide or lead carbonate in excess dilute nitric acid followed by evaporation of and/or cooling the solution for crystallization.

Reactions

Thermal dissociation above 205°C yields basic lead nitrate, nitrogen dioxide and oxygen:

$$2Pb(NO_3)_2 + H_2O \xrightarrow{205^\circ C} 2Pb(OH)NO_3 + 2NO_2 + O_2$$

When heated above 450°, it decomposes to lead monoxide and lead tetroxide:

$$4Pb(NO_3)_2 \xrightarrow{450^\circ C} PbO + Pb_3O_4 + 8NO_2$$

Reaction with sodium carbonate and powdered tellurium yields lead telluride, PbTe.

Reaction with sodium selenate yields lead selenate, $PbSeO_4$. Similarly, with sodium selenite or selenious acid, the product is lead selenite, $PbSeO_3$.

When its aqueous solution is mixed with hydrofluoric acid, lead fluoride precipitates out:

$$Pb(NO_3)_2 + 2HF \rightarrow PbF_2 + 2HNO_3$$

Reaction with sodium azide yields lead azide:

$$Pb(NO_3)_2 + NaN_3 \rightarrow Pb(N_3)_2 + 2NaNO_3$$

Analysis

Elemental composition: Pb 62.55%, N 8.46%, O 28.98%. The aqueous solution may be analyzed for lead by various instrumental techniques (See Lead). The nitrate ion may be identified by a nitrate ion-selective electrode or by ion chromatography following appropriate dilution of the solution. The compound may be identified in crystalline forms by x-ray and by its physical properties.

Toxicity

The toxic effects are greater than other lead salts because lead nitrate is more soluble. Moderately toxic by ingestion and other routes of exposure. The compound also is an irritant to eye, skin, and mucous membranes.

LEAD SULFATE

[7446-14-2]
Formula: $PbSO_4$; MW 303.26

Occurrence and Uses

Lead sulfate occurs in nature as the mineral, anglesite. It is an essential component of lead-sulfuric acid storage batteries and forms during discharge cycles. It is used as an additive to stabilize clay soil for construction. Other applications are in photography and as a pigment.

Physical Properties

White monoclinic or rhombic crystals; refractive index 1.877; density 6.20 g/cm^3; melts at 1,170°C; very slightly soluble in water, 42.5 mg/L at 25°C; K_{SP}1.82x10^{-8}; sparingly soluble in hydrochloric and nitric acids; slightly soluble in dilute sulfuric acid, more soluble in concentrated sulfuric acid; insoluble in alcohol; soluble in caustic soda and ammonium salts solutions.

Thermochemical Properties

$\Delta H_f°$	–219.9 kcal/mol
$\Delta G_f°$	–194.4 kcal/mol
S°	35.5 cal/degree mol
C_ρ	24.7 cal/degree mol

Preparation

Lead sulfate precipitates when an aqueous solution of lead nitrate or other soluble salt of lead is treated with sulfuric acid.

Alternatively, lead sulfate may be prepared by treating lead oxide, hydroxide, or carbonate with concentrated sulfuric acid under warm condition.

It also is produced when lead sulfide is roasted in air.

Analysis

Elemental composition: Pb 68.32%, S 10.57%, O 21.10%. the solid crystalline powder or the mineral anglesite may be characterized by x-ray techniques and physical properties. Lead can be analyzed in the solid compound or its nitric acid extract by various instrumental techniques (See Lead).

Toxicity

Low to moderate toxicity by ingestion. Irritant action on eye, skin, and mucous membranes.

LEAD SULFIDE

[1314-87-0]
Formula: PbS; MW 239.30
Synonyms: galena; lead glance

Occurrence and Uses

Lead sulfide occurs in nature as the mineral galena. Most lead comes from this ore. Additionally, lead sulfide has several industrial applications. It is used in infrared detectors; transistors; photoconductive cells; high temperature lubricants; and for glazing earthenware. It also is used as a catalyst in petroleum refining for removal of mercaptans from petroleum distillates.

Physical Properties

Black powder or cubic crystal; refractive index 3.91; density 7.60 g/cm^3; Moh's hardness 2.5; melts at 1,118°C; vapor pressure 1 torr at 852°C and 5 torr at 928°C; very slightly soluble in water (124 mg/L at 20°C); K_{SP} 9.04×10^{-29} at 25°C; soluble in acids.

Thermochemical Properties

$\Delta H_f°$	–24.0 kcal/mol
$\Delta G_f°$	–23.6 kcal/mol
S°	21.8 cal/degree mol
C_ρ	11.83 cal/degree mol

Preparation

Lead sulfide occurs naturally as the mineral galena. It can be prepared in the laboratory as a black precipitate by passing hydrogen sulfide through a dilute acid solution of inorganic lead salt, such as lead nitrate or lead acetate:

$$Pb^{2+} + H_2S \rightarrow PbS + 2H^+$$

It also is obtained by direct combination of elements by heating metallic lead with sulfur vapors.

Reactions

Lead sulfide decomposes in excess concentrated hydrochloric acid liberating hydrogen sulfide and probably forming chloroplumbus acid in solution:

$$PbS + 4HCl \rightarrow H_2PbCl_4 + H_2S$$

Two types of reactions occur with nitric acid depending on the concentration of the acid. Lead sulfide dissolves in dilute nitric acid, oxidizing to elemental sulfur:

$$PbS + 2HNO_3 \rightarrow Pb(NO_3)_2 + S + H_2$$

However, treatment with concentrated nitric acid yields lead(II) sulfate:

$$PbS + 4HNO_3 \rightarrow PbSO_4 + 4HNO_2$$

Lead sulfide also undergoes various oxidation reactions at elevated temperatures that occur in a reverberatory furnace, during the production of lead from galena. Sulfur dioxide and lead sulfate are formed as intermediate products. Some typical reactions are as follows:

$$PbS + 2O_2 \xrightarrow{\text{elevated temperature}} PbSO_4$$

$$2PbS + 3O_2 \xrightarrow[\text{temperature}]{\text{elevated}} 2PbO + 2SO_2$$

$$PbS + 2PbO \xrightarrow[\text{temperature}]{\text{elevated}} 3Pb + SO_2$$

$$PbS + PbSO_4 \xrightarrow[\text{temperature}]{\text{elevated}} 2Pb + 2SO_2$$

When roasted in an air blast furnace, basic lead sulfate, $PbO \cdot PbSO_4$ (also known as sublimed white lead), is formed.

Analysis

Elemental composition: Pb 86.60%, S 13.40%. Both mineral and synthetic forms can be identified by x-ray measurements. Lead can be analyzed by various instrumental techniques after digestion with nitric acid and appropriate dilution of the acid extract (See Lead).

LEAD TETRAACETATE

[546-67-8]
Formula: $Pb(C_2H_3O_2)_4$; MW 443.38
Synonyms: plumbic acetate; lead(IV) acetate

Uses

Lead tetraacetate is used as a highly selective oxidizing agent in organic synthesis. This includes oxidation of glycols into aldehydes, preparation of cyclohexyl acetate, production of oxalic acid, and in structural analysis of sugars.

Physical Properties

Colorless monoclinic crystals; turns pink; unstable in air; density 2.228 g/cm^3 at 17°C; melts at 175°C; decomposes in cold water and ethanol; soluble in chloroform, benzene, nitrobenzene, and hot glacial acetic acid; also soluble in concentrated hydrochloric acid.

Preparation

Lead tetraacetate is prepared by dissolving lead tetroxide in warm glacial acetic acid followed by cooling. On cooling, the tetraacetate crystallizes out while lead acetate remains in the solution:

$$Pb_3O_4 + 8CH_3COOH \xrightarrow{70^\circ C} Pb(CH_3COO)_4 + 2Pb(CH_3COO)_2 + 4H_2O$$

Yield is improved by adding chlorine gas to the mixture. Alternatively, the compound may be prepared by adding a mixture of glacial acetic acid and acetic anhydride to lead tetroxide and heating the solution gently. Acetic anhydride converts the water formed in the reaction into acetic acid, thus preventing hydrolysis of the product lead tetraacetate.

Reactions

Lead tetraacetate, on treatment with water, hydrolyzes to lead dioxide and acetic acid:

$$Pb(CH_3COO)_4 + 2H_2O \rightarrow PbO_2 + 4CH_3COOH$$

Lead tetraacetate is a selective oxidizing agent causing oxidative cleavage of polyhydroxy compounds. It cleaves compounds that have hydroxyl groups on adjacent carbon atoms, breaking the carbon-carbon bonds to form carbonyl compounds, such as aldehydes, ketones or acids. The reaction is carried out in organic solvents. A typical example is as follows:

$$\underset{\text{(ethylene glycol)}}{OH—CH_2—CH_2—OH} + Pb(CH_3COO)_4 \rightarrow \underset{\text{(formaldehyde)}}{2CH_2O} + Pb(CH_3COO)_2 + \underset{\text{(acetic acid)}}{2CH_3COOH}$$

Analysis

Elemental composition: Pb 46.73%, C 21.67%, H 2.73%, O 28.87%. The compound may be identified from its physical properties and elemental analyses. Additionally, a measured quantity of the compound may be hydrolyzed with water and the product, the brown lead dioxide formed may be determined by x-ray method or analyzed for lead by instrumental techniques (See Lead.)

LEAD TETRACHLORIDE

[13463-30-4]
Formula: $PbCl_4$; MW 349.00
Synonym: lead(IV) chloride

Physical Properties

Yellow oily liquid; fumes in air; unstable at ordinary temperatures; solidifies at –15°C; decomposes at 50°C.

Thermochemical Properties

$\Delta H_f°$ (liq) –78.7kcal/mol

Preparation

Lead tetrachloride may be prepared by dissolving lead dioxide in cold concentrated hydrochloric acid at 0°C:

$$PbO_2 + 4HCl \xrightarrow{0^\circ C} PbCl_4 + 2H_2O$$

However, in the above method some amount of lead dichloride may form, especially if the temperature is above 0°C.

The preferred preparation method is to introduce chlorine into the solution while dissolving lead dioxide in cold concentrated HCl. This prevents decomposition of $PbCl_4$ to $PbCl_2$ and enhances the formation of chloroplumbic acid, H_2PbCl_6 in solution. Addition of ammonium chloride precipitates out yellow ammonium chloroplumbate, $(NH_4)_2PbCl_6$, which is filtered out. The yellow precipitate, on treatment with cold concentrated sulfuric acid, forms lead tetrachloride, which separates out as a yellow oily liquid. The reactions are:

$$PbO_2 + 6HCl \xrightarrow[0°C]{Cl_2} H_2PbCl_6 + 2H_2O$$

$$H_2PbCl_6 + 2NH_4Cl \rightarrow (NH_4)_2PbCl_6 + 2HCl$$

$$(NH_4)_2PbCl_6 + H_2SO_4 \xrightarrow{0^\circ C} PbCl_4 + (NH_4)_2SO_4 + 2HCl$$

Reactions

Lead tetrachloride decomposes at 20°C, forming lead dichloride and evolving chlorine:

$$PbCl_4 \xrightarrow{20^\circ C} PbCl_2 + Cl_2$$

Reaction with ammonium chloride yields yellow precipitate of the complex salt, ammoniumhexachloroplumbate(IV):

$$PbCl_4 + NH_4Cl \rightarrow (NH_4)_2PbCl_6$$

The tetrachloride rapidly hydrolyzes in water forming lead dioxide:

$$PbCl_4 + 2H_2O \rightarrow PbO_2 + 4HCl$$

Analysis

Elemental composition: Pb 59.37%, Cl 40.63%. The compound is hydrolyzed in water to PbO_2, which is separated, digested with nitric acid, diluted, and analyzed for lead. The aqueous solution containing the hydrolysis product HCl is determined by acid-base titration. The chloride ion is measured by an electrode or ion chromatography, or by titration with a standard solution of silver nitrate using potassium chromate indicator. The compound liberates chlorine gas at ordinary temperatures, which may be determined from its physical properties or by GC-TCD or collected in water and measured by colorimetry.

LEAD TETRAETHYL

[78-00-2]
Formula: $Pb(C_2H_5)_4$; MW 323.44
Synonyms: tetraethyllead; tetraethylplumbane; TEL

Uses

Lead tetraethyl was used extensively as an additive to gasoline to prevent “knocking” in motors. Its use, however, is reduced drastically because of environmental pollution.

Physical Properties

Colorless liquid; burns with orange flame with green margin; refractive index 1.5198; density 1.653 g/mL at 20°C; insoluble in water; slightly soluble in ethanol; soluble in benzene, toluene, gasoline, and petroleum ether.

Thermochemical Properties

$\Delta H_f°$	(liq)	–12.6 kcal/mol
$\Delta H_f°$	(gas)	–26.2 kcal/mol

Preparation

Lead tetraethyl is prepared by heating ethyl chloride in the presence of a catalyst in an autoclave at 40 to 60°C with an alloy of lead and sodium:

$$Pb + 4Na + 4C_2H_5Cl \xrightarrow[\text{catalyst}]{40\text{-}60°C} Pb(C_2H_5)_4 + 4NaCl$$

Also, it can be prepared by the reaction of lead with ethylene and hydrogen in the presence of Ziegler catalyst, triethylaluminum:

$$Pb + 4C_2H_4 + 2H_2 \xrightarrow[\text{ether}]{Al(C_2H_5)_3} Pb(C_2H_5)_4$$

Analysis

Elemental composition: Pb 64.06%, C 29.70%, H 6.23%. Tetraethyl lead is dissolved in benzene or toluene, diluted appropriately, and analyzed by GC/MS. The ethyl group may be determined by NMR spectroscopy.

Toxicity

Tetraethyl lead is a highly toxic compound manifesting both acute and chronic effects. These effects are insomnia, hypotension, hypothermia, tremor, weight loss, hallucination, nausea, convulsion and coma. LD_{50} oral (rats): 12 mg/kg

LEAD TETRAFLUORIDE

[7783-59-7]
Formula: PbF_4; MW 283.18

Uses

Lead tetrafluoride is used as a fluorinating agent for hydrocarbons.

Physical Properties

White tetragonal crystals; density 6.7 g/cm^3; melts at about 600°C; hydrolyzes readily when exposed to moist air.

Thermochemical Properties

$\Delta H_f°$ –225.10 kcal/mol

Preparation

The tetrafluoride is obtained by fluorination of lead difluoride. The method involves passing a mixture of fluorine and nitrogen or carbon dioxide over lead difluoride at 300°C.

$$PbF_2 + F_2 \xrightarrow{N_2, 300^\circ C} PbF_4$$

Reactions

Lead tetrafluoride is readily hydrolyzed by moisture, turning brown and forming lead dioxide:

$$PbF_4 + 2H_2O \rightarrow PbO_2 + 4HF$$

The tetrafluoride also hydrolyzes in dilute hydrofluoric acid. However, in concentrated acid, it forms fluoplumbic acid, H_2PbF_6:

$$PbF_4 + 2HF \rightarrow H_2PbF_6$$

When an alkali metal fluoride or ammonium fluoride is added to a solution of lead tetrafluoride in concentrated hydrofluoric acid, salts of fluoplumbic acid are obtained:

$$H_2PbF_6 + 2NaF \rightarrow Na_2PbF_6 + 2HF$$

Analysis

Elemental composition: Pb 73.16%, F 26.84%. A small measured quantity of the compound is hydrolyzed in water and the aqueous solution is appropriately diluted and analyzed for fluoride ion, either by ion-specific electrode or by ion chromatography. The solution is digested with nitric acid and analyzed for lead by AA, ICP, or other instrumental methods (See Lead).

LEAD TETROXIDE

[1314-41-6]
Formula: Pb_3O_4; MW 685.60
Synonyms: red lead; minium; trilead tetroxide; lead orthoplumbite; mineral red; Paris red.

Uses

Lead tetroxide has many applications. The most important use is in paint and storage-batteries. It is used as a pigment in corrosion-protecting paints for steel surfaces. It also is used in positive battery plates; in colored glasses and ceramics; in glass sealants for television picture tubes; in propellants and explosives; in radiation shields for x-rays and gamma rays; in the vulcanization of rubber; in glass-writing pencils; in adhesives for tire cords; in foaming agents and waterproofing materials; in plasters and ointments; in lead dioxide matches; and as a catalyst for oxidation of carbon monoxide in exhausts.

Physical Properties

Bright-red crystalline substance or amorphous powder; density 9.1 g/cm³; decomposes on heating to 500°C, melts at 830°C under pressure and oxygen; insoluble in water and alcohol; soluble in glacial acetic acid, hot hydrochloric acid, and a dilute nitric acid-hydrogen peroxide mixture.

Thermochemical Properties

$\Delta H_f°$	–171.7 kcal/mol
$\Delta G_f°$	–143.7 kcal/mol
S°	50.5 cal/degree mol
C_ρ	35.1 cal/degree mol

Preparation

Lead tetroxide is made by heating lead monoxide in the presence of air at temperatures between 450 to 500°C. The temperature should be maintained below 500°C, above which the tetroxide decomposes.

$$6PbO + O_2 \xrightarrow{450\text{–}500^\circ C} 2Pb_3O_4$$

Alternatively, the tetroxide may be prepared by heating a mixture of lead monoxide and lead dioxide at 250°C:

$$2PbO + PbO_2 \xrightarrow{250^\circ C} Pb_3O_4$$

Reactions

When heated above 550°C, the tetroxide decomposes to monoxide, evolving oxygen:

$$6Pb_3O_4 \xrightarrow{500\text{–}550^\circ C} 6PbO + O_2$$

Lead tetroxide reacts with dilute nitric acid forming lead nitrate and precipitating lead dioxide:

$$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

The above reaction may be explained by assuming lead tetroxide as formally equivalent to plumbus plumbate having a structure $Pb_2^{II}[Pb^{IV}O_4]$ in which Pb^{2+} dissolves in dilute nitric acid forming lead(II) nitrate while Pb^{4+} precipitates out as lead(IV) oxide.

Lead tetroxide reacts with anhydrous acetic acid at 80°C producing lead(II) acetate and lead(IV) acetate. Alternatively, the tetroxide is added into a mixture of glacial acetic acid and acetic anhydride and heated gently:

$$Pb_3O_4 + 8CH_3COOH \xrightarrow[\text{heat}]{\substack{\text{acetic}\\ \text{anhydride}}} 2Pb(CH_3COO)_2 + Pb(CH_3Coo)_4 + 4H_2O$$

On cooling, the tetraacetate crystallizes, leaving diacetate in the solution. Acetic anhydride is added to react with water produced in the reaction to form acetic acid and thus prevent hydrolysis.

Lead tetroxide can be reduced to metallic lead when heated with reducing agents, such as hydrogen, carbon, or carbon monoxide:

$$Pb_3O_4 + 4H_2 \xrightarrow{heat} 3Pb + 4H_2O$$

LEAD TRIOXIDE

[1314-27-8]
Formula: Pb_2O_3; MW 462.40
Synonyms: lead sesquioxide; dilead trioxide; plumbous metaplumbate

Uses

Lead trioxide is a catalyst for oxidation of carbon monoxide in exhaust gases. Other uses are vulcanizing neoprene rubber; fireproofing plastics; detecting radiation; and manufacturing high-purity diamonds.

Physical Properties

Orange-yellow amorphous powder; decomposes at 370°C; insoluble in cold water; decomposes in hot water and acids.

Thermochemical Properties

S°	36.3 cal/degree mol
C_ρ	25.7 cal/degree mol

Preparation

Lead trioxide is prepared by adding sodium hypochlorite or bromine to an aqueous solution of sodium plumbite.

Reaction

When heated in air at 370°C, the trioxide converts to tetroxide, Pb_3O_4. It dissociates to lead monoxide on heating at 530°C. It decomposes in acids forming lead dioxide and the corresponding salts of the acids. With concentrated sulfuric acid, the products are lead dioxide and lead sulfate with evolution of oxygen:

$$Pb_2O_3 + H_2SO_4 \rightarrow PbO_2 + PbSO_4 + O_2 + H_2O$$

Analysis

Elemental composition: Pb 89.62%, O 10.38%. The composition of this oxide may be determined from analysis of lead in acid extract. The compound may be characterized by x-ray analysis and from physical properties.

LITHIUM

[7439-93-2]
Symbol Li; atomic number 3; atomic weight 6.941; a Group IA (Group 1) alkali metal element; lightest metal; electron configuration: $1s^22s^1$; atomic radius 1.225Å; ionic radius Li^+ 0.59Å (for CN 4), and 0.76Å (for CN 6); first ionization potential 5.392eV; valence +1; two naturally occurring stable isotopes, Li-7 (92.4%) and Li-6 (7.6%), and three radioactive isotopes, Li-5, Li-8, and Li-9.

History, Occurrence, and Uses

Lithium was first discovered in 1817 by Arfvedsen in its silicoaluminate mineral, petalite. However, the metal first was isolated from its mineral by Bunsen and Matthiesen in 1855. Lithium is distributed widely in nature. Its concentration in the earth's crust is 20 mg/kg, and in seawater is 0.18mg/L. It is found in many chloride brines at varying but significant amounts. The principal minerals are:

spodumene (spar): $LiAlSi_2O_6$ (theoretical Li_2O content 8.03%)
petalite: $LiAlSi_4O_{10}$ (theoretical Li_2O content 4.88%)
lepidolite (lithium mica): $K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$ (varying compositions; theoretical Li_2O content 3–4%)

amblygonite: $LiAlFPO_4$ (theoretical Li_2O content >8%)
hectorite: $Na_{0.33}(Mg,Li)_3Si_4O_{10}(F,OH)_2$ (theoretical Li_2O content 0.7–1.3%)

The metal has numerous industrial applications. It is used to make high-energy lithium batteries. Lithium and its aluminum alloys are used as anodes in non-aqueous solid-state batteries. Also, many of its salts are used as electrolytes in these batteries. Another major application is in metallurgy. Lithium is alloyed with lead, magnesium, aluminum and other metals. Its alloy Bahnmetall is used for wheel bearings in railroad cars, and its magnesium alloy is used in aerospace vehicles. Probably the most important applications of lithium are in preparative chemistry. It is the starting material to prepare lithium hydride, amide, nitride, alkyls and aryls. Lithium hydrides are effective reducing agents. The alkyls are used in organic syntheses.

Physical Properties

Soft silvery-white metal; body-centered cubic structure; density 0.531 g/cm^3; burns with a carmine-red flame, evolving dense white fumes; melts at 180.54°C; vaporizes at 1,342°C; vapor pressure 1 torr at 745°C and 10 torr at 890°C; electrical resistivity 8.55 microhm-cm at 0°C and 12.7 microhm-cm at 100°C; viscosity 0.562 centipoise at 200°C and 0.402 centipoise at 400°C; reacts with water; soluble in liquid ammonia forming a blue solution.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	38.09 kcal/mol
ΔG_f° (gas)	30.28 kcal/mol
S° (cry)	6.96 cal/degree mol
S° (gas)	33.14 cal/degree mol
C_ρ (cry)	5.92 cal/degree mol
C_ρ (gas)	4.97 cal/degree mol
ΔH_{fus}	0.716 kcal/mol
ΔH_{vap}	35.34 kcal/mol
Thermal conductivity at 0°C	0.17cal/sec/cm/cm^2/°C
Coefficient of linear expansion at 20°C	56x10^{-6}/°C

Production

Lithium is obtained primarily from its ore, spodumene. Another important source is natural brine found in many surface and ground waters, from which the metal also is produced commercially.

The first production step involves recovery of the metal from spodumene. The naturally occurring ore, alpha-spodumene is heated in a brick-lined rotary kiln at a temperature between 1,075 to 1,100°C. This converts the alpha form to a more reactive form, beta-spodumene. The beta form is heated in a rotary kiln at 250°C with an excess of 93% sulfuric acid. The metal reacts with acid forming lithium sulfate. The kiln discharge is leached with water to separate water-soluble lithium sulfate from several impurity metals. Aqueous solution containing excess sulfuric acid is then neutralized by treatment with an excess of ground calcium carbonate (limestone). The solution is filtered to remove unreacted limestone along with the products calcium sulfate and the sulfates of aluminum and iron. The solution containing saturated calcium sulfate and magnesium ions from limestone are then treated with calcium hydroxide upon which magnesium precipitates as hydroxide. The magnesium hydroxide is filtered from the solution. Addition of sodium carbonate to the filtrate precipitates calcium carbonate leaving lithium sulfate behind in the solution. The pH of the solution is then adjusted to between 7 and 8 with sulfuric acid. The solution is concentrated by evaporation after which it is treated with 28% sodium carbonate solution. Upon heating at 90 to 100°C, lithium carbonate precipitates. The precipitate is separated by centrifugation and washed and dried for further treatment.

Alternatively, limestone may be used instead of sulfuric acid to recover lithium from spodumene. Such recovery processes, known as alkaline methods, involve heating the ore with a mixture of ground limestone and calcium sulfate or chloride to form lithium sulfate or chloride. Leaching the kiln discharge with water yields an aqueous solution of lithium sulfate or chloride.

Several ion-exchange methods are also known that offer efficient recovery of lithium from its ores. In such processes, ore is heated with an acid, or its sodium or potassium salt, at moderate temperatures between 100 to 350°C. Often an aqueous solution of sodium or potassium salt such as sodium carbonate is employed which is heated with the ground ore in a steam autoclave. Lithium ions are liberated into aqueous solution from the silicate complex, exchanging hydrogen, sodium or potassium ions.

Lithium may be recovered from natural chloride brines. Such recovery processes may require additional steps depending on the magnesium and calcium content of the brine. The process involves evaporation of brine, followed by removal of sodium chloride and interferring ions such as calcium and magnesium. Calcium is removed by precipitation as sulfate while magnesium is removed by treating the solution with lime upon which insoluble magnesium hydroxide separates out. Addition of sodium carbonate to the filtrate solution precipitates lithium carbonate.

Lithium metal is produced commercially by electrolysis of a fused eutectic mixture of lithium chloride-potassium chloride (45% LiCl) at 400 to 450°C. The eutectic mixture melts at 352°C in comparison to the pure LiCl melting at 606°C. Also, the eutectic melt is a superior electrolyte to LiCl melt. (Landolt, P.E. and C. A. Hampel. 1968. *Lithium*. In *Encyclopedia of Chemical Elements*.C. A. Hampel, Ed. Reinhold Book Corp. New York.) Electrolysis is carried out using graphite anodes and steel cathodes. Any sodium impurity in lithium chloride may be removed by vaporizing sodium under vacuum at elevated temperatures. All commercial processes nowadays are based on electrolytic recovery of the metal. Chemical reduction processes do not yield high purity-grade metal. Lithium can be stored indefinitely under airtight conditions. It usually is stored under mineral oil in metal drums.

Reactions

Lithium metal is highly reactive but less so than other alkali metals. Its chemical properties, however, are more like those of the alkaline earth metals.

At ordinary temperatures, lithium does not react with dry oxygen. However, it reacts above 100°C, forming lithium oxide, Li_2O:

$$Li + O_2 \xrightarrow{100^\circ C} 2Li_2O$$

The metal ignites in air near its melting point, burning with intense white flame, forming Li_2O.

Lithium reacts with water forming lithium hydroxide with evolution of hydrogen:

$$2Li + 2H_2O \rightarrow 2LiOH + H_2$$

The reaction is violent when lithium metal is in finely divided state.

Lithium reacts violently with dilute acids, liberating hydrogen:

$$Li + 2HCl \rightarrow LiCl + H_2$$

Reaction with cold concentrated sulfuric acid is slow.

The metal dissolves in liquid ammonia, forming a blue solution, lithium amide, $LiNH_2$:

$$2Li + 2NH_3 \rightarrow 2LiNH_2 + H_2$$

The same product also is obtained from ammonia gas.

Unlike other alkali metals, lithium reacts with nitrogen in the presence of moisture at ordinary temperatures, forming the black lithium nitride, Li_3N:

$$6Li + N_2 \rightarrow 2Li_3N$$

The above reaction is exothermic.

Lithium reacts with hydrogen at red heat forming lithium hydride:

$$2Li + H_2 \xrightarrow{>400^\circ C} 2LiH$$

Reactions with sulfur and selenium in liquid ammonia yield lithium sulfide and selenide, respectively:

$$2Li + S \xrightarrow{liq \cdot NH_3} Li_2S$$

The metal combines with chlorine and other halogens, forming their halides:

$$Li + Cl_2 \rightarrow 2LiCl$$

When heated with carbon at 800°C, the product is lithium carbide:

$$2Li + 2C \xrightarrow{800^\circ C} Li_2C_2$$

The metal reacts with carbon dioxide at elevated temperatures, forming lithium carbonate, Li_2CO_3.

Lithium forms alloys with several metals including aluminum, calcium, copper, magnesium, mercury, sodium, potassium, silver, tin and zinc.

It combines with phosphorus, arsenic and antimony on heating, forming their binary salts:

$$3Li + P \xrightarrow{heat} Li_3P$$

The metal behaves as a reducing agent at high temperatures. It reduces aluminum chloride to aluminum and boron oxide to boron:

$$3Li + AlCl_3 \xrightarrow{high\ temperature} 3LiCl + Al$$

$$6Li + B_2O_3 \xrightarrow{high\ temperature} 3Li_2O + 2B$$

Lithium liberates hydrogen from ethanol, forming lithium ethoxide:

$$2Li + 2C_2H_5OH \rightarrow 2C_2H_5OLi + H_2$$

Several organolithium compounds have important applications in organic syntheses. These may be readily synthesized by reactions of lithium with organics. The metal reacts with alkyl or aryl halides or mercury alkyls or aryls to produce alkyl or aryl lithium. Some examples are:

$$\underset{\text{(diethylmercury)}}{(C_2H_5)_2Hg + 2Li} \xrightarrow{hexane} \underset{\text{(diethyllithium)}}{2C_2H_5Li + Hg}$$

$$\underset{\text{(methyl bromide)}}{CH_3Br + 2Li} \xrightarrow{cyclohexane} \underset{\text{(methyllithium)}}{CH_3Li + LiBr}$$

$$\underset{\text{(}n\text{-butyl chloride)}}{CH_3(CH_2)_3Cl + 2Li} \xrightarrow{hexane} \underset{\text{(}n\text{-butyllithium)}}{CH_3(CH_2)_3Li} + LiCl$$

$$\underset{\text{(diphenylmercury)}}{(C_6H_5)_2Hg + 2Li} \xrightarrow{toluene} \underset{\text{(phenyllithium)}}{2C_6H_5Li + Hg}$$

$$\underset{\text{(bromobenzene)}}{C_6H_5Br + 2Li} \xrightarrow{ethyl\ ether} \underset{\text{(phenyllithium)}}{C_6H_5Li + LiBr}$$

Analysis

Lithium metal can be determined by several instrumental methods, including flame AA, ICP-AES, ICP-MS, x-ray fluorescence and flame emission photometry. Flame AA measurement may be done at the wavelength 670.8 nm in the absorption mode using air-acetylene flame—or in the emission mode at the same wavelength.

Hazard

Lithium metal is less reactive than other alkali metals. However, violent explosions may occur when lithium is combined with halogenated hydrocarbons, such as chloroform or carbon tetrachloride. Violent reactions can occur with many other substances at high temperatures.

LITHIUM ALUMINUM HYDRIDE

[16853-85-3]
Formula: $LiAlH_4$; MW 37.95; ionic bond between Li^+ and AlH_4^- ions.
Synonyms: lithium tetrahydroaluminate; aluminum lithium hydride; lithium aluminum tetrahydride

Uses

Lithium aluminum hydride is among the most important industrial reducing agents. It is used extensively in organic syntheses and also in catalytic hydrogenation.

Physical Properties

White crystalline powder when pure; monoclinic crystals; grey in the presence of aluminum impurity; stable below 120°C in dry air; turns grey on standing; hygroscopic; density 0.917 g/cm^3; melts at 190°C (decomposes); reacts with water and alcohols; soluble in diethylether and tetrahydrofuran (about 30 and 13 g/100g, respectively at 25°C; also soluble in dimethylcellosolve; sparingly soluble in dibutylether; slightly soluble in dioxane (1g/L) and practically insoluble in hydrocarbons; can be solubilized in benzene by crown ether.

Preparation

Lithium aluminum hydride is prepared by reaction of lithium hydride with aluminum chloride in diethylether:

$$4LiH + AlCl_3 \xrightarrow{(C_2H_5)_2O} LiAlH_4 + 3LiCl$$

Reactions

Lithium aluminum hydride reacts violently with water evolving hydrogen. About 2.36L H_2 is evolved per 1 g of the compound at NTP.

$$LiAlH_4 + 2H_2O \rightarrow LiAlO_2 + 4H_2$$

Also, it reacts with alcohols evolving hydrogen:

$$\mathrm{LiAlH_4 + ROH \rightarrow Li[AlH(OR)_3] + 3H_2}$$

Reactions with metal chlorides yield metal hydrides:

$$\mathrm{LiAlH_4 + 4NaCl \rightarrow 4NaH + LiCl + AlCl_3}$$

It also reduces sodium methoxide, $NaOCH_3$ into sodium hydride, NaH.

Lithium aluminum hydride reacts with many inorganic and organic neutral ligands, forming coordinated alumina complexes associated with lithium ions:

$$\mathrm{LiAlH_4 + NH_3 \xrightarrow{\mathit{ether}} Li[Al(NH_2)_4]}$$

$$\mathrm{LiAlH_4 + PH_3 \xrightarrow{\mathit{ether}} Li[Al(PH_2)_4]}$$

$$\mathrm{LiAlH_4 + bipyridyl \xrightarrow{tetrahydrofuran} Al(bipy)_3}$$

Almost all organic functional groups except for olefinic double bonds are reduced by lithium aluminum hydride. It reduces acids, esters, acid chlorides, amides, imides, imines, nitriles, nitroorganics, epoxides, and lactones.

Most carboxylic acids are completely reduced to primary alcohols.

$$\begin{array}{lllll} \mathrm{RCOOH} & \xrightarrow[(C_2H_5)_2O]{LiAlH_4} & [\ \mathrm{RCHO}] & \xrightarrow[(C_2H_5)_2O]{LiAlH_4} & \mathrm{RCH2OH} \\ \text{(carboxylic acid)} & & \text{(aldehyde)} & & \text{(primary alcohol)} \end{array}$$

Reduction of acetic acid to ethanol is complete:

$$\begin{array}{lll} \mathrm{CH_3COOH} & \xrightarrow[(C_2H_5)_2O]{LiAlH_4} & \mathrm{CH_3CH_2OH} \\ & & (100\%) \end{array}$$

Carboxylic acids containing tertiary carbon atoms yield a lower product.

$$\begin{array}{lll} \mathrm{(CH_3)_3CCOOH} & \xrightarrow[(2)\ H_2O]{(1)\ LiAlH_4/ether} & \mathrm{(CH_3)_3CCH_2OH} \\ \text{(2,2-dimethylpropanoic} & & \text{(neopentyl alcohol)} \\ \text{acid)} & & (92\%) \end{array}$$

A balanced equation for conversion of carboxylic acid to alcohol and other products is:

$$4RCOOH + 3LiAlH_4 \xrightarrow{ether} [(RCH_2O)_4Al]Li + 4H_2 + 2LiAlO_2$$

$$[(RCH_2O)_4Al]Li + H_2O \rightarrow 4RCH_2OH + Al(OH)_3 + LiOH$$

Esters are reduced to alcohols, the products depending upon alkyl groups in the ester:

$$RCOOR' \xrightarrow[(2)\ H_2O]{(1)\ LiAlH_4/ether} RCH2OH + R'OH$$

Another synthetic reaction involves the reduction of cyanohydrins to yield β-amino alcohols:

$$\underset{\text{(cyclohexanone)}}{C_6H_{10}O} \xrightarrow{HCN} C_6H_{10}\text{–}CN\text{–}OH \xrightarrow[(2)\ ether]{(1)\ LiAlH_4} \underset{\text{(cyclohexyl cyanohydrin)}}{C_6H_{10}\text{–}CH_2NH_2\text{–}OH}$$

Esters are completely reduced to alcohols; while unsaturated esters are converted to unsaturated alcohols. Other reduction reactions include conversion of phenyl isocyanate to N-methylaniline:

$$C_6H_5NCO \xrightarrow[ether]{LiAlH_4} C_6H_5NHCH_3$$

and dechlorination of polyvinyl chloride at 100°C in tetrahydrofuran.

Hazard

Lithium aluminum hydride is a flammable substance. It ignites spontaneously on grinding and reacts violently with water and many organic substances. Diethyl ether, tetrahydrofuran or another suitable solvent should be used in its synthetic applications. Dry or powdered limestone is an appropriate fire extinguishing agent.

LITHIUM AMIDE

[7782-89-0]
Formula: $LiNH_2$; MW 22.96

Uses

Lithium amide is used in synthesis of histamine and analgesic drugs. The compound also is used in many organic synthetic reactions including alkylation of ketones and nitriles, Claisen condensation, and in synthesis of antioxidants and acetylenic compounds.

Physical Properties

Colorless needles; tetragonal structure; density 1.178 g/cm^3 at 17.5°C; melts around 375°C; starts to decompose at 320°C; decomposes at 400°C; soluble in cold water; decomposes in hot water; slightly soluble in ethanol and liquid ammonia; insoluble in benzene and ether.

Preparation

Lithium amide is obtained by dissolution of lithium metal in liquid ammonia. The reaction is slow, but may be catalyzed by cobalt nitrate:

$$2Li + 2NH_3 \xrightarrow{Co(NO_3)_2} 2LiNH_2 + H_2$$

It also is obtained by passing gaseous ammonia over lithium hydride:

$$LiH + NH_3 \rightarrow LiNH_2 + H_2$$

Reactions

Lithium amide decomposes to imide when heated above 400°C:

$$2LiNH_2 \rightarrow Li_2NH + NH_3$$

It is used in several organic syntheses. Some of these synthetic reactions are based on the mechanism that the terminal alkynes react with the stronger base, the anion, forming the weaker conjugate base:

$$R{-}C{\equiv}C{-}H + :\ddot{N}H_2^- \xrightarrow[NH_3]{liquid} R{-}C{\equiv}\bar{C}: + :NH_3$$

It converts *vic* dibromide to bromoalkene and then alkyne:

$$RCH(Br)CH(Br)R + LiNH_2 \xrightarrow[\text{heat}]{\text{mineral oil}} \underset{\text{(bromoalkene)}}{RCH{=}C(Br)R} + NH_3 + LiBr$$

$$\underset{\text{(bromoalkene)}}{RCH{=}C(Br)R} + LiNH_2 \xrightarrow[\text{heat}]{\text{mineral oil}} \underset{\text{(alkyne)}}{RC{\equiv}CR} + NH_3 + LiBr$$

Ketones can be converted into alkynes:

$$\underset{\text{(methyl cyclohexyl ketone)}}{C_6H_{11}COCH_3} \xrightarrow[0°C]{PCl_5} \underset{\text{(a \textit{gem}-dichloride)}}{C_6H_{11}C(Cl_2)CH_3} \xrightarrow[\text{mineral oil, heat}]{LiNH_2} \underset{\text{(cyclohexylacetylene) (46\%)}}{C_6H_{11}C{\equiv}CH}$$

LITHIUM BOROHYDRIDE

[16949-15-8]
Formula: $LiBH_4$; MW 21.78
Synonyms: lithium tetrahydroborate; lithium boron hydride

Uses

Lithium borohydride is used as a strong reducing agent. Its principal applications are in organic syntheses for reducing carbonyl groups such as aldehydes, ketones, and esters. It also is used for selectively reducing a carbonyl group in the presence of a nitrile group. Such selective reduction cannot be achieved with lithium aluminum hydride, which is a much stronger reducing agent. The compound also is used to detect free carbonyl groups in proteins and peptides.

Physical Properties

White orthorhombic crystals; density 0.67 g/cm^3; decomposes in moist air; melts at 268°C; decomposes at 380°C; reacts with water; dissolves in ether, tetrahydrofuran, and diethylamine; solubility in ether, 25g/L at 25°C.

Thermochemical Properties

$\Delta H_f°$	–45.60 kcal/mol
$\Delta G_f°$	–29.90 kcal/mol
S°	18.13 cal/degree mol
C_ρ	19.73 cal/degree mol

Preparation

Lithium borohydride is prepared by reacting ethyllithium with aluminum borohydride:

$$C_2H_5Li + Al(BH_4)_3 \xrightarrow{ether} 3LiBH_4 + Al(C_2H_5)_3$$

Alternatively, the compound may be obtained by the reaction of ethyllithium with diborane:

$$C_2H_5Li + B_2H_6 \xrightarrow{ether} LiBH_4 + C_2H_5BH_2$$

Reactions

Lithium borohydride reacts with water with liberation of hydrogen:

$$LiBH_4 + 2H_2O \rightarrow LiBO_2 + 4H_2$$

Reaction with methanol yields lithium boromethoxide and hydrogen:

$$LiBH_4 + 2CH_3OH \rightarrow LiB(OCH_3)_2 + 3H_2$$

Reaction with hydrogen chloride yields diborane, lithium chloride and hydrogen:

$$2LiBH_4 + 2HCl \rightarrow 2LiCl + B_2H_6 + 2H_2$$

Reactions with oxidizing agents are violent.

Analysis

Elemental composition: Li 31.85%, B 49.66%, H 18.50%. The compound is dissolved in water cautiously and the evolved hydrogen is measured by GC using a TCD. The aqueous solution is treated with nitric acid and the diluted nitric acid extract is analyzed for lithium by atomic absorption or emission spectroscopy (See Lithium).

LITHIUM BROMIDE

[7550-35-8]
Formula: $LiBr$; MW 86.85; forms stable hydrates, $LiBr \cdot H_2O$, $LiBr \cdot 2H_2O$, and $LiBr \cdot 3H_2O$.

Uses

Lithium bromide is used in absorption, refrigeration and air-conditioning systems. A highly concentrated solution of the salt is an efficient absorbent of water vapor. The vapor pressure of such solution is very low. Other applications include the use of the salt as a swelling agent for wool, hair and other organic fibers; as a catalyst in dehydrohalogenation reactions; and as a sedative and hypnotic in medicine.

Physical Properties

White cubic crystals; hygroscopic; refractive index 1.784; density 3.464 g/cm^3; melts at 550°C; vaporizes at 1,265°C; highly soluble in water (145g/100g at 4°C), much greater solubility in hot water (254g/100g at 90°C); soluble in methanol, ethanol and ether; slightly soluble in pyridine; vapor pressure of aqueous solutions at 52 and 68% concentrations at 25°C are 5 and 0.7 torr, respectively.

Thermochemical Properties

$\Delta H_f°$ (LiBr)	–83.94 kcal/mol
$\Delta H_f°$ ($LiBr \cdot H_2O$)	–158.36 kcal/mol
$\Delta H_f°$ ($LiBr \cdot 2H_2O$)	–230.10 kcal/mol
$\Delta H_f°$ (LiBr)(aq)	–95.61 kcal/mol
$\Delta G_f°$ (LiBr)	–81.74 kcal/mol
$\Delta G_f°$ ($LiBr \cdot H_2O$)	–142.05 kcal/mol
$\Delta G_f°$ ($LiBr \cdot 2H_2O$)	–200.90 kcal/mol
$\Delta G_f°$ (LiBr)(aq)	–94.95 kcal/mol
S° (LiBr)	17.75 cal/degree mol
S° ($LiBr \cdot H_2O$)	26.2 cal/degree mol

S° ($LiBr\cdot 2H_2O$)	38.8 cal/degree mol
S° (LiBr)(aq)	22.9 cal/degree mol
C_ρ (LiBr)(aq)	–17.5 cal/degree mol

Preparation

Lithium bromide is prepared by neutralizing lithium hydroxide or lithium carbonate with an aqueous solution of hydrobromic acid, followed by concentration and crystallization:

$$LiOH + HBr \rightarrow LiBr + H_2O$$

$$Li_2CO_3 + HBr \rightarrow LiBr + CO_2 + H_2O$$

The salt is usually obtained as hydrates. Anhydrous lithium bromide is obtained by heating hydrated salt under vacuum.

Analysis

Elemental composition (Anhydrous LiBr): Li 7.98%, Br 92.02%. The water of crystallization in hydrated salt can be measured by gravimetry. Lithium and bromide ions may be analyzed in diluted aqueous solutions of the salt by AA or ICP spectroscopy and ion chromatography, respectively.

LITHIUM CARBONATE

[554-13-2]
Formula: Li_2CO_3; MW 73.89

Uses

Lithium carbonate is used in enamels, specialty glasses and special ceramic wares. It is used to produce glazes on ceramics and porcelains. It also is used as an additive to molten aluminum fluoride electrolyte in Hall-Heroult process. It is the starting material to prepare many other lithium salts. The compound also is used in medicine as an antidepressant.

Physical Properties

White monoclinic crystals; refractive index 1.428; density 2.11 g/cm^3; melts at 723°C; decomposes at 1,310°C; low solubility in water (1.54 g/100g) at 0°C; 1.32 g//100g at 20°C), solubility decrease with temperature (0.72g/100g at 100°C); insoluble in acetone and ethanol.

Thermochemical Properties

$\Delta H_f°$	–290.60 kcal/mol
$\Delta G_f°$	–270.58 kcal/mol
S°	21.60 cal/degree mol
C_ρ	23.69 cal/degree mol

Preparation

Lithium carbonate is obtained as an intermediate product in recovery of lithium metal from its ore, spodumene (See Lithium). It is prepared by mixing a hot and concentrated solution of sodium carbonate with lithium chloride or sulfate solution.

$$Li_2SO_4 + Na_2CO_3 \rightarrow Li_2CO_3 + Na_2SO_4$$

Reactions

Lithium carbonate reacts with dilute acids, liberating carbon dioxide:

$$Li_2CO_3 + HCl \rightarrow LiCl + CO_2 + H_2O$$

Thermal decompostion yields lithium oxide and carbon dioxide:

$$Li_2\ CO_3 \xrightarrow{\text{high temperatue}} Li_2O + CO_2$$

Reaction with lime produces lithium hydroxide:

$$Li_2CO_3 + Ca(OH)_2 \rightarrow 2LiOH + CaCO_3$$

The carbonate reacts with molten aluminum fluoride converting to lithium fluoride:

$$3Li_2CO_3 + 2AlF_3 \xrightarrow{\text{elevated temperature}} 6LiF + 3CO_2 + Al_2O_3$$

It combines with carbon dioxide in aqueous slurry forming soluble bicarbonate, which decomposes to carbonate upon heating:

$$Li_2CO_3 + CO_2 + H_2O \rightarrow 2LiHCO_3$$

The bicarbonate can not be separated in solid form. It exists only in solution when carbonate dissolves in water saturated with CO_2 under pressure.

Analysis

Elemental composition: Li 18.78%, C 16.25%, O 64.96%. It evolves CO_2 with effervescence when treated with dilute acids, which turns limewater milky. Lithium may be analyzed in an aqueous solution by atomic absorption or emission spectroscopy and carbonate anion may be determined by ion chromatography.

LITHIUM CHLORIDE

[7447-41-8]
Formula: LiCl; MW 42.39

Uses

Lithium chloride is used in the production of lithium metal by electrolysis. It also is used in metallurgy as a eutectic melting composition with potassium chloride (LiCl 41 mol%: KCl 59 mol%). Other applications are in low temperature dry-cell batteries; as a dehumidifier in air conditioning; in welding and soldering flux; as a desiccant; in fireworks; and in mineral waters and soft drinks.

Physical Properties

White cubic crystals; granules or powder; hygroscopic; sharp salt-like taste; refractive index 1.662; density 2.068 g/cm^3; melts at 605°C; vaporizes around 1,360°C; readily dissolves in water (64g/100mL at 0°C); also highly soluble in alcohol and pyridine; moderately soluble in acetone (4.1 g/100mL at 25°C).

Thermochemical Properties

$\Delta H_f°$ (LiCl)	–97.66 kcal/mol
$\Delta H_f°$ ($LiCl \cdot H_2O$)	–170.3 kcal/mol
$\Delta H_f°$ ($LiCl \cdot 2H_2O$)	–242.0 kcal/mol
$\Delta H_f°$ ($LiCl \cdot 3H_2O$)	–313.4 kcal/mol
$\Delta G_f°$ (LiCl)	–91.87 kcal/mol
$\Delta G_f°$ ($LiCl \cdot H_2O$)	–151.0 kcal/mol
S° (LiCl)	14.18 cal/degree mol
S° ($LiBr \cdot H_2O$)	24.58 cal/degree mol
C_ρ (LiCl)	11.47 cal/degree mol

Preparation

Lithium chloride may be prepared by reaction of lithium carbonate or lithium hydroxide with hydrochloric acid followed by crystallization:

$$Li_2CO_3 + 2HCl \rightarrow 2LiCl + CO_2 + H_2O$$

$$LiOH + HCl \rightarrow LiCl + H_2O$$

Crystallization above 95°C yields anhydrous salt. Hot solution upon cooling forms crystals of monohydrate, $LiCl \cdot H_2O$.

Lithium chloride can be synthesized from its elements by heating lithium metal with chlorine gas. It also may be obtained from natural brine.

Analysis

Elemental composition: Li 16.37%, Cl 83.63%. The aqueous solution of the salt may be analyzed for lithium metal by AA or ICP (See Lithium) and for chloride by titration against a standard solution of silver nitrate or mercury nitrate, or by ion chromatography.

LITHIUM FLUORIDE

[7789-24-4]
Formula: LiF; MW 25.94

Uses

The important uses of lithium fluoride are as flux in glasses, vitreous enamels and glazes; in soldering and welding aluminum; and its prisms in infrared spectrophotometers. The compound also is used for storing solar energy.

Physical Properties

White cubic crystals; refractive index 1.3915; density 2.635 g/cm^3; melts at 845°C; vaporizes at 1,676°C; very slightly soluble in water 0.27 g/100g at 18°C; soluble in hydrofluoric acid; insoluble in alcohol.

Thermochemical Properties

$\Delta H_f°$	–147.22 kcal/mol
$\Delta G_f°$	–140.47 kcal/mol
S°	8.52 cal/degree mol
C_ρ	9.94 cal/degree mol

Preparation

Lithium fluoride is prepared by treating an aqueous solution of lithium hydroxide or lithium carbonate with aqueous hydrofluoric acid:

$$LiOH + HF \rightarrow LiF + H_2O$$

Analysis

Elemental composition: Li 26.75%, F 73.25%. An aqueous solution prepared by dissolving 100 mg in a liter of water may be analyzed for lithium by AA or ICP spectrophotometry and for fluoride by ion chromatography or by using a fluoride ion selective electrode.

LITHIUM HYDRIDE

[7580-67-8]
Formula: LiH; MW 7.949

Uses

Lithium hydride is used as a reducing and condensation agent in organic reactions. It converts acid chlorides to aldehydes. It also is used in several other organic syntheses; and to prepare lithium aluminum hydride. Lithium hydride also is used as a portable source of hydrogen; and for preparing many lithium salts. It also is used for storing thermal energy for space power stations.

Physical Properties

White crystalline solid; cubic crystals; density 0.82 g/cm^3; melts at 686.4°C; decomposes in water; soluble in acids.

Thermochemical Properties

$\Delta H_f°$	–21.64 kcal/mol
$\Delta G_f°$	–16.34 kcal/mol
S°	4.783 cal/degree mol
C_ρ	6.66 cal/degree mol

Preparation

Lithium hydride is prepared by heating lithium metal with hydrogen above 440°C. The reaction is exothermic and can be controlled once it is initiated, without external heating. The heat of formation is greater than that of sodium hydride:

$$2Li + H_2 \xrightarrow{>400^\circ C} 2LiH$$

Reactions

Lithium hydride reacts vigorously with water, forming lithium hydroxide with the evolution of hydrogen:

$$LiH + H_2O \rightarrow LiOH + H_2$$

The hydride also reacts with ammonia forming lithium amide and evolving hydrogen:

$$LiH + NH_3 \rightarrow LiNH_2 + H_2$$

Lithium hydride is a strong reducing agent and would, therefore, react with compounds that contain oxygen. Even many highly stable oxides of metals and nonmetals can be reduced. It reduces metal oxides to metals and carbon dioxide to carbon:

$$Fe_3O_4 + 4LiH \rightarrow 3Fe + 4NaOH$$

$$2LiH + CO_2 \rightarrow Li_2O + C + H_2O$$

It undergoes violent reactions with oxidizing agents.

Lithium hydride reacts with aluminum hydride forming lithium aluminum hydride, a powerful reducing agent:

$$LiH + AlH_3 \xrightarrow{ether} LiAlH_4$$

Lithium hydride consisting of Li^+ and H^- ions exhibits properties of an ionic salt, both cationic and anionic; such as a strong electrolyte. Thus, when electrolyzed at temperatures slightly below its melting point, it dissociates to Li^+

and H^- ions. Hydrogen gas is liberated at the anode.

The hydride ion, $H:^-$ being a strong base, would react with alcohols, forming alkoxides and liberating hydrogen:

$$\underset{\text{(ethanol)}}{CH_3CH_2OH} + LiH \rightarrow \underset{\text{(lithium ethoxide)}}{CH_3CH_2OLi} + H_2$$

$$\underset{\text{(\textit{tert}-butanol)}}{(CH_3)_3COH} + LiH \rightarrow \underset{\text{(lithium \textit{tert}-butoxide)}}{(CH_3)_3COLi} + H_2$$

LITHIUM HYDROXIDE

[1310-65-2]
Formula: LiOH; MW 23.95
Synonym: lithium hydrate

Uses

Lithium hydroxide is used as an electrolyte in certain alkaline storage batteries; and in the production of lithium soaps. Other uses of this compound include its catalytic applications in esterification reactions in the production of alkyd resins; in photographic developer solutions; and as a starting material to prepare other lithium salts.

Physical Properties

White tetragonal crystals; refractive index 1.464; density 1.46 g/cm^3; melts at 450°C; decomposes at 924°C; dissolves in water (12.8g/100g at 20°C and 17.5 g/100g at 100°C); slightly soluble in alcohol.

The monohydrate is white monoclinic crystalline solid; refractive index 1.460; density 1.51 g/cm^3; soluble in water, more soluble than the anhydrous salt (22.3g and 26.8g/100g at 10 and 100°C, respectively); slightly soluble in alcohol; insoluble in ether.

Thermochemical Properties

$\Delta H_f°$	–115.90 kcal/mol
$\Delta G_f°$	–104.92 kcal/mol
S°	10.23 cal/degree mol
C_ρ	11.87 cal/degree mol

Preparation

Lithium hydroxide is prepared by the reaction of lithium carbonate with calcium hydroxide:

$$Li_2CO_3 + Ca(OH)_2 \rightarrow 2LiOH + CaCO_3$$

Calcium carbonate is filtered out and the solution is evaporated and crystallized. The product obtained is the monohydrate, $LiOH{\cdot}H_2O$. The anhydrous compound is obtained by heating the hydrate above 100°C in vacuum or carbon dioxide-free air.

The hydroxide also may be prepared by treating lithium oxide with water.

Reactions

Lithium hydroxide is a base. However, it is less basic than sodium or potassium hydroxide.

The compound undergoes neutralization reactions with acids:

$$LiOH + HCl \rightarrow LiCl + H_2O$$

Heating the compound above 800°C in vacuum yields lithium oxide:

$$2LiOH \xrightarrow[\text{vacuum}]{800°C} Li_2O + H_2O$$

Lithium hydroxide readily absorbs carbon dioxide, forming lithium carbonate:

$$2LiOH + CO_2 \rightarrow Li_2CO_3 + H_2O$$

Passing chlorine through a solution of lithium hydroxide yields lithium hypochlorite:

$$LiOH + Cl_2 \rightarrow LiOCl + HCl$$

Saponification of fatty acids with lithium hydroxide produces lithium soaps.

$$\underset{\text{(stearic acid)}}{LiOH + CH_3(CH_2)_{16}COOH} \rightarrow \underset{\text{(lithium stearate)}}{CH_3(CH_2)_{16}COOLi + H_2O}$$

Analysis

Elemental composition: Li 28.98%, H 4.21%, O 66.80%. An aqueous solution of the compound may be analyzed for lithium by various methods (See Lithium). The basicity of the solution can be measured by acid-base titration using a standard solution of HCl and either a color indicator or a pH meter.

LITHIUM IODIDE

[10377-51-2]
Formula: LiI; MW 133.85
The monohydrate, $LiI{\cdot}H_2O$ [17023-24-4]; dihydrate, $LiI{\cdot}2H_2O$ [17023-25-5]; and the trihydrate, $LiI{\cdot}3H_2O$ [7790-22-9] are also known.

Uses

Lithium iodide is used in photography; and its aqueous solution as an absorbent in refrigeration.

Physical Properties

White cubic crystals; refractive index 1.955; density 4.076 g/cm^3; melts at 449°C; vaporizes around 1,180°C; highly soluble in water (165 g/100g at 20°C), solubility greatly increases in hot water (433g/100g at 80°C); also very soluble in methanol (343 g/100g at 20°C) and ammonia; soluble in acetone (42.6g/100g at 18°C).

The trihydrate, $LiI \cdot 3H_2O$, is a yellowish solid (due to the release of iodine when exposed to air); hexagonal crystals; hygroscopic; density 3.48 g/cm^3; loses iodine when heated in air; loses one molecule of water of crystallization at 73°C becoming dihydrate, $LiI \cdot 2H_2O$ and loses the second molecule at 80°C, forming monohydrate, $LiI \cdot H_2O$ and becomes anhydrous at 130°C; highly soluble in water; soluble in ethanol and acetone.

Thermochemical Properties

$\Delta H_f°$ (LiI)	–64.63 kcal/mol
$\Delta H_f°$ ($LiI \cdot H_2O$)	–141.09 kcal/mol
$\Delta H_f°$ ($LiI \cdot 2H_2O$)	–212.81 kcal/mol
$\Delta H_f°$ ($LiI \cdot 3H_2O$)	–284.93 kcal/mol
$\Delta H_f°$ (LiI)(aq)	–79.75 kcal/mol
$\Delta G_f°$ (LiI)	–64.60 kcal/mol
$\Delta G_f°$ ($LiI \cdot H_2O$)	–127.00 kcal/mol
$\Delta G_f°$ ($LiI \cdot 2H_2O$)	–186.50 kcal/mol
$\Delta G_f°$ (LiI)(aq)	–82.40 kcal/mol
S° (LiI)	20.74 cal/degree mol
S° ($LiI \cdot H_2O$)	29.40 cal/degree mol
S° ($LiI \cdot 2H_2O$)	44.0 cal/degree mol
S° (LiI)(aq)	29.80 cal/degree mol
C_ρ (LiI)	–12.20 cal/degree mol
C_ρ (LiI)(aq)	–17.60 cal/degree mol

Preparation

The trihydrate salt is obtained by neutralization of lithium hydroxide or lithium carbonate solution with pure hydriodic acid followed by concentration of the solution for crystallization:

$$LiOH + HI \rightarrow LiI + H_2O$$

When heated in a vacuum, the trihydrate dehydrates to anhydrous salt.

Analysis

Elemental composition (anhydrous LiI): Li 5.18%, I 94.82%. The water of crystallization may be measured by gravimetry. An aqueous solution may be appropriately diluted and analyzed for lithium by AA or ICP spectrophotometry (See Lithium) and for the iodide ion by ion chromatography. Iodide may be alternatively analyzed by the leuco crystal violet method. Upon addition of potassium peroxymonosulfate, $KHSO_5$, iodide is selectively oxidized to iodine, which instantaneously reacts with the colorless indicator reagent known as leuco crystal violet [4,4',4"-methylidynetris(N,N-dimethylaniline)] to produce a violet colored dye. Absorbance or transmittance of the solution measured at 592nm by a spectrophotometer or a filter photometer is proportional to concentration of iodide in solution (APHA, AWWA and WEF. 1998. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington, D.C.: American Public Health Association.)

LITHIUM NITRATE

[7790-69-4]
Formula: $LiNO_3$; MW 68.946
Forms a stable trihydrate, $LiNO_3 \cdot 3H_2O$

Uses

Lithium nitrate is used in fireworks to impart carmine-red color to the flame. Its mixtures with other alkali nitrates produce very low melting eutectics, which are used as heat-transfer media.

Physical Properties

White trigonal crystals; hygroscopic; refractive index 1.735; density 2.38 g/cm^3; melts to a clear melt at 264°C; decomposes at 600°C; highly soluble in water (90g/100g at 28°C; solubility greatly increases with temperature (234g/100g at 100°C); also, soluble in methanol, pyridine and ammonia solution.

The trihydrate, $LiNO_3 \cdot 3H_2O$, consists of colorless needles; loses water of crystallization on strong heating; soluble in water, methanol and acetone.

Thermochemical Properties

$\Delta H_f°$	($LiNO_3$)	–147.47 kcal/mol
$\Delta H_f°$	($LiNO_3 \cdot 3H_2O$)	–328.5 kcal/mol
$\Delta G_f°$	($LiNO_3$)	–91.1 kcal/mol
$\Delta G_f°$	($LiNO_3 \cdot 3H_2O$)	–263.8 kcal/mol
S°	($LiNO_3$)	21.5 cal/degree mol
S°	($LiNO_3 \cdot 3H_2O$)	53.4 cal/degree mol

Preparation

Lithium nitrate is prepared by neutralization of lithium hydroxide or lithium carbonate with nitric acid followed by evaporation of the solution and strong heating at 200°C in vacuum to yield the anhydrous salt:

$$LiOH + HNO_3 \rightarrow LiNO_3 + H_2O$$

$$Li_2CO_3 + HNO_3 \rightarrow LiNO_3 + CO_2 + H_2O$$

Analysis

Elemental composition (anhydrous salt): Li 10.07%, N 20.32%, O 69.62%. A diluted aqueous solution may be analyzed for lithium by AA or ICP method (See Lithium) and nitrate ion by either ion-specific electrode or by ion chromatography.

LITHIUM NITRIDE

[26134-62-3]
Formula: Li_3N; MW 34.83

Uses

Lithium nitride is used as a catalyst to prepare boron nitride. It also is used as a reducing and nucleophilic reagent in organic synthesis, and to convert metals into their nitrides.

Physical Properties

Red hexagonal crystals or free-flowing fine red powder; density 1.27 g/cm^3; melts at 813°C; an excellent solid ionic conductor; conductivity 4×10^{-2} mho/cm at 227°C; decomposes in water.

Preparation

Lithium nitride is prepared by passing dry nitrogen gas over lithium metal:

$$6Li + N_2 \rightarrow 2Li_3N$$

The reaction is exothermic and occurs at ordinary temperatures. The reaction may be controlled by adjusting temperature and nitrogen flow rate. The reaction proceeds rapidly when the metal is heated in nitrogen.

Reactions

Lithium nitride is a strong reducing agent. Thus, all its reactions involve reduction. It ignites in air and reacts with water to form lithium hydroxide and ammonia:

$$Li_3N + 3H_2O \rightarrow 3LiOH + NH_3$$

Lithium nitride reduces metal oxides and many metal chlorides to metallic state. It reduces copper(I) chloride to copper. Most of these reactions are exothermic.

Hazard

Lithium nitride ignites in air. Violent decomposition can occur when mixed with oxidizing agents.

LITHIUM OXIDE

[12057-24-8]
Formula: Li_2O; MW 29.88
Synonym: lithium monoxide

Uses

Lithium oxide in its highly porous sintered form is used as an absorbent for carbon dioxide.

Physical Properties

White cubic crystals; refractive index 1.644; density 2.013 g/cm^3; melts at 1,570°C; dissolves and decomposes in water (6.67 g/100g at 0°C and 10.02 g/100g at 100°C).

Thermochemical Properties

$\Delta H_f°$ (cry)	–142.91 kcal/mol
$\Delta H_f°$ (gas)	–38.4 kcal/mol
$\Delta G_f°$ (cry)	–134.13 kcal/mol
$\Delta G_f°$ (gas)	–43.3 kcal/mol
S° (cry)	8.98 cal/degree mol
S° (gas)	55.30 cal/degree mol
C_ρ (cry)	12.93 cal/degree mol
C_ρ (gas)	11.91 cal/degree mol

Preparation

Lithium oxide is prepared by heating lithium metal in dry oxygen above 100°C:

$$4Li + O_2 \xrightarrow{heat} 2Li_2O$$

Another method of preparation that yields pure lithium oxide involves thermal decomposition of lithium peroxide:

$$2Li_2O_2 \xrightarrow{heat} 2Li_2O + O_2$$

Also, the oxide can be produced by heating the pure lithium hydroxide at 800°C in a vacuum:

$$2LiOH \xrightarrow[\text{vacuum}]{800°C} Li_2O + H_2O$$

Reactions

Lithium oxide absorbs carbon dioxide forming lithium carbonate:

$$Li_2O + CO_2 \rightarrow Li_2CO_3$$

The oxide reacts slowly with water forming lithium hydroxide:

$$Li_2O + H_2O \rightarrow 2LiOH$$

There is no reaction with oxygen at high temperature or high pressure to form any peroxide or higher oxide.

The oxide reacts with acids forming lithium salts.

Analysis

Elemental composition: Li 46.45%, O 53.55%. The oxide may be identified from its physical properties and characterized by x-ray analysis. Lithium composition in the oxide may be determined by analyzing the nitric acid extract by AA or ICP (See Lithium).

LITHIUM SULFATE

[10377-48-7]
Formula: Li_2SO_4; MW 109.94
Also forms a stable monohydrate, $Li_2SO_4 \cdot H_2O$ [10102-25-7]

Uses

Lithium sulfate is used in making a special type of high strength glass. It also is used in medicine as an antidepressant.

Physical Properties

Colorless monoclinic or hexagonal crystals; transforms to cubic form at 500°C; refractive index 1.465; density 2.221 g/cm^3; sublimes at 845°C; soluble in water, solubility decreases with an increase in temperature (26.1 and 23.2 g at 0 and 100°C, respectively); insoluble in absolute ethanol and acetone.

The monohydrate constitutes colorless monoclinic crystals; refractive index 1.465; density 2.06 g/cm^3; loses water of crystallization at 130°C; soluble in water, (more soluble than the anhydrous salt (34.9 and 29.2 g/100g at 25 and 100°C), respectively; insoluble in acetone and pyridine.

Thermochemical Properties

$\Delta H_f°$ (Li_2SO_4)	–343.33 kcal/mol
$\Delta H_f°$ ($Li_2SO_4 \cdot H_2O$)	–414.80 kcal/mol
$\Delta H_f°$ (Li SO_4)(aq)	–350.44 kcal/mol
$\Delta G_f°$ (Li_2SO_4)	–315.91 kcal/mol
$\Delta G_f°$ ($Li_2SO_4 \cdot H_2O$)	–374.2 kcal/mol
$\Delta G_f°$ (Li SO_4)(aq)	–318.18 kcal/mol
S° (Li_2SO_4)	27.5 cal/degree mol
S° ($Li_2SO_4 \cdot H_2O$)	39.1 cal/degree mol
S° (Li SO_4)(aq)	11.3 cal/degree mol

C_ρ (Li_2SO_4)	28.10 cal/degree mol
C_ρ ($Li_2SO_4 \cdot H_2O$)	36.1 cal/degree mol

Preparation

Lithium sulfate is prepared by neutralization of lithium hydroxide or lithium carbonate with sulfuric acid followed by crystallization:

$$2LiOH + H_2SO_4 \rightarrow Li_2SO_4 + H_2O$$

$$Li_2CO_3 + H_2SO_4 \rightarrow Li_2SO_4 + CO_2 + H_2O$$

The product obtained from crystallization in a concentrated solution is the monohydrate, $Li_2SO_4 \cdot H_2O$. Anhydrous salt is obtained by heating the monohydrate in a vacuum.

Analysis

Elemental composition (anhydrous Li_2SO_4): Li 12.63%, S 29.12%, O 59.28%. The waters of crystallization may be determined by gravimetry. Lithium may be analyzed in a dilute aqueous solution by AA or ICP (See Lithium), while sulfate may be measured by ion chromatography.

LUTETIUM

[7439-94-3]
Symbol Lu; atomic number 71; atomic weight 174.97; a lanthanide series element; an *f*-block inner-transition metal; electron configuration $[Xe]4f^{14}5d^16s^2$; valence +3; atomic radius (coordination number 12) 1.7349Å; ionic radius (Lu^{3+}) 0.85Å; two naturally-occurring isotopes: Lu-176 (97.1%) and Lu-175(2.59%); Lu-172 is radioactive with a half-life of $4x10^{10}$ years (beta-emission); several artificial isotopes known, that have mass numbers 155, 156, 167–174, 177–180.

History, Occurrence, and Uses

Lutetium was independently discovered by Urbain and von Welsbach in 1907. The element was named after Lutetia, the ancient name for Paris. The metal also is known as cassiopeium in Germany.

Lutetium occurs in nature in small amounts in yttrium-containing minerals. It is found in xenotime, precambrian granites, and North American shales. It also exists at 0.001% in monazite, from which the metal is produced commercially. Lutetium has very little commercial application. The metal emits beta particles after thermal neutron activation, and is used to catalyze organic reactions.

Physical Properties

Silvery-white metal; hexagonal close-packed structure; density 9.84 g/cm^3; melts at 1,663°C; vaporizes at 3,402°C; electrical resistivity 59 microhm-cm; slightly paramagnetic; thermal neutron cross section 108 barns; soluble in acids.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	102.2 kcal/mol
ΔG_f° (gas)	96.7 kcal/mol
S° (cry)	12.18 cal/degree mol
S° (gas)	44.14 cal/degree mol
C_ρ (cry)	6.42 cal/degree mol
C_ρ (gas)	4.99 cal/degree mol
ΔH_{fus} (cry)	4.60 kcal/mol
ΔH_{vap} (cry)	102.2 kcal/mol\

Production

Lutetium is produced commercially from monazite. The metal is recovered as a by-product during large-scale extraction of other heavy rare earths (See Cerium, Erbium, Holmium). The pure metal is obtained by reduction of lutetium chloride or lutetium fluoride by a alkali or alkaline earth metal at elevated temperatures;

$$2LuCl_3 + 3Ca \xrightarrow{\textit{elevated temperature}} 2Lu + 3CaCl_2$$

Chemical Properties

In aqueous media lutetium occurs as tripositive Lu^{3+} ion. All its compounds are in +3 valence state. Aqueous solutions of all its salts are colorless, while in dry form they are white crystalline solids. The soluble salts such as chloride, bromide, iodide, nitrate, sulfate and acetate form hydrates upon crystallization. The oxide, hydroxide, fluoride, carbonate, phosphate, and oxalate of the metal are insoluble in water. The metal dissolves in acids forming the corresponding salts upon evaporation of the solution and crystallization.

Analysis

The metal may be analyzed by AA, ICP-AES, ICP/MS, x-ray fluorescence and other instrumental techniques.

MAGNESIUM

[7439-95-4]
Symbol Mg; atomic number 12; atomic weight 24.305; a Group II A (Group 2) alkaline-earth metal; atomic radius 1.60Å; ionic radius (Mg^{2+}) 0.72Å; atomic volume 14.0 cm³/mol; electron configuration [Ne]$3s^2$; valence +2; ionization potential 7.646 and 15.035eV for Mg^+ and Mg^{2+}, respectively; three natural isotopes: Mg-24(78.99%), Mg-25(10.00%), Mg-26(11.01%).

History, Occurrence and Uses

Magnesium was discovered by Davy in 1808. He produced an amalgam of magnesium both by chemical and electrolytic methods. Metallic mercury was used in both methods. In the chemical method, Davy passed potassium vapors over magnesia at red heat and extracted the 'new element' with mercury. In the electrolytic reduction, magnesium sulfate was electrolyzed using a mercury cathode. Both the methods yielded the amalgam of the new element. Magnesium in the metallic form was first isolated by French chemist Bussy in 1828 by heating magnesium chloride with potassium metal at elevated temperatures. Faraday in 1833 produced metallic magnesium by electrolysis of magnesium chloride.

Magnesium is probably one of the most common metals distributed in nature, constituting about 2.4% of the earth's crust. The metal, however, does not occur in nature in elemental form. The principal minerals are dolomite $[CaMg(CO_3)_2]$, magnesite $MgCO_3$; carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$, and silicate materials, such as talc $Mg_3(Si_4O_{10})(OH)_2$ and asbestos $H_4Mg_3Si_2O_9$. Magnesium also is found in seawater, natural underground brines and salt deposits. Its concentration in sea water is 1,350 mg/L. Magnesium also occurs in all plants. Its porphyrin complex, chlorophyll, is essential for photosynthesis. It also is an essential nutrient element for humans. The dietary requirement for adults is about 300 mg per day.

Magnesium metal and its alloys have numerous uses in chemical, electrochemical, metallurgy, and electronic industries. Its thermal and electrical properties, lightness, and ease of fabrication into useful shapes make it an attractive choice in industrial applications. The metal is alloyed with aluminum for various structural uses. Its alloys with zinc, copper, nickel, lead, zirconium and other metals have many uses too. Magnesium alloys are used in automobile parts, aircraft, missiles, space vehicles, ship hulls, underground pipelines, memory discs, machine tools, furniture, lawn mowers, ladders, toys, and sporting goods. It also is used in making small and lightweight dry cell batteries. Chemical applications of magnesium include its use as a reducing agent, to prepare Grignard reagent for organic syntheses, and to purify gases. Magnesium also is used in blasting compositions, explosive sensitizers, incendiaries, signal flares, and pyrotechnics. Magnesium salts have numerous uses. They are discussed individually.

Physical Properties

Silvery-white metal; close-packed hexagonal structure; density 1.74 g/cm^3 at 20°C, 1.57 g/cm^3 at 650°C (liquid melt); melts at 650°C; vaporizes at 1,090°C; vapor pressure 5 torr at 678°C and 20 torr at 763°C; electrical resistivity 4.46 microhm-cm at 20°C, 28.0 microhm-cm at 650°C (liquid melt); surface tension 563 dynes/cm at 681°C; modulus of elasticity 6.5x10^6 lb/sq in; Poisson's ratio 0.35; thermal neutron absorption cross section 0.059 barn; soluble in dilute acids.

Thermochemical Properties

ΔH_f° (cry)	0.0
$\Delta H_f^{\circ\circ}$ (gas)	35.16 kcal/mol
ΔG_f° (gas)	26.89 kcal/mol
S° (cry)	7.82 cal/degree mol

S° (gas)	35.52 cal/degree mol
C_ρ (cry)	5.95 cal/degree mol
C_ρ (gas)	4.97 cal/degree mol
ΔH_{fus}	2.03 kcal/mol
ΔH_{vap}	49.9 kcal/mol
Thermal conductivity at 27°C	1.56 W/cm. K
Coefficeint of linear expansion (20–100°C)	26.1×10^{-6}/°C

Production

Although many commercial processes have been developed since the first electrolytic isolation of Mg metal by Davy and Faraday, and Bussy, by chemical reduction, the principles of the manufacturing processes have not changed. At present, the metal is most commonly manufactured by electrolytic reduction of molten magnesium chloride, in which chlorine is produced as a by-product. In chemical reduction processes, the metal is obtained by reduction of magnesium oxide, hydroxide, or chloride at elevated temperatures.

All the magnesium produced in the world currently is derived from its minerals dolomite and carnallite, as well as from the underground brines and seawaters. In most processes, magnesium is recovered from its mineral or brine either as magnesium chloride or converted to the latter for electrolytic production.

Many subterranean brines are very rich in magnesium chloride, often containing about 11% $MgCl_2$. Sodium and calcium chlorides are the other two major components (c.12% NaCl and 2% $CaCl_2$) in such brines. Solar evaporation of the brine solution and repeated heating increases the $MgCl_2$ concentration in the brine to above 25% at which the solubility of NaCl significantly decreases and it can be filtered out. Repeated spray drying and purification by chlorination yields anhydrous magnesium chloride.

Magnesium chloride produced from dolomite for electrolysis involves a series of steps that include calcinations of the mineral to oxide and then conversion to magnesium hydroxide, neutralization of the hydroxide with hydrochloric acid to form hydrated chloride, addition of sulfuric acid to separate out calcium as its insoluble sulfate, and dehydration of the hydrated salt to yield anhydrous $MgCl_2$. Similar steps are also followed to obtain the metal from seawater. The average concentration of magnesium ion in seawater is about 1,200 mg/L, thus making ocean water an enormous source of magnesium. Magnesium is precipitated as hydroxide by treatment with lime in an agitated flocculator:

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$$

The insoluble $Mg(OH)_2$ is filtered off and the seawater containing calcium chloride is returned to the sea. The hydroxide is then neutralized with hydrochloric acid. Evaporation of the solution yields hexahydrate, $MgCl_2 \cdot 6H_2O$. The hexahydrate is either fully dehydrated to anhydrous $MgCl_2$ by heating in dryers or partially dehydrated to monohydrate for electrolytic production of metal. Magnesium hydroxide produced from seawater alternatively may be calcined to magnesium oxide, MgO. The latter is reduced with carbon and converted to magnesium chloride by heating in an electric furnace in the presence of chlorine gas:

$$MgO + C + Cl_2 \xrightarrow{\textit{electric furnace}} MgCl_2 + CO$$

$$MgO + CO + Cl_2 \xrightarrow{\textit{electric furnace}} MgCl_2 + CO_2$$

Manufacturing processes, based on thermal reduction of magnesium oxide employ ferrosilicon or carbon as a reducing agent and use dolomite as the starting material. In these processes, the mineral is first calcined to produce oxides of magnesium and calcium, $MgO \cdot CaO$. In one such batch process, known as the Pidgeon process, calcined dolomite is mixed with pulverized ferrosilicon powder, briquetted, and charged into an electrically-heated retort made of nickel-chrome-steel alloy and operated under vacuum (0.1 to 0.2 mm Hg). The reaction is carried out at about 1,150°C for several hours (8 hours). Silicon reduces magnesium oxide to metallic magnesium produced as vapor. The vapors condense into crystals in the cooler zone of the retort (500°C). The reactions are as follows:

$$2(MgO \cdot CaO) + Si(Fe) \rightarrow 2\,Mg + 2CaO \cdot SiO_2(Fe)$$

The ferrosilicon alloy required in the above process is produced by thermal reduction of silica with carbon in the presence of iron:

$$SiO_2 + 2C + Fe \rightarrow Si(Fe) + 2CO$$

In the Pidgeon process discussed above, a secondary side reaction occurs between the CaO and SiO_2 forming dicalcium silicate:

$$2CaO + SiO_2 \xrightarrow{1500^\circ C} Ca_2SiO_4$$

In a modified method known as Magnetherm process, sufficient aluminum oxide is added to melt this Ca_2SiO_4 slag. This allows the products to be removed in the molten state and, in addition, heats the reactor by the electrical resistance of the slag.

Magnesium also is produced by thermal reduction of its oxide by carbon:

$$MgO + C \rightarrow Mg + CO$$

The above reaction is reversible above 1,850°C. The metal produced as vapor must be cooled rapidly to prevent any reversible reactions. Rapid cooling (shock cooling) can quench the reaction giving finely divided pyrophoric dust of the metal. The separation, however, is difficult. This makes the carbon reduction process less attractive than the other two thermal reduction processes, namely Pidgeon and Magnetherm processes.

Reactions

At room temperature magnesium is not attacked by air. However, when heated it burns with a dazzling white light, forming the oxide, MgO and nitride, Mg_3N_2. The formation of oxide is an exothermic reaction. The heat of reaction causes a portion of the metal to combine with the nitrogen of air:

$$2Mg + O_2 \rightarrow 2\ MgO$$

$$3Mg + N_2 \rightarrow 2\ Mg_3N_2$$

When the metal is in a finely divided state or a thin foil, both the reactions above are rapid.

Magnesium reacts very slowly with water at ordinary temperatures. Although the metal occupies a position higher than hydrogen in the electrochemical series, the reaction practically stops after a thin protective film of insoluble hydroxide deposits over the surface of the metal. The reaction is moderately fast in hot water and rapid in steam. The products are magnesium hydroxide and hydrogen:

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

In the presence of ammonium chloride or a substance that dissolves $Mg(OH)_2$, the above reaction proceeds at ambient temperatures, the metal continues to dissolve in water, displacing hydrogen.

Magnesium reacts readily with most mineral acids, evolving hydrogen:

$$Mg + 2H^+ \rightarrow Mg^{2+} + H_2$$

However, with certain acids, such as hydrofluoric acid, a protective layer of insoluble magnesium fluoride terminates the reaction. Likewise, the metal has little action on chromic acid.

At ordinary temperatures magnesium is stable in alkalies, both dilute and concentrated. However, hot solutions of alkalies above 60°C attack the metal.

Magnesium combines with halogens at elevated temperatures forming halides:

$$Mg + Cl_2 \rightarrow MgCl_2$$

$$Mg + Br_2 \rightarrow MgBr_2$$

The metal reacts with nitrogen, phosphorus, sulfur and selenium at elevated temperatures forming their binary compounds:

$$3Mg + N_2 \rightarrow Mg_3N_2$$

$$Mg + S \rightarrow MgS$$

$$3Mg + 2P \rightarrow Mg_3P_2$$

Magnesium exhibits single displacement reactions, thus replacing lower metals in electrochemical series from their salt solutions or melt. For example, magnesium will replace iron from molten iron(II) chloride forming magnesium chloride:

$$Mg + FeCl_2 \rightarrow MgCl_2 + Fe$$

Or it will reduce Fe^{2+} to metallic iron from the aqueous solution of $FeCl_2$:

$$Mg + Fe^{2+} + 2Cl^- \rightarrow Mg^{2+} + 2Cl^- + Fe$$

Magnesium also reduces nonmetallic oxides, such as carbon dioxide, carbon monoxide, sulfur dioxide and nitrous oxide, burning at elevated temperatures.

$$2Mg + CO_2 \rightarrow 2MgO + C$$

The metal reduces ammonia to magnesium nitride:

$$3Mg + 2NH_3 \rightarrow Mg_3N_2 + 3H_2$$

Two important reduction reactions of magnesium that are of commercial interest are the production of titanium by Kroll process and obtaining uranium from its fluoride:

$$2Mg + TiCl_4 \rightarrow 2MgCl_2 + Ti$$

$$2Mg + UF_4 \rightarrow 2MgF_2 + U$$

Magnesium forms hydride when heated with hydrogen under pressure:

$$Mg + H_2 \rightarrow MgH_2$$

Probably the most important reaction of magnesium in terms of synthetic applications involves preparation of Grignard reagent, RMgX where R is an alkyl or aryl group and X is a halogen other than fluorine. Grignard reagents provide convenient routes for various organic syntheses. These reagents are made by the reaction of magnesium with an alkly or aryl halide in ether:

$$Mg + C_2H_5Br \xrightarrow{\text{ether}} \underset{\text{(ethyl magnesium bromide)}}{C_2H_5MgBr}$$

Analysis

Magnesium in trace amounts can be measured conveniently in aqueous and solid matrices by flame atomic absorption or by ICP emission spectroscopy. The sample is digested with nitric acid and diluted. The recommended wavelength for flame AA measurement is 285.2nm and for ICP/AES analysis 279.08 or 279.55 nm. The metal also can be measured by the gravimetric method in which diammonium hydrogen phosphate $(NH_4)_2HPO_4$ is added to an ammoniacal solution of magnesium or its compound to produce a yellow precipitate of magnesium ammonium phosphate which on ignition yields magnesium pyrophosphate, $Mg_2P_2O_7$. The solid or aqueous sample is digested with nitric acid and then hydrochloric acid, evaporated and diluted prior to adding $(NH_4)_2HPO_4$ and ammonia solution. The method is less sensitive than the AA or ICP techniques and also subject to interference from calcium, aluminum, iron, silica and ammonium chloride.

MAGNESIUM ACETATE

[142-72-3]
Formula: $Mg(OOCCH_3)_2$; MW 142.39; also exists as stable tetrahydrate, $Mg(OOCCH_3)_2 \cdot 4H_2O$ [16674-78-5] and monohydrate $Mg(OOCCH_3)_2 \cdot H_2O$ [60582-92-5].

Uses

Magnesium acetate is used in the manufacture of rayon fiber for cigarette filters; and as a fixative for dyes in textile printing. It also is used as an antiseptic and disinfectant.

Physical Properties

Anhydrous magnesium sulfate is a white crystalline solid occurring in alpha form as orthorhomic crystals or as a beta form having triclinic structure; density 1.507 and 1.502 g/cm^3 for alpha- and beta-forms, respectively; decomposes at 323°C; very soluble in water; moderately soluble in methanol (5.25g/100 mL at 15°C).

The tetrahydrate constitutes colorless monoclinic crystals; hygroscopic; density 1.454 g/cm^3; melts at 80°C; highly soluble in water (120 g/100mL at 15°C); very soluble in methanol and ethanol.

Preparation

Magnesium acetate is prepared by treating magnesium oxide with acetic acid. Magnesium oxide reacts with concentrated acetic acid in boiling ethyl acetate to produce the alpha form of anhydrous magnesium acetate. The beta form is obtained by treating the oxide with 5–6% acetic acid. In slightly hydrated isobutyl alcohol medium the product is a monohydrate, $Mg(OOCCH_3)_2 \cdot H_2O$. In aqueous solution magnesium acetate crystallizes as a tetrahydrate, the commercial product. The tetrahydrate dehydrates to anhydrous salt at 134°C.

Analysis

Elemental composition for anhydrous acetate: Mg 17.08%, C 33.73%, H 4.25%, O 44.74%. The water of crystallization in the commercial product can be measured by gravimetry. Acetate anion can be estimated from elemental analysis for C, H and O, or by ion chromatography in a very dilute aqueous solution. Mg can be determined by AA or ICP methods.

MAGNESIUM BROMIDE

[7789-48-2]
Formula: $MgBr_2$; MW 184.11; forms stable hexahydrate, $MgBr_2 \cdot 6H_2O$ [13446-53-2] and decahydrate, $MgBr_2 10H_2O$ [75198-45-7].

Occurrence and Uses

Magnesium bromide occurs in sea water, surface and subterranean brines, and salt deposits. It is an electrolyte component in certain dry cells. In medicine, it is a sedative and anticonvulsant for treatment of nervous disorder. It also is used in organic synthesis forming several addition compounds.

Physical Properties

The anhydrous $MgBr_2$ is a white crystalline substance; hexagonal crystals; deliquescent; density 3.72 g/cm^3; melts at 700°C; highly soluble in water (101.5g/100mL at 20°C); moderately soluble in methanol and ethanol (21.8 and 6.9 g/mL at 20°C, respectively).

The hexahydrate, $MgBr_2 \cdot 6H_2O$ consists of colorless monoclinic crystals; bitter taste; hygroscopic; fluoresce in x-rays; density 2.07 g/cm^3; melts at 172.4°C; intensely soluble in water, 316 g/100 mL at 0°C; dissolves in methanol and ethanol; slightly soluble in ammonia solution.

Thermochemical Properties

$\Delta H_f°$ (cry)	–125.3 kcal/mol
$\Delta H_f°$ (gas)	–74.0 kcal/mol
$\Delta H_f°$ (aq)	–169.7 kcal/mol
$\Delta G_f°$ (cry)	–120.4 kcal/mol
S° (cry)	28.0 cal/degree mol

Preparation

Magnesium bromide is prepared by treating magnesium oxide with hydrobromic acid and subsequent crystallization above 0°C. The product is hexahydrate, $MgBr_2 \cdot 6H_2O$:

$$MgO + 2HBr \rightarrow MgBr_2 + H_2O$$

The anhydrous $MgBr_2$ may be obtained by heating the hexahydrate with dry hydrogen bromide gas.

Magnesium bromide also can be made from its elements. Heating magnesium metal with bromine vapor yields the salt:

$$Mg + Br_2 \rightarrow MgBr_2$$

Magnesium bromide, like the chloride salt, is obtained from sea water (see Magnesium and Magnesium chloride). In this process, magnesium hydroxide precipitated from sea water is neutralized with hydrobromic acid, and $MgBr_2$ is obtained by crystallization.

Analysis

Elemental composition: Mg 13.20%, Br 86.80%. The aqueous solution is analyzed for Mg by AA or ICP technique and the bromide ion measured by ion chromatography.

MAGNESIUM CARBONATE

[13717-00-5]

Formula: $MgCO_3$; MW 84.31; several hydrated and basic carbonates are also known that are stable and occur in nature. The types, names, formulas and CAS Registry numbers of anhydrous, hydrated and basic magnesium carbonates are tabulated below:

Compound	Mineral	Formula	CAS No.
anhydrous salt	magnesite	$MgCO_3$	[13717-00-5]
dihydrate	barringtonite	$MgCO_3 \cdot 2H_2O$	[5145-48-2]
trihydrate	nesquehonite	$MgCO_3 \cdot 3H_2O$	[14457-83-1]
pentahydrate	lansfordite	$MgCO_3 \cdot 5H_2O$	[61042-72-6]
basic carbonate	artinite	$MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$	[12143-96-3]
basic carbonate	hydromagnestite	$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$	[12072-90-1]
basic carbonate	dypingite	$4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$	[12544-02-4]
basic carbonate	—	$4MgCO_3 \cdot Mg(OH)_2 \cdot 8H_2O$	[75300-49-1]

Occurrence and Uses

Magnesium carbonate occurs in nature in several minerals as hydrated, basic and double salts, as shown above. The two principal minerals are magnesite, $MgCO_3$ and dolomite, a double salt, $CaCO_3 \cdot MgCO_3$. Both minerals are used as source materials in the production of magnesium metal. Also, they are calcined to produce basic refractory bricks. Other applications of magnesium carbonate are in flooring, fireproofing and fire-extinguishing compositions; as a filler material and smoke suppressant in plastics; as a reinforcing agent in neoprene rubber; as a drying agent and for color retention in foods; in cosmetics; in dusting powder; and in toothpaste. The high purity magnesium carbonate is used as an antacid in medicine; and as an additive to table salt. Another important application of magnesium carbonate is as a starting material in producing a number of magnesium compounds.

Physical Properties

The anhydrous salt consists of white trigonal crystals; refractive index 1.717; density 2.958 g/cm^3; decomposes at 350°C; practically insoluble in water (106 mg/L at room temperature); K_{sp} 1.0×10^{-5}; low to moderate solubility under partial pressure of CO_2 (3.5 and 5.9 g $MgCO_3$/100g saturated solution at CO_2 pressure 2 and 10 atm, respectively); insoluble in acetone and ammonia; dissolves in acids.

The di– and trihydrates, $MgCO_3 \cdot 2H_2O$ and $MgCO_3 \cdot 3H_2O$ are colorless crystals having triclinic and monoclinic structures, respectively; the refractive index 1.458 and 1.412, respectively; and their densities are 2.825 and 1.837 g/cm^3. The pentahydrate, $MgCO_3 \cdot 5H_2O$, occurring naturally as the mineral lansfordite is a white crystalline solid; monoclinic crystals; refractive index 1.456; density 1.73g/cm^3; decomposes in air; slightly soluble in water (0.375 g/100 mL at 20°C).

All three basic carbonates, artinite, hydromagnestite and dypingite, are white crystalline substances of monoclinic crystal structures; refractive index 1.488, 1.523 and 1.508, respectively; the index of refraction for the basic carbonate octahydrate is 1.515; the densities are 2.02 and 2.16 g/cm^3 for artinite and hydromagensite; the basic carbonates are all practically insoluble in water.

Thermochemical Properties

$\Delta H_f°$ ($MgCO_3$)	–261.9 kcal/mol
$\Delta G_f°$ ($MgCO_3$)	–241.9 kcal/mol
$\Delta G_f°$ ($MgCO_3 \cdot 3H_2O$)	–412.6 kcal/mol
$\Delta G_f°$ ($MgCO_3 \cdot 5H_2O$)	–525.7 kcal/mol
S° ($MgCO_3$)	15.7 cal/degree mol
C_ρ ($MgCO_3$)	18.05 cal/degree mol

Preparation

Magnesium carbonate is obtained mainly by mining its natural mineral magnesite. The trihydrate salt, $MgCO_3 \cdot 3H_2O$, is prepared by mixing solutions of magnesium and carbonate ions in the presence of carbon dioxide. Alternatively, it may be produced by carbonation of a magnesium hydroxide slurry with carbon dioxide under pressure (3.5 to 5 atm) and at a temperature below 50°C which yields soluble magnesium bicarbonate:

$$Mg(OH)_2 + 2CO_2 \rightarrow Mg(HCO_3)_2$$

The solution is filtered to remove impurities and the filtrate is subjected to vacuum or aeration to yield insoluble magnesium carbonate as a hydrated salt:

$$Mg^2 + 2HCO_3^- \rightarrow MgCO_3 + CO_2 + H_2O$$

Under ordinary conditions, anhydrous magnesium carbonate cannot be prepared in aqueous systems. The anhydrous salt, however, can be made under very high partial pressures of carbon dioxide.

Basic magnesium carbonate occurs in nature as the mineral hydromagnesite. The basic salt is obtained by mining the ore followed by purification. The basic carbonates also can be made by drying the magnesium carbonate trihydrate at about 100°C. Alternatively it can be prepared by simply boiling a solution of magnesium bicarbonate. The bicarbonate is obtained by carbonation of a magnesium hydroxide slurry below 50°C and under a CO_2 partial pressure of 3.5 to 5 atm. Composition of the basic carbonate produced by the above methods is $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$.

Another basic salt, $MgCO_3 \cdot Mg(OH)_3 \cdot 3H_2O$ is precipitated when magnesium salt solution is treated with sodium carbonate solution. The reactions probably are:

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$$

$$2Mg^{2+} + CO_3^{2-} + 2OH^- \rightarrow MgCO_3 \cdot Mg(OH)_2$$

Reactions

Magnesium carbonate dissolves in dilute mineral acids, evolving carbon dioxide:

$$MgCO_3 + HCl \rightarrow MgCl_2 + CO_2 + H_2O$$

$$MgCO_3 + H_2\ SO_4 \rightarrow MgSO_4 + CO_2 + H_2O$$

Thermal dissociation at elevated temperatures yields magnesium oxide and CO_2:

$$MgCO_3 \rightarrow MgO + CO_2$$

The trihydrate, $MgCO_3 \cdot 3H_2O$ or other hydrates on heating form basic magnesium carbonates, the product compositions depending on degree of water of crystallization and temperature.

Magnesium carbonate forms several double salts with salts of alkali and alkaline earth metals and ammonium ion. Some examples are:

$MgCO_3 \cdot Na_2CO_3$;
$MgCO_3 \cdot K_2CO_3 \cdot 8H_2O$;
$MgCO_3 \cdot KHCO_3 \cdot 4H_2O$ (Engle's salt);
$MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4H_2O$;
$MgCO_3 \cdot MgCl_2 \cdot 7H_2O$, and
$MgCO_3 \cdot MgBr_2 \cdot 7H_2O$

Analysis

Elemental composition: Mg28.83%, C 14.24%, O 56.93%. A measured amount of magnesium carbonate is treated with dilute HCl and liberated CO_2 is identified by the limewater test (CO_2 turns limewater milky). Carbon dioxide also may be identified and quantified by GC-TCD or preferably by GC/MS (characteristic mass ion 44). The acid solution can be analyzed for magnesium by AA or ICP techniques.

MAGNESIUM CHLORIDE

[7786-30-3]
Formula: $MgCl_2$; MW 95.218; also occurs as hexahydrate, $MgCl_2 \cdot 6H_2O$ [13778-96-6].

Occurrence and Uses

Magnesium chloride is a constituent of sea water. It also is found in most natural brines and many minerals such as carnallite, $KCl \cdot MgCl_2 \cdot H_2O$. Its hexahydrate occurs in nature as mineral bischofite, $MgCl_2 \cdot 6H_2O$.

The most important use of magnesium chloride is in the electrolytic production of magnesium metal. The compound is also used to make oxychloride cement, or what is known as Sorel cement for flooring, fire-resistant panel, and fireproofing of steel beams and other materials. Other applications are: as a dust binder on roads; as a flocculating agent in water treatment; for dressing cotton and woolen fabrics; as a fire-extinguishing agent and a fireproofing material; in processing of sugar-beets; and as a catalyst.

Physical Properties

Anhydrous salt consists of white lustrous hexagonal crystals; refractive index 1.675; density 2.32 g/cm^3; melts at 714°C; decomposes at a lower temperature of 300°C when heated slowly, releasing chlorine; vaporizes at 1,412°C; highly soluble in water, releasing heat (solubility 54.2 g/100 mL at 20°C and 72.7 g/100mL at 100°C) moderately soluble in ethanol (7.4 g/100mL at 30°C).

Hexahydrate constitutes colorless monoclinic crystals; deliquescent; refractive index 1.495; density 1.569 g/cm^3; decomposes on heating at 116°C; highly soluble in water (157 g/100mL at 20°C); solubility increased on heating; soluble in alcohol.

Thermochemical Properties

$\Delta H_f°$ ($MgCl_2$)	–153.28 kcal/mol
$\Delta H_f°$ ($MgCl_2 \cdot 6H_2O$)	–597.28 kcal/mol
$\Delta G_f°$ ($MgCl_2$)	–141.45 kcal/mol
$\Delta G_f°$ ($MgCl_2 \cdot 6H_2O$)	–505.49 kcal/mol
S° ($MgCl_2$)	21.42 cal/degree mol
S° ($MgCl_2 \cdot 6H_2O$)	87.50 cal/degree mol
C_ρ ($MgCl_2$)	17.06 cal/degree mol
C_ρ ($MgCl_2 \cdot 6H_2O$)	75.30 cal/degree mol

Production

Magnesium chloride is prepared by treating magnesium carbonate, hydroxide or oxide with hydrochloric acid followed by crystallization by evaporation. The hexahydrate of the salt $MgCl_2 \cdot 6H_2O$ is obtained upon crystallization.

In most commercial processes, the compound is either derived from the sea water or from the natural brines, both of which are rich sources of magnesium chloride. In the sea water process, the water is treated with lime or calcined dolomite (dolime), $CaO \cdot MgO$ or caustic soda to precipitate magnesium hydroxide. The latter is then neutralized with hydrochloric acid. Excess calcium is separated by treatment with sulfuric acid to yield insoluble calcium sulfate. When produced from underground brine, brine is first filtered to remove insoluble materials. The filtrate is then partially evaporated by solar radiation to enhance the concentration of $MgCl_2$. Sodium chloride and other salts in the brine concentrate are removed by fractional crystallization.

The crude product containing magnesium oxide or hydroxide is purified by heating with chlorine.

Magnesium chloride can be also recovered from its mineral carnallite by similar processes involving concentration of the liquor by solar evaporation followed by separation of other salts by fractional crystallization.

The product obtained is always the hexahydrate, $MgCl_2 \cdot 6H_2O$. It is dehydrated to anhydrous magnesium chloride by spray drying and heating with dry hydrogen chloride gas. In the absence of HCl, heating hexahydrate yields the basic salt, Mg(OH)Cl:

$$MgCl_2 \cdot 6H_2O \rightarrow Mg(OH)Cl + HCl + 5H_2O$$

Pure anhydrous chloride can be prepared by heating the double salt $MgCl_2 \cdot NH_4Cl \cdot 6H_2O$:

$$MgCl_2 \cdot NH_4Cl \cdot 6H_2O \rightarrow MgCl_2 \cdot NH_4Cl + 6H_2O$$

Ammonium chloride sublimes on further heating, leaving pure anhydrous $MgCl_2$:

$$MgCl_2 \cdot NH_4Cl \rightarrow MgCl_2 + NH_4Cl$$

Other methods of preparation involve heating magnesium oxide with coke powder in the presence of chlorine:

$$MgO + C + Cl_2 \rightarrow MgCl_2 + CO$$

Magnesium chloride also is a by-product during reduction of titanium(IV) chloride with magnesium metal:

$$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$$

The anhydrous salt and the hexahydrate are both highly corrosive. They are handled in equipment made out of inconel.

Analysis

Elemental composition (anhydrous $MgCl_2$): Mg 25.54%, Cl 74.46%. Aqueous solution of the salt may be analyzed for Mg by AA or ICP method (See Magnesium). The chloride ion can be identified by ion chromatography or measured by titration with a standard solution of silver nitrate using potassium chromate as indicator.

MAGNESIUM FLUORIDE

[7783-40-6]
Formula: MgF_2; MW 62.31
Synonym: magnesium flux

Occurrence and Uses

Magnesium fluoride occurs in nature as the mineral, sellaite. It is used in glass and ceramics. Single crystals are used for polarizing prisms and lenses.

Physical Properties

Colorless tetragonal crystals; faint violet luminescence; refractive index 1.378; density 3.148 g/cm³; Moh's hardness 6; melts at 1261°C; vaporizes at 2,260°C; practically insoluble in water (76 mg/L at 18°C); soluble in nitric acid; slightly soluble in dilute acids and acetone; insoluble in ethanol.

Thermochemical Properties

$\Delta H_f°$	–268.5 kcal/mol
$\Delta G_f°$	–255.8 kcal/mol
S°	13.68 cal/degree mol
C_ρ	14.72 cal/degree mol

Preparation

Magnesium fluoride is prepared by treating a magnesium salt solution with hydrofluoric acid or sodium fluoride:

$$MgSO_4 + 2HF \rightarrow MgF_2 + 2H^+ + SO_4^{2-}$$

or by adding hydrofluoric acid to magnesium carbonate:

$$MgCO_3 + 2HF \rightarrow MgF_2 + CO_2 + H_2O$$

Analysis

Elemental composition: Mg 39.02%, F 60.98%. The compound is digested with nitric acid-hydrofluoric acid mixture, diluted and analyzed for magnesium by AA or ICP method. The crystals may be characterized nondestructively by x-ray crystallography.

MAGNESIUM HYDRIDE

[60616-74-2]
Formula: MgH_2; MW 26.321

Uses

Magnesium hydride is a reducing agent; a source of hydrogen; and serves to prepare many complex hydrides.

Physical Properties

White tetragonal crystals; rutile structure; density 1.45 g/cm^3; decomposes at 200°C; reacts with water.

Preparation

Magnesium hydride is obtained by combining the elements at about 500°C. A convenient method of preparation involves passing hydrogen under pressure over heated magnesium powder in the presence of magnesium iodide as catalyst.

$$Mg + H_2 \xrightarrow[MgI_2]{\text{high temperature and pressure}} MgH_2$$

Magnesium hydride also is produced by thermal decomposition of diethylmagnesium at 200°C:

$$(C_2H_5)_2Mg \rightarrow MgH_2 + C_4H_8$$

An active form of the hydride obtained as a solvated pyrophoric powder and used as a reducing agent is prepared by the reaction of dibutylmagnesium $(C_4H_9)_2Mg$ with phenylsilane, $C_6H_5SiH_3$ in ether-heptane solvent mixture.

Reactions

Magnesium hydride is not readily decomposed by heat. However, in high vacuum decomposition takes place at 280°C, the hydride dissociating to its elements.

Magnesium hydride is a strong reducing agent, reducing oxidizable substances and compounds containing oxygen. The reactions often progress with violence. It ignites spontaneously in air, forming magnesium oxide and water:

$$MgH_2 + O_2 \rightarrow MgO + H_2O$$

It reacts violently with water, evolving hydrogen.

Similar reaction occurs with methane forming magnesium methoxide and evolving hydrogen:

$$MgH_2 + 2CH_3OH \rightarrow Mg(OCH_3)_2 + 2H_2$$

Magnesium hydride forms double hydrides with aluminum hydride and boron hydride:

$$MgH_2 + B_2H_6 \xrightarrow{ether} MgB_2H_8$$

$$MgH_2 + 2AlH_3 \xrightarrow{ether} MgAl_2H_8$$

Analysis

Elemental composition: Mg 92.35%, H 7.65%. The compound may be identified from its chemical properties that involve the evolution of hydrogen when cautiously treated with water or methanol (See Hydrogen). Magnesium may be analyzed by various instrumental techniques after digesting the compound into aqueous phase aided by nitric acid.

Hazard

Flammable solid, ignites spontaneously in air. Reaction with water is violent with the evolution of hydrogen.

MAGNESIUM HYDROXIDE

[1309-42-8]
Formula: $Mg(OH)_2$; MW 58.327
Synonym: brucite

Occurrence and Uses

Magnesium hydroxide occurs in nature as mineral brucite, often associated with several other minerals such as calcite, magnesite, or talc. Magnesium hydroxide is used as an intermediate in making magnesium metal. It also is used to manufacture magnesium oxide, magnesium carbonate and several other magnesium salts. Milk of magnesia, a finely divided suspension of magnesium hydroxide in water, is used in medicine as a laxative and antacid.

Physical Properties

Colorless hexagonal plate; refractive index 1.559; density 2.36 g/cm^3; loses water at 350°C; practically insoluble in water (9mg/L at 18°C and 40 mg/L at 100°C); soluble in acids and in aqueous solutions containing NH_4^+ ion.

Thermochemical Properties

$\Delta H_f°$	–220.97 kcal/mol
$\Delta G_f°$	–199.23 kcal/mol
S°	15.10 cal/degree mol
C_ρ	18.41 cal/degree mol

Production

Magnesium hydroxide is commonly produced from seawater, which is rich in Mg^{2+} ion. The average concentration of Mg^{2+} in seawater is about 1,300 mg/L. The first step of the process involves removal of interfering substances from seawater, the most notable being the water-soluble calcium bicarbonate. Bicarbonate removal is crucial, as it can form insoluble calcium carbonate, a side product that cannot be separated from magnesium hydroxide readily. Acidification of seawater converts bicarbonate into carbon dioxide, which is degassed by heating. Alternatively, seawater is treated with lime to convert calcium bicarbonate to carbonate:

$$Ca(HCO_3)_2 + CaO \rightarrow 2CaCO_3 + H_2O$$

Lime is obtained by calcination of dolomite, $CaCO_3 \cdot MgCO_3$, or limestone, $CaCO_3$, under controlled conditions to remove all CO_2. After bicarbonate removal, the seawater is then treated with calcium hydroxide, slaked dolime or sodium hydroxide to precipitate magnesium hydroxide:

$$Mg^{2+} + 2OH^{-} \rightarrow Mg(OH)_2$$

The solution is seeded with magnesium hydroxide to enhance crystal growth.

Magnesium hydroxide also is obtained from waste liquors from the potash industry. It is precipitated from mother liquors containing magnesium salts.

In the laboratory, magnesium hydroxide may be prepared by double decomposition reactions by adding a soluble hydroxide to solutions of magnesium salts; i.e., adding caustic soda solution to magnesium sulfate solution:

$$Mg^{2+} + SO_4^{2-} + 2Na^{+} + 2OH^{-} \rightarrow Mg(OH)_2 + 2Na^{+} + SO_4^{2-}$$

The above precipitation reaction does not occur with ammonium hydroxide in the presence of excess ammonium chloride.

Reactions

Solid magnesium hydroxide is decomposed by heat, forming magnesium oxide:

$$Mg(OH)_2 \rightarrow MgO + H_2O$$

Magnesium hydroxide is a weak base. However, it is sufficiently strong to neutralize acids, forming their salts. For example, treatment with sulfuric acid followed by evaporation and crystallization yields magnesium sulfate:

$$Mg(OH)_2 + H_2SO_4 \rightarrow MgSO_4 + 2H_2O$$

Magnesium hydroxide is soluble in solutions containing excess ammonium ion:

$$Mg(OH)_2 + 2NH_4^{+} \rightarrow Mg^{2+} + 2NH_4OH$$

Carbonation of its slurry with carbon dioxide at 4 to 5 atm pressure yields magnesium bicarbonate:

$$Mg(OH)_2 + CO_2 \rightarrow Mg(HCO_3)_2$$

Treatment with sodium carbonate solution yields basic carbonate. The probable reaction step is as follows:

$$2Mg^{2+} + 2OH^{-} + CO_3^{2-} \rightarrow MgCO_3 \cdot Mg(OH)_2$$

Similarly, basic magnesium chloride of indefinite composition is produced when magnesium hydroxide is mixed with magnesium chloride and water. The product is used as oxychloride cement (see Magnesium Oxide).

MAGNESIUM IODIDE

[10377-58-9]
Formula: MgI_2; MW 278.12; forms two stable hydrates, hexahydrate $MgI_2 \cdot 6H_2O$ [75535-11-4] and octahydrate $MgI_2 \cdot 8H_2O$ [7790-31-0].

Uses

Magnesium iodide has few commercial applications. The salt is used to prepare several addition compounds with organic solvents, some of which are used in organic synthesis.

Physical Properties

The anhydrous iodide is white hexagonal solid; deliquescent; density 4.43 g/cm^3; decomposes at 637°C; highly soluble in water (148 g/100mL at 18°C); soluble in alcohol, ether and ammonia.

The octahydrate is white orthorhombic crystals; deliquescent; density 2.098 g/cm^3; decomposes at 41°C; very soluble in water (81g/100 mL at 20°C); soluble in alcohol and ether.

Thermochemical Properties

$\Delta H_f°$	–87.0 kcal/mol
$\Delta G_f°$	–85.6 kcal/mol
S°	31.0 cal/degree mol

Preparation

Magnesium iodide is prepared by the reaction of magnesium oxide, hydroxide or carbonate with hydriodic acid, followed by evaporation of the solution and crystallization:

$$MgO + 2HI \rightarrow MgI_2 + H_2O$$

$$Mg(OH)_2 + 2HI \rightarrow MgI_2 + 2H_2O$$

$$MgCO_3 + 2HI \rightarrow MgI_2 + CO_2 + H_2O$$

Analysis

Elemental composition (anhydrous MgI_2): Mg 8.72%, I 91.26%. Aqueous solution may be analyzed for Mg by AA or ICP, and for iodide by ion chromatography following appropriate dilution.

MAGNESIUM NITRATE

[10377-60-3]
Formula: $Mg(NO_3)_2$; MW 148.31; forms two stable hydrates; the hexahydrate $Mg(NO_3)_2 \cdot 6H_2O$ [13446-18-9] and the dihydrate, $Mg(NO_3)_2 \cdot 2H_2O$ [15750-45-5].

Occurrence and Uses

The hexahydrate, $Mg(NO_3)_2 \cdot 6H_2O$, occurs in nature as mineral nitromagnesite. Magnesium nitrate is used in pyrotechnics; and in the manufacture of concentrated nitric acid to remove water and concentrate the acid vapors to 90–95% HNO_3. It also is used to aid coating and prilling in production of ammonium nitrate. The salt also is used as an analytical standard for magnesium and a matrix modifier in furnace atomic absorption spectroscopic analysis. It also finds some limited application as a nitrogenous fertilizer.

Physical Properties

The anhydrous salt consists of white cubic crystals; density 2.3 g/cm^3; very soluble in water. The dihydrate is white crystalline solid having density 1.45 g/cm^3; decomposes at about 100°C; soluble in water and ethanol. The hexahydrate, $MgNO_3 \cdot 6H_2O$ is a colorless solid having monoclinic crystal structure and density 1.46 g/cm^3. The salt is hygroscopic and very soluble in water and moderately soluble in ethanol.

Thermochemical Properties

$\Delta H_f°$	–189.0 kcal/mol
$\Delta G_f°$	–147.4 kcal/mol
S°	39.2 cal/degree mol
C_ρ	33.9 cal/degree mol

Preparation

Magnesium nitrate is prepared by the action of nitric acid on magnesium carbonate, oxide or hydroxide:

$$MgCO_3 + 2HNO_3 \rightarrow Mg(NO_3)_2 + CO_2 + H_2O$$

$$Mg(OH)_2 + 2HNO_3 \rightarrow Mg(NO_3)_2 + 2H_2O$$

The salt crystallizing at room temperature after evaporation is the hexahydrate, $Mg(NO_3)_2 \cdot 2H_2O$.

Reactions

Thermal decomposition of anhydrous $Mg(NO_3)_2$ yields magnesium oxide and nitrogen oxides. Heating the hexahydrate above its melting point forms basic nitrates, such as $Mg(NO_3)_2 \cdot 4\,Mg(OH)_2$. The latter decomposes at 400°C, forming magnesium oxide and oxides of nitrogen. Magnesium nitrate forms addition compounds with a number of nitrogen-containing organics such as pyridine, aniline, and urea.

Analysis

Elemental composition (anhydrous $Mg(NO_3)_2$); Mg 16.39%, N 18.88%, O 64.73%. The water of crystallization can be measured by gravimetry. Magnesium content of the salt can be measured by analysis of the metal in an aqueous solution using AA or ICP. Nitrate anion can be measured by ion chromatography—or by using a nitrate ion-selective electrode.

MAGNESIUM OXIDE

[1309-48-4]
Formula: MgO; MW 40.30
Synonym: magnesia; magnesia usta

Uses

Magnesium oxide occurs in nature as the mineral periclase. The commercial product is manufactured in several grades, depending on the purity, particle size and the reactivity desired. Dead-burned magnesia (consisting of sintered micro-crystals) is used in production of basic refractory brick for cement kilns, furnaces and crucibles. The caustic-burned magnesia, more reactive than the dead-burned reactive grade, is used to manufacture various magnesium salts; in extraction of uranium oxide from uranium ore; as mineral supplement in animal feed; and in many catalytic applications. Caustic-burned magnesia of higher reactive-grade, available as light or heavy magnesia, is used in cosmetics as fillers; as an accelerator for vulcanization of rubber; as an ingredient of antacids; and to prepare magnesium metal and various metal salts. Fused magnesia in crushed form is used in electrical arc furnaces and domestic appliances as insulation.

Physical Properties

Periclase: Colorless, transparent cubic crystals or white very-fine powder; refractive index 1.736; density 3.58 g/cm^3; hardness 5.5 Mohs; melts at

2,852°C; vaporizes at 3,600°C; electrical resistivity 1.3×10^{15} ohm–cm at 27°C; practically insoluble in water (86 mg/L at 30°C); soluble in acids and ammonium salt solutions; insoluble in alcohol.

Thermochemical Properties

$\Delta H_f°$	–143.81 kcal/mol
$\Delta G_f°$	–136.10 kcal/mol
S°	6.44 cal/degree mol
C_ρ	8.88 cal/degree mol
Thermal conductivity at 27°C	60.0 W/m.K

Production

Magnesium oxide is produced either from its minerals or from seawater or brine. Among minerals, magnesite, $MgCO_3$ and dolomite, $MgCO_3 \cdot CaCO_3$ are the two primary sources. It also may be obtained from its hydroxide ore, brucite, $Mg(OH)_2$. Calcination of these minerals yields magnesium oxide. The minerals generally contain several impurities, such as silica, alumina, iron oxide, and oxides and silicates of calcium and other metals. The ore is crushed, sized and impurities are separated by various processes, including froth flotation, magnetic separation, dissolution, and a wide-range of chemical process depending on the chemical properties of impurities. Often magnesium ore is converted into one of its salts, such as carbonate, hydroxide, chloride, or sulfate by chemical processes. The salt on calcination yields magnesium oxide:

$$MgCO_3 \xrightarrow{calcination} MgO + CO_2$$

$$Mg(OH)_2 \xrightarrow{calcination} MgO + H_2O$$

If dolomite is the source, thermal decomposition of $MgCO_3$ at 350°C produces MgO. At this temperature, $CaCO_3$ does not decompose. The decomposition temperature for the latter is 850°C.

Magnesium oxide also is produced from sea water and subterranean brine. Magnesium ion is precipitated as hydroxide by treating seawater with calcium or sodium hydroxide following a series of concentration steps (See magnesium). The hydroxide is then calcined to yield oxide. If brine is the source, it is concentrated, purified and calcined:

$$MgCl_2 + H_2O \rightarrow MgO + 2HCl$$

Calcination temperature is very important in the production process and dictates the particle size, purity and reactivity of the product. A dead-burned, sintered dense microcrystalline product is obtained at calcination temperature of 1,400 to 1,700°C. A caustic-burned product is obtained when magnesium carbonate or hydroxide is calcined at 600 to 700°C. A light grade (specific gravity 2.9) highly reactive caustic-burned magnesia that contains some moisture and carbon dioxide is obtained at about 600°C. A denser form from heavy caustic-burned oxide is produced when the carbonate or hydroxide is calcined at 800 to 900°C.

Magnesium oxide also can be prepared by heating magnesium metal in oxygen.

Reactions

Unlike calcium oxide, at ordinary temperatures magnesium oxide is stable in water. There is very little formation of magnesium hydroxide. The reaction, however, is rapid at elevated temperatures. The acids form their magnesium salts which, if water-soluble, may be obtained by evaporation of the solution:

$$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$$
$$MgO + 2HCl \rightarrow MgCl_2 + H_2O$$

Heating the oxide with carbon dioxide yields magnesium carbonate, $MgCO_3$.

The oxide can be reduced to metallic magnesium by heating with a reducing agent such as carbon or hydrogen at elevated temperatures:

$$MgO + C \rightarrow Mg + CO$$
$$MgO + H_2 \rightarrow Mg + H_2O$$

Analysis

Elemental composition: Mg 60.32%, O 39.68%. The oxide can be identified nondestructively by x-ray methods. Oxygen content may be determined by elemental microanalysis. Magnesium may be analyzed by AA or ICP following dissolution of the oxide in nitric acid and appropriate dilution with water.

MAGNESIUM PERCHLORATE

[10034-81-8]
Formula: $Mg(ClO_4)_2$; MW 223.21; forms several hydrates including a stable hexahydrate, $Mg(ClO_4)_2 \cdot 6H_2O$
Synonyms: Anhydrone; Dehydrite

Uses

Magnesium perchlorate is a drying agent for gases; and also an oxidizing agent.

Physical Properties

White granular or flaky powder; highly deliquescent; density 2.21 g/cm^3; decomposes at 251°C; very soluble in water (99.3g/100mL at 18°C); soluble in ethanol (24g/100mL) at 25°C.

Hexahydrate constitutes white rhombohedral crystals; refractive index

1.482; density 1.98 g/cm³; melts around 185°C; very soluble in water, releasing heat.

Preparation

Magnesium perchlorate may be prepared by adding perchloric acid to an aqueous solution of magnesium hydroxide. Crystallization yields hexahydrate, $Mg(ClO_4)_2 \cdot 6H_2O$.

$$Mg(OH)_2 + 2HClO_4 \rightarrow Mg(ClO_4)_2 + H_2O$$

Reactions

Magnesium perchlorate is a strong oxidizing agent. In aqueous solutions and in acid medium the most conspicuous reactions are those involving oxidation—characteristic of the oxidizing action of perchlorate ion, ClO_4^-.

Thermal decomposition in the presence of a catalyst, such as manganese dioxide, yields magnesium chloride and oxygen:

$$Mg\ (ClO_4)_2 \xrightarrow[\text{catalyst}]{\text{heat}} MgCl_2 + 4O_2$$

Analysis

Elemental composition (for anhydrous salt): Mg 10.89%, Cl 31.77%, O 57.34%. In the aqueous solution of the compound, Mg is analyzed by AA or ICP and perchlorate ion by ion chromatography or by redox titration. Also the solid salt may be mixed with MnO_2 and heated. Oxygen liberated may be tested by flaming of a glowing splinter, and the $MgCl_2$ residue may be dissolved in water, filtered, and the aqueous solution may be analyzed for Cl^- by titration or ion chromatography and Mg determined by AA or ICP (See Magnesium Chloride).

MAGNESIUM PHOSPHATES, BASIC

Magnesium phosphate forms three basic salts, as follows:

(i) Monobasic salt: $MgH_4(PO_4)_2$; MW 218.28; CAS No. [13092-66-5]

Synonyms: magnesium biphosphate; primary magnesium phosphate; acid magnesium phosphate; magnesium tetrahydrogen phosphate

(ii) Dibasic salt: $MgHPO_4$; MW 120.29; CAS No. [7757-86-0]; also forms a stable trihydrate, $MgHPO_4 \cdot 3H_2O$; the trihdrate is found in nature as the minerals, newberyite and phosphorroeslerite.

Synonyms: magnesium hydrogen phosphate; secondary magnesium phosphate

(iii) Tribasic salt: $Mg_3(PO_4)_2$; MW 262.86; CAS No. [7757-87-1]; forms stable hydrates $Mg_3(PO_4)_2 \cdot 4H_2O$, $Mg_3(PO_4)_2 \cdot 8H_2O$, and $Mg_3(PO_4)_2 \cdot 22H_2O$; the octahydrate occurs naturally as the mineral bobierrite.

Synonyms: magnesium orthophosphate, neutral magnesium phosphate, trimagnesium phosphate

Uses

All basic magnesium phosphates find applications in plastics as stabilizers. Other than this, monobasic salt is used in fireproofing wood. The dibasic phosphate is a food additive; and also a laxative. The tribasic phosphate is an antacid; and a nutritional food supplement. The compound also is an adsorbent; and a polishing agent in dental work.

Physical Properties

The monobasic phosphate as dihydrate is a white crystalline powdery material; hygroscopic; decomposes on heating; dissolves in water; soluble in acids with reaction; insoluble in alcohol.

The dibasic magnesium phospate trihydrate is a white crystalline powder; orthorhombic structure; refractive index 1.514; density 2.123 g/cm^3 at 15°C; melts at 205°C losing a molecule of water; decomposes between 550 to 650°C; slightly soluble in water; soluble in acid; insoluble in ethanol. The heptahydrate $MgHPO_4 \cdot 7H_2O$ constitutes white monoclinic needles; density 1.728 g/cm^3 at 15°C; sparingly soluble in water (3g/L at 20°C); soluble in acids; insoluble in ethanol.

The tetrahydrate of the tribasic phosphate, $Mg_3(PO_4)_2 \cdot 4H_2O$ is a bulky and soft white powdery material; monoclinic crystals; density 1.64 g/cm^3 at 15°C; slightly soluble in water (0.2 g/L at 20°C); soluble in acids. The naturally occurring octahydrate, bobierite, is a white crystalline solid, containing monoclinic plates; refractive index 1.510; density 2.195 g/cm^3 at 15°C; loses three molecules of water of crystallization at 150°C; loses all water at 400°C; insoluble in water; soluble in dilute mineral acids.

Magnesium orthophosphate $Mg_3(PO_4)_2$ constitutes rhombic crystals; melts at 1,184°C; insoluble in water; soluble in ammonium salt solution.

Thermochemical Properties [$Mg_3(PO_4)_2$]

$\Delta H_f°$	–903.6 kcal/mol
$\Delta G_f°$	–845.8 kcal/mol
S°	45.2 cal/degree mol
C_ρ	51.0 cal/degree mol

Preparation

The basic phosphates that occur naturally may be mined from their respective minerals. They may be prepared by reactions of phosphoric acid with magnesium oxide and hydroxide followed by crystallization. Monobasic and dibasic magnesium phosphate are prepared by the action of phosphoric acid on magnesium hydroxide and magnesium oxide, respectively. The tribasic phosphate is made by treating magnesium oxide with phosphoric acid at high temperature.

Analysis

Basic magnesium phosphates may be characterized by x-ray and thermogravimetric analyses and elemental analysis. Magnesium may be determined by AA or ICP after digestion in nitric acid followed by dilution. Alternatively, the compounds can be analyzed for magnesium nondestructively, but with lesser sensitivity, using x-ray fluorescence. The phosphorus content may be measured by dissolving the basic phosphate in sulfuric acid, diluting the acid extract and treating the diluted acid solution with ammonium molybdate-ammonium metavanadate reagent, and measuring the intensity of the yellow color formed using a spectrophotometer at 400 to 490 nm wavelength. Alternatively, the acid solution may be treated with ammonium molybdate and stannous chloride reagent to produce an intense blue color that may be measured at 690 or 650 nm. The concentration may be determined from a phosphate standard calibration curve (APHA, AWWA, and WEF. 1999. *Standard Methods for the Examination of Water and Wastewater,* 20th ed. Washington D.C.: American Public Health Association.)

MAGNESIUM SILICATES

Magnesium forms an array of silicates having varying structures. Such a wide variety of silicates include metasilicate, orthosilicate, pyrosilicate, polysilicates, and a number of complex silicates, such as asbestos and talc in combination with other metal ions. Many such silicates occur in nature either as complex silicates or as discrete magnesium silicate. Some important magnesium silicates are listed below:

(i) Magnesium metasilicate: $MgSiO_3$ [13776-74-4]; MW 100.39; occurs in nature as minerals enstatite, clinoenstatite, and protoenstatite. It has pyroxene-type structure consisting of $(SiO_3^{2-})_n$ chain. The metasilicate consists of white monoclinic crystals having density 3.19 g/cm^3. The compound decomposes at 1550°C.

(ii) Magnesium orthosilicate: Mg_2SiO_4 [26686-77-1]; MW 140.69; occurs in nature as the mineral forsterite. It is a white crystalline solid consiting of orthorhombic crystals. It has a density 3.21 g/cm^3 and melts at 1,898°C.

(iii) Magnesium trisilicate: $Mg_2Si_3O_8$; also known as magnesium mesotrisilicate; occurs in nature as minerals sepiolite, parasepiolite, and meerschaum. The compound is obtained as a fine white powder. Its pentahydrate occurs in nature as the mineral sellagen.

(iv) Chrysotile [12001-29-5], a white serpentine fibrous silicate, is a major asbestos mineral. It is a tetrasilicate compound of magnesium, having the formula $Mg_6Si_4O_{10}(OH)_8$ containing $(Si_4O_{11}^{6-})_n$ chain.

(v) Complex silicates: magnesium silicate is a component of several complex silicates, including tremolite, an amphibole-type tetrasilicate $Ca_2Mg_5(Si_4O_{11})_2$ containing double-strand cross-linked $(Si_4O_{11}^{6-})_n$; and diopside, a calcium magnesium metasilicate $[CaMg(SiO_3)_2]$ consisting of pyroxene-type single-strand chains of composition $(Si_4O_3^{2-})_n$.

(vi) Talc [14807-96-6] or talcum: a very finely powdered hydrous magnesium silicate. Its formula is $Mg_3SiO_{10}(OH)_2$ or $3MgO\bullet4SiO_2\bullet HOH$. It occurs in nature in compact and lump form, known as steatite or soapstone. The latter is an impure variety of steatite. Talc is a white or grayish-white powder, density 2.7 g/cm^3 and adheres readily to skin.

Magnesium silicates have numerous applications in several industries, such as ceramics, glass, refractories, paints, rubber, chemicals, and food. Some general applications include manufacture of dry resins and resinous compositions; filler for rubber, paper and soap; bleaching agent for vegetable oils; anticaking agent in food; catalyst; pigment in paints and varnishes; dusting and shoe powder; toilet preparations; heat and electric insulators; and antacid and gastric sedative in medicine and a filler for pills. Florisil, a porous and granular form of activated magnesium silicate, is used for cleanup of sample extracts from interfering substances in gas chromatographic analysis.

Thermochemical Properties (Mg_2SiO_4)

$\Delta H_f°$	–519.6 kcal/mol
$\Delta G_f°$	–491.2 kcal/mol
$S°$	22.7 cal/degree mol
C_ρ	28.3 cal/degree mol

Production

Magnesium silicate occurs in nature in a variety of minerals, and is mined. The pyrosilicate is prepared by treating an aqueous solution of a magnesium salt with a solution of sodium silicate. The active form can be made by adjusting drying temperature and degree of hydration.

Analysis

Magnesium silicates are characterized by x-ray diffraction and Raman spectroscopy. Magnesium is analyzed in an aqueous acid extract by AA or ICP following digestion of the solid with nitric acid and appropriate dilution.

MAGNESIUM SULFATE

[7487-88-9]

Formula: $MgSO_4$; MW 120.36. Forms several stable hydrates, many of which occur in nature. The hydrates, their formulas, mineral names, and CAS Registry Numbers are tabulated below:

Hydrate	Mineral Name	Formula	CAS No.
monohydrate	kieserite	$MgSO_4 \cdot H_2O$	[14168-73-1]
tetrahydrate	starkeyite	$MgSO_4 \cdot 4H_2O$	[24378-31-2]
pentahydrate	pentahydrite	$MgSO_4 \cdot 5H_2O$	[15553-21-6]
hexahydrate	hexahydrite	$MgSO_4 \cdot 6H_2O$	[13778-97-7]
heptahydrate	epsomite	$MgSO_4 \cdot 7H_2O$	[10034-99-8]

Occurrence and Uses

Magnesium sulfate is found in nature in many salt deposits and mineral waters, occurring as hydrates or double salts. The heptahydrate or Epsom salt was discovered in 1695, found in the mineral water at Epsom. Kieserite and epsomite are the two most important minerals. Other than these and the above hydrates, magnesium sulfate also is found in several other minerals, including:

langbeinite,	$K_2SO_4 \cdot 2MgSO_4$	[13826-56-7]
leonite	$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$	[15226-80-9]
vanthoffite	$3Na_2SO_4 \cdot MgSO_4$	[15557-33-2]
bloedite	$Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$	[15083-77-9]
kainite	$4KCl \cdot 4MgSO_4 \cdot 11H_2O$	[67145-93-1]
polyhalite	$K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$	[15278-29-2].

Magnesium sulfate is used widely in several industries including fertilizer, cement, textile, chemicals, and medicine. In the cement industry, it is used in manufacturing oxysulfate cement. In medicine, it is an analgesic and cathartic. An important application of anhydrous magnesium sulfate in the laboratory involves drying organic solvents required for syntheses and GC analysis.

In the textile industry, magnesium sulfate is used in finishing composition for dressing cotton; for weighting and sizing silk; as a mordant for fixing basic dyestuffs on wool; and in fireproofing fabrics. It also is a component of certain types of electrolytic plating baths; of various photographic solutions; of cosmetic lotions. It is a catalyst carrier; a dietary supplement in cattle feed; a coagulant for rubber and plastic; and is used in making citric acid and several magnesium salts, such as magnesium stearate.

Physical Properties

The anhydrous salt consists of colorless rhombohedral crystals; density 2.66 g/cm^3; decomposes at 1,124°C; dissolves in water (269 g/100mL at 0°C), ethanol and glycerol; sparingly soluble in ether (1.16 g/mL at 18°C); insoluble in acetone.

The monohydrate $MgSO_2 \cdot H_2O$, as the mineral kieserite, consists of colorless monoclinic crystals; refractive index 1.523; density 2.445 g/cm^3; becomes anhydrous on heating at 200°C; soluble in water.

Epsom salt, or heptahydrate $MgSO_2 \cdot 7H_2O$, constitutes colorless monoclinic or rhombohedral crystals; refractive index 1.433; density 1.68 g/cm^3; loses six molecules of water of crystallization at 150°C and converts to anhydrous form at 200°C; highly soluble in water (71 g/100mL at 20°C); slightly soluble in alcohol and glycerol.

Thermochemical properties

$\Delta H_f°$ ($MgSO_4$)	–307.1 kcal/mol
$\Delta H_f°$ ($MgSO_4 \cdot 2H_2O$)	–453.2 kcal/mol
$\Delta H_f°$ ($MgSO_4 \cdot 4H_2O$)	–596.7 kcal/mol
$\Delta H_f°$ ($MgSO_4 \cdot 6H_2O$)	–737.8 kcal/mol
$\Delta H_f°$ ($MgSO_4 \cdot 7H_2O$)	–809.9 kcal/mol
$\Delta G_f°$ ($MgSO_4$)	–279.8 kcal/mol
$\Delta G_f°$ ($MgSO_4 \cdot 6H_2O$)	–629.1 kcal/mol

ΔG_f° ($MgSO_4 \cdot 7H_2O$)	–686.4 kcal/mol
S° ($MgSO_4$)	21.9 cal/degree mol
S° ($MgSO_4 \cdot 6H_2O$)	83.2 cal/degree mol
S° ($MgSO_4 \cdot 7H_2O$)	89.0 cal/degree mol
C_ρ ($MgSO_4$)	23.0 cal/degree mol
C_ρ ($MgSO_4 \cdot 6H_2O$)	83.2 cal/degree mol

Production

Hydrated magnesium sulfate occurs in nature as the minerals kieserite and epsomite. The salt is mined in large scale from these and other naturally occurring minerals. The salt also is prepared in the laboratory by the action of sulfuric acid on magnesium oxide, hydroxide, or carbonate followed by evaporation and crystallization:

$$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$$

$$Mg(OH)_2 + H_2SO_4 \rightarrow MgSO_4 + 2H_2O$$

$$MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + CO_2 + H_2O$$

Crystallization at temperatures between 1.8 and 48°C yields heptahydrate, $MgSO_4 \cdot 7H_2O$. Below 1.8°C, a dodecahydrate , $MgSO_4 \cdot 12H_2O$ crystallizes out. Above 48°C crystals of lower hydrates form. The anhydrous salt is obtained by heating the heptahydrate at about 500°C in a rotary drum; or dehydrating above 150°C in the presence of sulfuric acid.

Reactions

The anhydrous salt decomposes at elevated temperatures to magnesium oxide, oxygen, sulfur dioxide, and sulfur trioxide. The decomposition commences around 900°C and is complete at about 1,100°C. The overall reaction is:

$$3\,MgSO_4 \xrightarrow{900\text{–}1100^\circ C} 3MgO + O_2 + 2SO_2 + SO_3$$

On the other hand, heating hydrated sulfate above 150°C yields magnesium oxysulfate, a hydrolysis reaction. No dehydration or thermal decomposition occurs.

The anhydrous salt may be reduced to magnesium oxide when heated with carbon at 750°C:

$$MgSO_4 + C \rightarrow MgO + SO_2 + CO$$

Magnesium sulfate undergoes three important types of reactions in aqueous solutions: double decomposition, double salt formation, and formation of oxysulfate cements. Many insoluble magnesium salts may be precipitated out by double decomposition reactions:

$$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2 + 2Na^+ + SO_4^{2-}$$

$$3MgSO_4 + 2Na_3PO_4 \rightarrow Mg_3(PO_4)_2 + 6Na^+ + 3\,SO_4^{2-}$$

Magnesium sulfate forms several double salts having varying stoichiometric compositions. When gaseous ammonia is bubbled through magnesium sulfate solution, several hydrated double salts are obtained by crystallization.

Magnesium sulfate double salts have the compositions $MgSO_4 \cdot NH_3 \cdot 3H_2O$; $MgSO_4 \cdot 2NH_3 \cdot 4H_2O$; and $MgSO_4 \cdot 2NH_3 \cdot 2H_2O$ (Copp, A. N. 1981. *Magnesium Compounds*, In Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. 14, pp. 636-40, New York: Wiley Interscience.) Similarly, in sulfuric acid, crystals of double salts $MgSO_4 \cdot H_2SO_4 \cdot 3H_2O$, $MgSO_4 \cdot H_2SO_4$, and $MgSO_4 \cdot 3H_2SO_4$ are obtained.

Addition of magnesium oxide to magnesium sulfate solutions yields crystalline oxysulfates at varying stoichiometric compositions, such as $MgSO_4 \cdot 3MgO \cdot 11H_2O$ and $MgSO_4 \cdot 5MgO \cdot 8H_2O$.

Treatment of barium peroxide, BaO_2 with a concentrated solution of magnesium sulfate yields magnesium peroxide MgO_2, a white powdery material used as a bleaching and oxidizing agent, and as an antacid in medicine.

Analysis

Elemental composition (of anhydrous $MgSO_4$) Mg 20.20%, S 26.63%, O 53.16%. The water of crystalization may be measured by thermogravimetric methods. Magnesium may be analyzed by AA or ICP-AES following acid digestion.

MANGANESE

[7439-96-5]
Symbol: Mn; atomic number 25; atomic weight 54.938; a Group VIIB (Group 7) transition metal; electron configuration $[Ar]4s^2 3d^7$; atomic radius 1.27Å; valence 0, +1, +2, +3, +4, +5, +6, +7; most common oxidation states +2, +4 and +7; stable natural isotope Mn-55 (100%)

History, Occurrence, and Uses

Manganese was recognized as an element by Scheele, Bergman and others in 1774 and isolated by Gahn in the same year. Gahn obtained the metal by thermal reduction of pyrolusite with carbon. The element derived its name from the Latin word, *magnes* which means magnet, referring to the magnetic properties of its ore pyrolusite.

Manganese is distributed widely in nature, mostly as oxide, silicate, and carbonate ores. Manganese ores often are found in association with iron ores in small quantities. The element, however, does not occur naturally in native form. Manganese is the twelfth most abundant element in the earth's crust.

Its concentration in the earth's crust is estimated to be 0.095%. Its average concentration in seawater is 2µg/L. Manganese also is found in large quantities in deep-sea nodules over the ocean floor at depths of 2.5 to 4 miles. The composition of some common manganese minerals is tabulated below:

Mineral	**CAS Registry Number**	**Composition**
Pyrolusite	[14854-26-3]	MnO_2
Manganite	[52019-58-6]	$Mn_2O_3 \cdot H_2O$
Hausmannite	[1309-55-3]	Mn_3O_4
Rhodochrosite	[598-62-9]	$MnCO_3$
Rhodonite	[14567-57-8]	$MnSiO_3$
Bementite	[66733-93-5]	$Mn_8Si_6O_{15}(OH)_{10}$
Braunite	— — —	$3Mn_2O_3 \cdot MnSiO_3$
Psilomelane	[12322-95-1]	$BaMn^{II}Mn^{IV}{}_8O_{16}(OH)_4$

Manganese is used widely in industry: the most important use is in ferrous metallurgy. It also is used in chemical, electrochemical, food and pharmaceutical applications. Ferromanganese alloys are used in steel manufacturing. Manganese serves as a deoxidizer of molten steel and controls its sulfur content. Manganese metal also enhances strength and hardness of the alloy, and its resistance to corrosion. Manganese is used in high-temperature steels, stainless steels, manganese steel and various nickel-chromium and manganese-aluminum alloys. Practically all aluminum and magnesium alloys contain manganese.

Manganese is an essential element for plants and animals. Its shortage in soil can cause chlorosis or lack of chlorophyll in plants—manifested by the appearance of yellow or grey streaks on the leaves or mottling. It activates certain plant enzymes, such as *oxalosuccinic decacarboxylase* in the oxidation of carbohydrates. Manganese deficiency can cause deformity of bones in animals.

In chemical industries, manganese is used to prepare several compounds. It also is used as a catalyst. Its salts have numerous applications in oxidation, catalysis, and medicine.

Physical Properties

Reddish-gray metal; exists in four allotropic modifications: alpha-, beta-, gamma- and delta forms. Alpha form has cubic crystal structure; 58 atoms per unit cell; density 7.43 g/cm^3; brittle; transforms to beta form at 720°C. Beta-manganese is brittle and has a cubic lattice structure; containing 20 atoms per unit cube; transforms to gamma form at 1,100°C or back to alpha form on cooling; density 7.29 g/cm^3. The gamma form exists as face-centered cubic crystal containing 4 atoms per unit cell; density 7.18 g/cm^3; converts to delta form at 1,136°C. Delta-manganese consists of body-centered cubic crystals containing 2 atoms per unit cube; density 6.30 g/cm^3; stable up to 1,244°C above which it melts to liquid.

Manganese vaporizes at 2,097°C; vapor pressure 0.9 torr at 1,244°C; hardness 5.0 (Mohs scale); magnetic susceptibility 9.9 cgs units at 18°C; electrical resistivities 185, 44, and 60 microhm–cm at 20°C for alpha-, beta- and gamma allotropes respectively; thermal neutron absorption 13.2 barns.

Thermochemical Properties

$\Delta H_f°$ (Mn-alpha)	0.0 kcal/mol
$\Delta H_f°$ (Mn-gamma)	0.37 kcal/mol
$\Delta H_f°$ (Mn-gas)	67.1 kcal/mol
$\Delta G_f°$ (Mn-alpha)	0.0 kcal/mol
$\Delta G_f°$ (Mn-gamma)	0.34 kcal/mol
$\Delta G_f°$ (Mn-gas)	57.0 kcal/mol
S° (Mn-alpha)	7.65 cal/degree mol
S° (Mn-beta)	8.22 cal/degree mol
S° (Mn-gamma)	7.75 cal/degree mol
S° (Mn-gas)	41.49 cal/degree mol
C_ρ (Mn-alpha)	6.29 cal/degree mol
C_ρ (Mn-beta)	6.34 cal/degree mol
C_ρ (Mn-gamma)	6.59 cal/degree mol
C_ρ (Mn-gas)	4.97 cal/degree mol
ΔH_{fus}	3.516 kcal/mol
Coefficeint of linear expansion (at 25°C)	$22x10^{-6}$/°C

Production

Manganese is recovered primarily from its oxide ores, the most important being pyrolusite, MnO_2. The basic method of producing the metal has not changed much since Gahn first isolated it by reducing manganese dioxide with carbon. Several processes to produce manganese meet its high demand in ferrous metallurgy. The oxides are reduced thermally in an electric furnace or a blast furnace. The ore is smelted at high temperatures in the presence of carbon, which reduces higher oxides of manganese, MnO_2, Mn_2O_3, and Mn_3O_4 into MnO, and then forms metallic manganese which has a relatively high vapor pressure:

$$MnO_2 + C \rightarrow MnO + CO$$

$$Mn_3O_4 + C \rightarrow 3MnO + CO$$

$$MnO + C \rightarrow Mn + CO$$

Selection of the process depends on the requirement of the product, such as high-carbon or low-carbon ferromanganese or silicomanganese of varying carbon contents. Usually coke is used as a reducing agent for high-carbon ferromanganese for the steel industry. Low-carbon ferromanganese, silicomanganese, or refined ferromanganese that has low carbon content ranging from 0.1 to 1.5% maximum carbon, may be obtained by using silicon as a reducing agent:

$$MnO_2 + Si \rightarrow Mn + SiO_2$$

$$Mn_3O_4 + 2Si \rightarrow 3Mn + SiO_2$$

$$2MnO + Si \rightarrow 2Mn + SiO_2$$

Often, the manganese ores contain several other naturally occurring metal oxides such as alumina, silica, magnesia, and lime. Some of these oxides may be blended into manganese ore as fluxes to the furnace charge.

Manganese may be produced by electrolytic processes. Aqueous solutions of manganese(II) sulfate are used as the electrolyte. Mn ore is roasted and reduced with carbon or silicon to convert the higher oxides of manganese into MnO. The products are then leached with dilute sulfuric acid at pH 3. MnO dissolves in the acid forming manganese(II) sulfate. The solution is filtered and separated from insoluble residues. It then is neturalized with ammonia to pH 6–7.

Iron and aluminum precipitate out when treated with ammonia and are removed by filtration. Other metals, such as copper, zinc, lead and arsenic are precipitated and removed as sulfides upon passing hydrogen sufide through the solution. Colloidal particles of metallic sulfides and sulfur are removed by treatment with iron(II) sulfide. The purified solution of manganese(II) sulfate is then electrolyzed in an electrolytic cell using lead anode and Hastelloy or Type 316 stainless steel cathode, both of which are resistant to acid. Manganese is deposited on the cathode as a thin film.

Manganese also is produced by electrolysis of fused salt. In one such process, the reduced MnO is blended to molten calcium fluoride and lime. The latter is used to neutralize silica in the ore. The fused composition of these salts is electrolyzed at 1,300°C in an electrolytic cell made up of high temperature ceramic material, using a carbon anode and a cathode consisting of iron bars internally cooled by water.

Reactions

Manganese forms compounds in several valence states: 0, +1, +2, +3, +4, +5, +6, and + 7. Of these, the valences 0, +1, and +5 are very uncommon. The divalent salts are the most stable. While in the divalent state, the metal is a reducing agent; in tetravalent state it is an oxidizing agent. Heptavalent manganese (Mn^{7+}) is a powerful oxidizing agent. Some examples of Mn compounds in all these oxidation states are tabulated below:

Oxidation State	**Example**
Mn(O)	$Mn_2(CO)_{10}$
Mn(I)	$C_9H_7Mn(CO)_3$
Mn(II)	$MnCl_2$; $MnSO_4$; MnO
Mn(III)	MnF_3; Mn_2O_3
Mn(IV)	MnO_2; K_2MnO_3
Mn(V)	K_3MnO_4
Mn(VI)	K_2MnO_4; $BaMnO_4$
Mn(VII)	$KMnO_4$; Mn_2O_7

Many chemical properties of manganese are similar to iron. Manganese burns in air or oxygen at elevated temperatures forming trimanganese tetroxide:

$$3Mn + 2O_2 \rightarrow Mn_3O_4$$

The metal reacts slowly with water in cold, forming manganous hydroxide with the evolution of hydrogen:

$$Mn + 2H_2O \rightarrow Mn(OH)_2 + H_2$$

The reaction is usually slow below 100°C, but proceeds rapidly upon heating.

Manganese reacts readily with dilute mineral acids forming their divalent salts and liberating hydrogen:

$$Mn + 2HCl \rightarrow MnCl_2 + H_2$$

$$Mn + H_2SO_4 \rightarrow MnSO_4 + H_2$$

Manganese forms manganese(II) halides when heated with halogens. With fluorine, reaction is very vigorous and the products are MnF_2 and MnF_3:

$$Mn + Cl_2 \rightarrow MnCl_2$$

$$Mn + F_2 \rightarrow MnF_2$$

$$2Mn + 3F_2 \rightarrow 2MnF_3$$

When heated with sulfur, the product is manganese(II) sulfide, MnS_2.

Manganese combines with carbon or silicon at elevated temperatures forming a series of carbides or silicides having compositions such as Mn_2C_7, Mn_3C, Mn_7C_3 and $Mn_{15}C_4$ or MnSi, Mn_3Si and Mn_5Si_3. Manganese reacts with nitrogen above 750°C forming various nitrides, such as Mn_3N_2, Mn_5N_2 and Mn_4N. The metal ignites in nitrogen at 1,200°C, then burns with a heavy, smoky flame forming the above nitrides. The principal product is Mn_3N_2. Also reaction with anhydrous ammonia above 350°C yields several nitrides of varying composition.

Manganese dissolves in concentrated alkali in boiling solutions forming manganese(II) hydroxide and hydrogen. However, in the presence of excess oxygen or under oxygen pressure, the product is a manganate:

$$2Mn + 4KOH + 3O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

Reactions with concentrated acids are slow at room temperature, but rapid when heated. No hydrogen forms in concentrated acids. With concentrated sulfuric and nitric acids, sulfur dioxide and nitric oxide form:

$$Mn + 2H_2SO_4 \rightarrow MnSO_4 + SO_2 + 2H_2O$$

$$Mn + 2HNO_3 \rightarrow MnNO_3 + NO + 2H_2O$$

Manganese combines with several metals at elevated temperatures forming binary compounds in varying compositions. Such metals include Al, Zn, Ni, Sn, As, Sb, Be, Pd, and Au.

Analysis

Manganese in aqueous solution may be analyzed by several instrumental techniques including flame and furnace AA, ICP, ICP-MS, x-ray fluorescence and neutron activation. For atomic absorption and emission spectrometric determination the measurement may be done at the wavelengths 279.5, 257.61 or 294.92 nm respectively. The metal or its insoluble compounds must be digested with nitric acid alone or in combination with another acid. Soluble salts may be dissolved in water and the aqueous solution analyzed. X-ray methods may be applied for non-destructive determination of the metal. The detection limits in these methods are higher than those obtained by the AA or ICP methods. ICP-MS is the most sensitive technique. Several colorimetric methods also are known, but such measurements require that the manganese salts be aqueous. These methods are susceptible to interference.

Manganese produces violet color in an oxidizing flame on a microcosmic or borax bead. The color disappears in a reducing flame.

Toxicity

Although trace amounts of manganese are essential for animals, in large quantities the metal can cause acute and chronic poisoning. Chronic inhalation of metal dust or fumes can cause manganism, a nonfatal disease affecting the central nervous system. The symptoms are mental disorder and disturbance in speech.

MANGANESE(II) CARBONATE

[598-62-9]
Formula: $MnCO_3$; MW 114.95
Synonyms: manganous carbonate; manganese spar; rhodochrosite

Occurrence and Uses

Manganese(II) carbonate occurs in nature as the mineral rhodochrosite [14476-12-1] (manganese spar). This ore also is used to produce manganese dioxide (by electrolytic process). The pure compound is used as gemstones; and as a pigment (manganese white).

Physical Properties

Pinkish-red translucent crystals; hexagonal-rhombohedral structure; refractive index 1.597; density 3.70 g/cm^3; hardness 3.8 Mohs; decomposes above 200°C; slightly soluble in water; K_{SP}2.24x10^{-11}; soluble in dilute acids.

Thermochemical Properties

$\Delta H_f°$ (cry)	–214.0 kcal/mol
$\Delta H_f°$ (ppt)	–210.9 kcal/mol
$\Delta G_f°$ (cry)	–195.9 kcal/mol
$\Delta G_f°$ (ppt)	–194.0 kcal/mol
S° (cry)	20.5 cal/degree mol
S° (ppt)	27.0 cal/degree mol

Preparation

Manganese(II) carbonate is mined from its naturally occurring mineral rhodochrosite. The compound may be prepared in the laboratory as a pale-pink precipitate by adding sodium bicarbonate to a solution of manganese(II) salt saturated with carbon dioxide. The product obtained is monohydrate, $MnCO_3 \cdot H_2O$. However, if the carbon dioxide-saturated solution, together with the above monohydrate precipitate, is heated in the absence of atmosphere oxygen, the monohydrate $MnCO_3 \cdot H_2O$ is converted into the anhydrous $MnCO_3$.

Reactions

The dry carbonate decomposes on heating, forming manganese(II) oxide and CO_2:

$$MnCO_3 \rightarrow MnO + CO_2$$

When heated above 330°C, MnO is partially oxidized by CO_2, thus the decomposition products also contain MnO_2 and CO.

When heated in air, the carbonate yields Mn_3O_4:

$$6MnCO_3 + O_2 \rightarrow 2Mn_3O_4 + 6CO_2$$

When heated in oxygen, manganese(III) oxide forms:

$$4MnCO_3 + O_2 \rightarrow 2Mn_2O_3 + 4CO_2$$

Reaction with dilute acids forms manganese salts of the acids, liberating CO_2:

$$MnCO_3 + H_2SO_4 \rightarrow MnSO_4 + CO_2 + H_2O$$

Analysis

Elemental composition: Mn 47.79%, C 10.45%, O 41.76%. The compound is dissolved in dilute HCl and CO_2 liberated is identified by the lime water test (turns lime water milky), by GC-TCD, or GC/MS. The characteristic mass for CO_2 is 44. The acid solution may be analyzed for Mn by AA, ICP or other instrumental technique (see Manganese).

MANGANESE(II) CHLORIDE

[7773-01-5]
Formula: $MnCl_2$; MW 125.84; forms a stable tetrahydrate, $MnCl_2 \cdot 4H_2O$
Synonyms: manganous chloride; manganese dichloride; scacchite

Uses

Manganese(II) chloride is used in dyeing and printing textiles and as a disinfectant. It also is used in dry cell batteries; for the preparation of drying agents for paints and varnishes; as a catalyst in chlorination reactions; in the production of several manganese salts, including methylcyclopentadienylmanganese tricarbonyl used as a colorant for brick. In metallurgy, the compound is used as an alloying agent and is added to molten magnesium to produce magnesium-manganese alloys.

Physical Properties

The anhydrous chloride is a pink solid; cubic crystals; deliquescent; density 2.977 g/cm^3 at 25°C; melts at 650°C; vaporizes at 1,190°C; very soluble in water (~72g/100 mL at 25°C); soluble in alcohol; insoluble in ether.

The tetrahydrate has a rose color; monoclinic crystal structure; deliquescent; density 2.01 g/cm^3; melts at 58°C; loses one molecule of water at 106°C and all water at 198°C; highly soluble in water (151 g/100mL at 8°C) and extremely soluble in boiling water (656 g/100mL at 100°C); soluble in ethanol; insoluble in ether.

Thermochemical Properties

$\Delta H_f°$ ($MnCl_2$)	–115.0 kcal/mol
$\Delta H_f°$ ($MnCl_2 \cdot 4H_2O$)	–403.3 kcal/mol
$\Delta G_f°$ ($MnCl_2$)	–105.3 kcal/mol
$\Delta G_f°$ ($MnCl_2 \cdot 4H_2O$)	–340.3 kcal/mol
S° ($MnCl_2$)	28.26 cal/degree mol
S° $MnCl_2 \cdot 4H_2O$)	72.5 cal/degree mol
C_ρ ($MnCl_2$)	17.43 cal/degree mol

Preparation

Manganese(II) chloride is prepared by heating manganese(II) oxide, manganese dioxide, manganese(II) carbonate or manganese(II) hydroxide with hydrochloric acid:

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$$

$$MnCO_3 + HCl \rightarrow MnCl_2 + H_2O + CO_2$$

When the product mixture is evaporated below 58°C, the tetrahydrate salt, $MnCl_2 \cdot 4H_2O$ is obtained.

Manganese(II) chloride is a by-product in the manufacture of chlorine from manganese dioxide and hydrochloric acid (the Weldon process).

Anhydrous chloride can be prepared by heating manganese(II) oxide or manganese(II) carbonate with dry hydrogen chloride; or by burning the metal in chlorine at 700°C to 1,000°C.

The anhydrous salt can also be obtained by slowly heating the tetrahydrate, $MnCl_2 \cdot 4H_2O$ in a rotary drier above 200°C or by dehydration in a stream of hydrogen chloride gas.

Reactions

Manganese(II) chloride forms double salts with alkali metal chlorides when mixed in stoichiometric amounts. Such double salts, which can decompose in water, may have compositions like $KMnCl_3$ or K_2MnCl_4.

Manganese(II) chloride forms adducts with ammonia, hydroxylamine and many other nitrogen compounds. Many adducts are stable at ordinary temperatures. Examples are $MnCl_2 \cdot 6NH_3$ and $MnCl_2 \cdot 2NH_2OH$.

An aqueous solution can readily undergo double decomposition reactions with soluble salts of other metals, producing precipitates of insoluble salts of Mn(II) or other metals.

Analysis

Elemental composition: Mn 43.66%, Cl 56.34%
An aqueous solution of the compound may be analyzed for Mn by AA, ICP, or other instrumental techniques, and for chloride by ion chromatography or titration against a standard solution of silver or mercuric nitrate.

MANGANESE DECACARBONYL

[10170-69-1]
Formula: $Mn_2(CO)_{10}$; MW 389.99; manganese in zero oxidation state.
Synonyms: dimanganese decacarbonyl; manganese carbonyl

Uses

Manganese decacarbonyl is used as an antiknock additive to gasoline; and as a catalyst.

Physical Properties

Golden-yellow monoclinic crystals; density 1.75 g/cm^3; melts at 154 to 155°C; decomposition commences around 110°C, slowly losing carbon monoxide; stable under carbon monoxide atmosphere; insoluble in water; soluble in most organic solvents.

Preparation

Manganese decacarbonyl is prepared by the reduction of methylcyclopentadienylmanganese tricarbonyl (MMT) with sodium in diglyme under carbon monoxide pressure.

Alternatively, the compound can be prepared by reduction of manganese(II) iodide with a Grignard reagent in the presence of carbon monoxide under pressure.

Analysis

Elemental composition: Mn 28.17%, C 30.80%, O 41.03%. The compound is cautiously digested with nitric acid, diluted and analyzed for manganese by instrumental techniques. Its solution in an organic solvent may be analyzed by GC/MS.

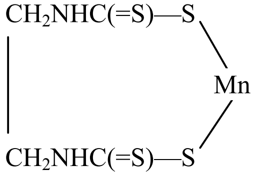
Toxicity

The compound is toxic by ingestion and possibly by other routes of exposure.

MANGANESE ETHYLENENEBIS(THIOCARBAMATE)

[12427-38-2]
Formula: $C_4H_6MnN_2S_4$; MW 256.29

Structure:



Synonyms: Maneb; [ethylenebis(dithiocarbamato)]manganese; manganous ethylenebis(dithiocarbamate)

Uses

The compound is a fungicide.

Physical Properties

Yellow powder; crystallizes from methanol or ethanol; melts between 192° to 204°C; low solubility in water; soluble in chloroform and pyridine.

Preparation

Manganese ethylenebis(thiocarbamate) is made by adding disodium ethylenebis(dithiocarbamate) (also, known as Nabam, commercially available) to an aqueous solution of manganese(II) sulfate:

$$NaSC(=S)NHCH_2CH_2NHC(=S)SNa + MnSO_4 \rightarrow C_4H_6MnN_2S_4 + Na_2SO_4$$

Alternatively, the compound may be prepared by neutralizing an aqueous solution of disodiummethylenebis(dithiocarbamate) (Nabam) with acetic acid followed by addition of manganese(II) chloride solution.

Analysis

Elemental composition: Mn 20.70%, S 48.35%, C 18.11%, N 10.56%, H 2.28%. A chloroform solution of the compound may be analyzed by GC/MS or by GC-FPD. Manganese may be determined by digesting the compound with nitric acid and analyzing the diluted acid extract by AA or ICP.

Toxicity

Maneb is toxic by ingestion.

MANGANESE(II) HYDROXIDE

[18933-05-6]
Formula: $Mn(OH)_2$; MW 88.953
Synonyms: manganous hydroxide; pyrochroite
Occurrence: Manganese(II) hydroxide occurs naturally as the mineral pyrochroite

Physical Properties

Pink hexagonal crystal; density 3.26 g/cm^3; refractive index 1.68; Mohs hardness 2.5; decomposes at 140°C; insoluble in water; K_{SP} 5.61×10^{-12}; soluble in acid; dissolves in alkaline solution on heating.

Thermochemical Properties

$\Delta H_f°$	–167.0 kcal/mol
$\Delta G_f°$	–148.0 kcal/mol
S°	23.0 cal/degree mol

Preparation

Manganese(II) hydroxide is obtained as a white precipitate by adding a solution of sodium or potassium hydroxide to a solution of manganese(II) salt, such as manganese(II) chloride:

$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2$$

The white precipitate rapidly turns brownish-pink in air. The reaction does not occur with ammonia in the presence of ammonium salt.

The hydroxide also is found in nature as mineral pyrochroite in the form of white transparent leaflets. The white leaflets turn pink on exposure to air.

Reactions

Manganese(II) hydroxide is a base exhibiting weak amphoteric behavior. It reacts with acids forming the corresponding manganese(II) salt:

$$Mn(OH)_2 + 2KOH \rightarrow K_2Mn(OH)_4$$

The hydroxide is rapidly oxidized in air forming manganese(III) oxide, Mn_2O_3.

Analysis

Elemental composition: Mn 61.76%, H 2.27%, O 35.97%. The compound is digested in nitric acid and analyzed for manganese by AA, ICP or other instrumental technique.

MANGANESE(II) OXIDE

[1344-43-0]
Formula: MnO; MW 70.94
Synonyms: manganous oxide; manganese monoxide; green manganese oxide; manganosite [1313-12-8]

Occurrence and Uses

Manganese(II) oxide occurs naturally as manganosite [1313-12-8]. The mineral is found very rarely in nature. Manganese(II) oxide is used in the fertilizer industry as a source of manganese in fertilizers; in feedstuff formulations; and as an intermediate in the production of several manganese compounds.

Physical Properties

Green cubic crystal; refractive index 2.16; density 5.37 g/cm^3 at 23°C; Moh's hardness 5.5; melts at 1945°C; insoluble in water.

Thermochemical Properties

$\Delta H_f°$	–92.07 kcal/mol
$\Delta G_f°$	–86.74 kcal/mol
S°	14.27 cal/degree mol
C_ρ	10.86 cal/degree mol

Production

Manganese(II) oxide is obtained commercially from manganese(IV) oxide (manganese dioxide) by the reduction with hydrogen, carbon monoxide or methane at elevated temperatures (>800°C):

$$MnO_2 + CO \rightarrow MnO + CO_2$$

$$MnO_2 + H_2 \rightarrow MnO + H_2O$$

The oxide also can be made by thermal decomposition of manganese(II) carbonate or manganese(II) oxalate in the absence of air:

$$MnCO_3 \rightarrow MnO + CO_2$$

Also, careful dehydration of manganese(II) hydroxide, $Mn(OH)_2$, under controlled conditions in the absence of air yields MnO.

Reactions

Manganese(II) oxide is the lowest oxide of manganese and it is purely a basic oxide. It reacts with acids to form their manganese(II) salts:

$$MnO + H_2SO_4 \rightarrow MnSO_4 + H_2O$$

$$MnO + 2HCl \rightarrow MnCl_2 + H_2O$$

The compound also is oxidized by air or oxygen to higher oxides of manganese. When heated cautiously in air, the product is manganese sesquioxide or manganese(III) oxide:

$$4MnO + O_2 \rightarrow 2Mn_2O_3$$

Analysis

Elemental composition: Mn 77.44%, O 22.55%. The oxide can be characterized nondestructively by x-ray methods. Also, manganese may be analyzed by AA or ICP technique following acid digestion with nitric acid and diluting the acid extract appropriately (see Manganese).

MANGANESE(III) OXIDE

[1317-34-6]
Formula: Mn_2O_3; MW 157.87
Synonyms: manganese sesquioxide; dimanganese trioxide

Occurrence and Uses

Manganese(III) oxide occurs in nature as the mineral braunite. The oxide is used in the production of ferrites and thermistors.

Physical Properties

Black cubic (or rhombic) crystals; density 4.50 g/cm^3; Moh's hardness 6–6.5 (for braunite); decomposes at about 875°C; insoluble in water; insoluble in alcohol and acetone; soluble in acids.

Thermochemical Properties

$\Delta H_f°$	–229.2 kcal/mol
$\Delta G_f°$	–210.6 kcal/mol
S°	26.40 cal/degree mol
C_ρ	25.73 cal/degree mol

Preparation

Manganese(III) oxide is obtained by heating manganese(II) oxide in air at 600 to 850°C. It also may be prepared by igniting manganese(II) salts in air or oxygen. The oxide also is produced by cautious heating of manganese(II) oxide in oxygen. Manganese(III) oxide also can be made by dehydrating manganese(III) metahydroxide, MnO(OH), in a vacuum at 250°C. In such preparation, an unstable tetragonal modification, beta-Mn_2O_3, is first obtained which on prolonged heating converts to the stable cubic modification, alpha-Mn_2O_3.

Analysis

Elemental composition: Mn 69.59%, O 30.41%. The oxide can be characterized by x-ray methods and analyzed for manganese by AA or ICP following acid extraction.

MANGANESE(II,III) OXIDE

[1317-35-7]
Formula: Mn_3O_4; MW 228.81
Synonyms: trimanganese tetraoxide; manganomanganic oxide; red oxide of manganese

Occurrence and Use

Manganese(II,III) oxide occurs in nature as the mineral hausmannite [1309-55-3]. It is used to make ferrites and thermistors. The oxide also is used in the thermite process for producing manganese.

Physical Properties

Black tetragonal crystal; exhibits two allotropic modifications—a stable alpha phase, occurring in tetragonal crystalline form (as hausmannite) and an unstable beta modification; density 4.85 g/cm^3; Moh's hardness 5.5; melts at 1,567°C; insoluble in water; soluble in hydrochloric acid.

Thermochemical Properties

$\Delta H_f°$	–331.7 kcal/mol
$\Delta G_f°$	–306.7 kcal/mol
S°	37.2 cal/degree mol
C_ρ	33.4 cal/degree mol

Preparation

Manganese(II,III) oxide is made by heating manganese(IV) oxide, MnO_2, or manganese(III) oxide, Mn_2O_3, above 950°C. When Mn_2O_3 is heated in air, the temperature should be above 940°C, but if heated in oxygen, the temperature should be above 1,090°C. Also, heating manganese(III) oxide at 230°C in hydrogen yields Mn_3O_4. However, further heating above 300°C converts Mn_3O_4 formed to green manganese(II) oxide, MnO.

Manganese(II,III) oxide also is obtained by heating the dioxide, MnO_2, with carbon at 600 to 700°C.

Reactions

Manganese(II,III) oxide reacts with dilute acids forming the corresponding manganous salt and manganese(IV) oxide, MnO_2:

$$Mn_3O_4 + 2H_2SO_4 \rightarrow 2MnSO_4 + MnO_2 + 2H_2O$$

The oxide, however, dissolves slowly in cold sulfuric acid forming a red solution that also contains manganic sulfate, $Mn_2(SO_4)_3$:

$$Mn_3O_4 + 4H_2SO_4 \rightarrow MnSO_4 + Mn_2(SO_4)_3 + 4H_2O$$

Reaction with acetic acid yields manganese(II) acetate and manganese(III) oxide:

$$Mn_3O_4 + 2CH_3COOH \rightarrow Mn(CH_3COO)_2 + Mn_2O_3 + H_2O$$

Manganese(II,III) oxide is reduced to manganese metal when heated with powdered aluminum (the Thermite process). The reaction is vigorous and exothermic:

$$3Mn_3O_4 + 8Al \rightarrow 4Al_2O_3 + 9Mn$$

Analysis

Elemental composition: Mn 72.03%, O 27.98%. The oxide can be characterized by x-ray methods. Manganese in the oxide can be analyzed by AA or ICP method after digesting the oxide in nitric acid.

MANGANESE(IV) OXIDE

[1313-13-9]
Formula: MnO_2; MW 86.937
Synonyms: manganese dioxide; manganese peroxide; black manganese oxide

Occurrence and Uses

Manganese(IV) oxide is the most important ore of manganese from which the metal is mostly manufactured. The oxide occurs in nature as the mineral pyrolusite as heavy gray lumps, or black when powdered.

The mineral is used to produce manganese metal, most manganese salts, and also manganese steel and other alloys. The metallurgical applications of manganese(IV) oxide mainly involve making ferromanganese and special manganese alloys. Another important application of manganese(IV) oxide is in manufacturing dry-cell batteries and alkaline cells. The oxide also is a colorant in brick, tile, porcelain and glass; a drier for paints and varnishes; a preparation for printing and dyeing textiles; a curing agent for polysulfide rubbers; an adsorbent for hydrogen sulfide and sulfur dioxide; an oxidizing agent in many organic syntheses such as quinone and hydroquinone; and a catalyst in laboratory preparation of oxygen from potassium chlorate. Manganese(IV) oxide also is used to make welding rods and fluxes, and ceramic magnets (ferrites); and is an additive to fertilizers.

Physical Properties

Black tetragonal crystals; density 5.08 g/cm³; Moh's hardness 6.3; decomposes at 535°C; insoluble in water.

Thermochemical Properties

$\Delta H_f°$	–124.3 kcal/mol
$\Delta G_f°$	–111.2 kcal/mol
S°	12.69 cal/degree mol
C_ρ	12.93 cal/degree mol

Preparation

Pure manganese(IV) oxide (precipitate form) may be prepared by reducing permanganate ion with a manganous salt:

$$2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$$

Manganese(IV) oxide can also be precipitated by oxidation of a manganese(II) salt using an oxidizing agent such as hypochlorite or peroxydisulphate:

$$Mn^{2+} + S_2O_8^{2-} + 2H_2O \rightarrow MnO_2 + 2SO_4^{2-} + 4H^+$$

Manganese(IV) oxide may also be made by thermal decomposition of manganese(II) nitrate; or from roasting manganese(II) carbonate in air:

$$Mn(NO_3)_2 \rightarrow MnO_2 + 2NO_2$$

$$MnCO_3 + ½\ O_2 \rightarrow MnO_2 + CO_2$$

A highly active gamma-MnO_2 can be produced by treating manganese(III) oxide with hot sulfuric acid:

$$Mn_2O_3 + H_2SO_4 \rightarrow MnO_2 + MnSO_4 + H_2O$$

Mn_2O_3 is derived from pyrolusite by heating the mineral at 600–800°C or reducing with powdered coal at 300°C.

Reactions

Thermal decomposition of manganese(IV) oxide at 600 to 800°C yields manganese(III) oxide:

$$4MnO_2 \rightarrow 2Mn_2O_3 + O_2$$

MnO_2 also is reduced to Mn_2O_3 at 300°C in the presence of a reducing agent such as hydrogen, methane or carbon.

Treatment with concentrated hydrochloric acid forms manganese(IV) chloride which readily decomposes to manganese(III) chloride and manganese(II) chloride, successively liberating chlorine:

$$MnO_2 + 4HCl \rightarrow MnCl_4 + 2H_2O$$

$$MnCl_4 \rightarrow MnCl_3 + \tfrac{1}{2}\ Cl_2$$

$$MnCl_3 \rightarrow MnCl_2 + \tfrac{1}{2}\ Cl_2$$

When heated with concentrated sulfuric acid, manganese(IV) oxide yields manganese(II) sulfate, evolving oxygen:

$$MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O + \tfrac{1}{2}\ O_2$$

When the solution is heated at 135°C, $MnSO_4$ is oxidized to $Mn_2(SO_4)_3$. Reaction with sulfuric acid in the presence of oxalic acid yields manganese(II) sulfate and carbon dioxide:

$$MnSO_2 + (COOH)_2 + H_2SO_4 \rightarrow MnSO_4 + 2CO_2 + 2H_2O$$

While the reaction with sulfuric acid in the presence of sodium chloride evolves chlorine:

$$MnO_2 + 2NaCl + 2H_2SO_4 \rightarrow MnSO_4 + Na_2SO_4 + 2H_2O + Cl_2$$

When heated with potassium hydroxide, manganese(IV) oxide partially decomposes to manganese(III) oxide and potassium manganate:

$$3MnO_2 + 2KOH \rightarrow Mn_2O_3 + K_2MnO_4 + H_2O$$

However, in the presence of oxygen or other oxidizing agents, all manganese is oxidized to manganate:

$$MnO_2 + 2KOH + \tfrac{1}{2}\ O_2 \rightarrow K_2MnO_4 + H_2O$$

Manganate(VI) can further oxidize to manganate(VII) (or permanganate) in alkaline solution with a strong oxidizing agent such as hypochlorite, chlorine or perchlorate, or under anodic oxidation. Alternatively, in less alkaline media (where the KOH concentration is less than about 15%), the manganate ion MnO_4^{2-} hydrolyzes, disproportionating to permanganate MnO_4^- and forming back manganese(IV) oxide:

$$3MnO_4^{2-} + 2H_2O \rightarrow 2MnO_4^- + MnO_2 + 4OH^-$$

The green color of manganate solution turns purple due to the permanganate formed.

Manganese(IV) oxide is an oxidizing agent. In acid medium, it oxidizes iodide to iodine:

$$MnO_2 + 2I^- + 4H^+ \rightarrow Mn^{2+} + 2H_2O + I_2$$

Thus, in the presence of dilute acids, MnO_2 is readily attacked by strong reducing agents. Similarly, reaction with sulfurous acid forms manganese(II) dithionate:

$$MnO_2 + 2H_2SO_3 \rightarrow MnS_2O_6 + 2H_2O$$

Or with nitrous acid in the presence of nitric acid, manganese(II) nitrate is formed:

$$MnO_2 + HNO_2 + HNO_3 \rightarrow Mn(NO_3)_2 + H_2O$$

Reaction with potassium bifluoride in the presence of hydrofluoric acid creates a stable complex fluoride, K_2MnF_6 in which Mn is in +4 oxidation state:

$$MnO_2 + 2KHF_2 + 2HF \rightarrow K_2MnF_6 + 2H_2O$$

When fused with basic oxides such as calcium oxide, manganites or manganate(IV) salts such as $CaO{\cdot}MnO_2$, $2CaO{\cdot}MnO_2$, $CaO{\cdot}3MnO_2$ are formed. The stoichiometric compositions of these manganites vary.

Manganese(IV) oxide reacts with aniline in the presence of sulfuric acid forming quinone, an intermediate product in the manufacture of hydroquinone:

$$4MnO_2 + 2C_6H_5NH_2 + 5H_2SO_4 \rightarrow 2C_6H_4O_2 + 4MnSO_4 + (NH_4)_2SO_4 + 4H_2O$$

Analysis

Elemental composition: Mn 63.19%, O 36.81%. The pure oxide may be characterized by x-ray crystallography. The MnO_2 content in pyrolusite may be measured by titration. An excess of a standard solution of oxalic acid is added to a solution of MnO_2 in sulfuric acid. After all solid MnO_2 dissolves, the excess oxalic acid is measured by titrating against a standard solution of potassium permanganate (see Reactions).

Alternatively, pyrolusite is heated with concentrated hydrochloric acid and the chlorine evolved is passed through a solution of potassium iodide. The iodine liberated is titrated against a standard solution of sodium thiosulfate using starch indicator. One mol MnO_2 is equivalent to two mol thiosulfate. Also, acid extracts of MnO_2 may be diluted and measured by AA or ICP techniques (See Manganese).

MANGANESE(II) SULFATE

[7785-87-7]
Formula: $MnSO_4$; MW 151.00; forms stable monohydrate, $MnSO_4 \cdot H_2O$ [10034-96-5] and tetrahydrate, $MnSO_4 \cdot 4H_2O$ [10101-68-5]
Synonym: manganous sulfate

Uses

Manganese(II) sulfate is used to produce manganese by an electrolytic process. The compound is used for dyeing textiles; for producing red glazes on porcelain; in varnish driers; in fertilizers; and in animal feeds to provide manganese as an essential trace element.

Physical Properties

The anhydrous salt is a white orthogonal crystal; density 3.25 g/cm^3; melts at 700°C; decomposes at 850°C; very soluble in water.

The monohydrate $MnSO_4 \cdot H_2O$ consists of red monoclinic crystals; density 2.95 g/cm^3; highly soluble in water. The tetrahydrate $MnSO_4 \cdot 4H_2O$ is a pink solid; monoclinic crystals; density 2.107 g/cm^3; highly soluble in water; more soluble than the anhydrous salt or the monohydrate.

Thermochemical Properties

$\Delta H_f°$ ($MnSO_4$)	–254.60 kcal/mol
$\Delta H_f°$ ($MnSO_4 \cdot H_2O$)	–329.00 kcal/mol
$\Delta H_f°$ ($MnSO_4 \cdot 4H_2O$)	–539.70 kcal/mol
$\Delta G_f°$ ($MnSO_4$)	–228.83 kcal/mol
S° ($MnSO_4$)	26.8 cal/degree mol
C_ρ ($MnSO_4$)	24.0 cal/degree mol

Preparation

Manganese(II) sulfate is prepared by prolonged heating of any manganese salt with concentrated sulfuric acid. The compound is produced commercially from pyrolusite (MnO_2) or rhodochrosite ($MnCO_3$). Either mineral is dissolved in sulfuric acid and the solution evaporated:

$$MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O + \tfrac{1}{2} O_2$$

Alternatively, manganese dioxide is heated strongly with dehydrated iron(II) sulfate:

$$2MnO_2 + 2FeSO_4 \rightarrow 2MnSO_4 + Fe_2O_3 + \tfrac{1}{2}\ O_2$$

Manganese(II) sulfate, prepared by methods involving evaporation of manganese salt with sulfuric acid, is the tetrahydrate, $MnSO_4 \bullet 4H_2O$. The tetrahydrate on gentle heating produces monohydrate, $MnSO_4 \bullet H_2O$.

Also, manganese(II) sulfate is a by-product in the manufacture of hydroquinone. The process involves reaction of aniline with manganese dioxide in sulfuric acid, followed by the removal of quinone by steam distillation under vacuum.

$$\underset{\text{(aniline)}}{2C_6H_5NH_2} + 5H_2SO_4 + 4MnO_2 \rightarrow \underset{\text{(quinone)}}{2C_6H_4O_2} + 4MnSO_4 + 2C_6H_4O_2 + 4MnSO_4$$

The unreacted acid is neutralized by lime, treated with water, and the solution filtered to separate any excess MnO_2 and insoluble residues. Evaporation of the filtrate yields a crude product containing about 80% $MnSO_4$ and 15% $(NH_4)_2SO_4$.

Manganese(II) sulfate also may be produced by the action of sulfur dioxide with manganese dioxide:

$$MnO_2 + SO_2 \rightarrow MnSO_4$$

Reactions

Aqueous solution of manganese(II) sulfate undergoes double decomposition reactions precipitating insoluble manganese(II) salts; for example, adding caustic soda solution precipitates manganese(II) hydroxide.

Manganese(II) sulfate forms several double salts, such as manganese(II) ammonium sulfate, $(NH_4)_2Mn(SO_4)_2 \bullet 6H_2O$.

Reaction with oxalic acid, stearic acid, phthalic acid or their alkali salts yield their corresponding manganese salts (manganese soaps).

Manganese(II) sulfate may be oxidized electrolytically to manganese dioxide (gamma form) in an electrolytic cell.

$$MnSO_4 + 2H_2O \rightarrow MnO_2 + H_2SO_4 + H_2$$

Manganous(II) sulfate is a reducing agent. Treatment with oxidizing agents can yield manganese compounds in a higher oxidation state.

Analysis

Elemental composition: Mn 36.38%, S 21.23%, O 42.38%. Manganese may be analyzed in an aqueous solution of the compound by AA, ICP or x-ray fluorescence methods. Sulfate can be determined by ion chromatography. Water of crystallization in hydrated sulfate may be measured by heating at 400°C (by gravimetry).

MENDELEVIUM

[7440-11-1]
Symbol: Md; atomic number 101; atomic weight (most stable isotope) 257; a man-made radioactive transuranium element; an inner-transition element of actinide series; electron configuration $[Rn]5f^{13}7s^2$; valence +2, +3. Isotopes, half-lives and their decay modes are:

Mass	Half-life	Decay Mode
Md–252	8 min	Orbital electron capture
Md–255	30 min	Orbital electron capture
Md–256	1.5 hr.	Orbital electron capture Alpha decay
Md–257	3.0 hr.	Orbital electron capture Alpha decay
Md–258	60 day	Alpha decay

History

The element first was made by Ghiorso, Harvey, Choppin, Thompson, and Seaborg in 1955 in Berkeley, California. It was synthesized by bombardment of einsteinium-253 with alpha particles of 41 MeV energy in a 60-inch cyclotron. The element was named Mendelevium in honor of Russian chemist Dimitri Mendeleev. Mendelevium –258 isotope with a half-life of 60 days was discovered in 1967. The element has no commercial use except in research to synthesize isotopes of other transuranium elements.

Synthesis

Mendelevium was synthesized first by bombarding Einstein-253 with helium ions. The nuclear reaction is:

$$^{253}_{99}Es + ^{4}_{2}He \rightarrow ^{256}_{101}Md + ^{1}_{0}n$$

All isotopes of medelevium have been synthesized by other nuclear reactions since its discovery. They are prepared by bombarding uranium, einsteinium, and californium isotopes with heavy ions, such as boron-11, carbon-12 and carbon-13.

$$^{238}_{92}U + ^{19}_{9}F \rightarrow ^{252}_{101}Md + 5\,^{1}_{0}n$$

For example, uranium-238 when bombarded with fluorine-19 produced Md-252. Also, certain nuclear reactions carried out by heavy ion projectiles involve ‘stripping’ reactions in which some protons and neutrons may transfer from the projectiles onto the target nucleus, but the latter might not capture the projectile heavy ion.

MERCURY

[7439-97-6]
Symbol: Hg; atomic number 80; atomic weight 200.59; a Group IIB (Group 12) element; atomic radius 1.51 Å; ionic radius, Hg^{2+}(CN6) 1.16 Å; electron configuration [Xe]$4f^{14}5d^{10}6s^2$; valence +1 and +2; ionization potential 10.437 eV(1st) and 18.756 eV (2nd); natural isotopes Hg-202 (29.80%), Hg-200 (23.13%), Hg-199 (16.84%), Hg-201 (13.22%), Hg-198 (10.02%), Hg-204 (6.85%), Hg-196 (0.146%); several radioisotopes in the mass range from 189 to 206 are known. Antitquated names: quicksilver; hydrargyrum

History, Occurrence, and Uses

Although mercury is known from early times and was used by alchemists, its first modern scientific applications date back to 1643 when Torricelli used it in the barometer to measure pressure and about eight decades later Fahrenheit used it in the thermometer to measure temperature. Before this, mercury's use was confined to decorative work, gold extraction and medicines. The element was named after the planet mercury and its symbol Hg is taken from the Latin word hydrargyrum, which means liquid silver.

The element does not occur in nature in native form. Its principal mineral is cinnabar, the red mercuric sulfide, HgS. Black mercuric sulfide, metacinnabar, also is found in nature. Other ores are livingstonite, $HgSb_4S_7$; coloradite, HgTe; tiemannite, HgSe; and calomel, HgCl. Its concentration in the earth's crust is estimated to be 0.08 mg/kg. The average concentration in sea water is about 0.03 µg/L.

Some of the most important uses of mercury are in the electrical and electrolytic applications. A broad range of such applications include mercury batteries and cells in portable radios, microphones, cameras, hearing aids, watches, smoke alarms, and wiring and switching devices. Other notable applications are in mercury vapor lamps, fluorescent tubes and electrical discharge tubes. Mercury electrodes are widely used in electrolytic cells. Mercury cathodes are employed in the electrolysis of sodium chloride to produce caustic soda and chlorine. Another major use, as mentioned earlier, is in thermometers, manometers, barometers and other pressure-sensing devices. Mercury also is used as a catalyst in making urethane foams and vinyl chloride monomers. Mercury and its compounds long have been used as fungicides in paints and in agriculture. Mercury compounds are used in medicines, pigments and analytical reagents.

Physical Properties

Heavy silvery-white liquid; does not wet glass; forms tiny globules; the only metal that occurs at ordinary temperatures as a liquid and one of the two liquid elements at ambient temperatures (the other one being bromine); density 13.534 g/cm^3; solidifies at –38.83°C; vaporizes at 356.73°C; vapor pressure 0.015 torr at 50°C, 0.278 torr at 100°C and 17.29 torr at 200°C; critical temperature 1,477°C; critical pressure 732 atm; critical volume 43cm^3/mol; resistivity 95.8×10^{-6} ohm/cm at 20°C; surface tension 485.5 dynes/cm at 25°C; viscosity 1.55 centipoise at 20°C.

Thermochemical Properties

$\Delta H_f°$ (liq)	0.0
$\Delta H_f°$ (gas)	14.68 kcal/mol
$\Delta G_f°$ (gas)	7.60 kcal/mol
S° (liq)	18.14 cal/degree mol
S° (gas)	41.82 cal/degree mol
C_ρ (liq)	6.69 cal/degree mol
C_ρ (gas)	4.97 cal/degree mol
ΔH_{vap}	14.1 kcal/mol
ΔH_{fus}	0.547 kcal/mol

Production

Mercury mostly is obtained from its sulfide ore, cinnabar. The process involves roasting cinnabar in a furnace between 600 to 700°C. Mercury vapors are cooled and condensed into metal:

$$HgS + O_2 \rightarrow Hg + SO_2$$

Mercury may also be extracted from cinnabar by reduction of the ore with lime at elevated temperature:

$$4HgS + 4CaO \rightarrow 4Hg + 3CaS + CaSO_4$$

Smaller quantities of metal are recovered from mercury-containing industrial and municipal wastes, such as amalgams and batteries. The scrap material is heated in a retort and the vapors of mercury are condensed into high-purity metal.

Reactions

Mercury is stable to dry air or oxygen at ordinary temperatures. However, in the presence of moisture, oxygen slowly attacks the metal forming red mercury(II) oxide. Also, when the metal is heated in air or oxygen at about 350°C it is gradually converted to its oxide. The oxide, however, dissociates back to its elements at 440°C.

$$2\ Hg + O_2 \rightarrow 2\ HgO \text{ (red oxide)}$$

Mercury readily combines with halogens at ordinary temperatures forming mercury(II) halides.

The metal reacts with hydrogen sulfide at room temperature, producing mercury(II) sulfide:

$$Hg + H_2S \rightarrow HgS + H_2$$

Mercury metal forms both mercury(I) and mercury(II) salts. Oxidizing acids in excess amounts and under hot conditions yields mercury(II) salts. Thus, heating mercury with concentrated nitric or sulfuric acid yields mercury(II) nitrate or mercury(II) sulfate:

$$Hg + 4HNO_3 \rightarrow Hg(NO_3)_2 + 2NO_2 + 2H_2O$$

$$Hg + 2H_2SO_4 \rightarrow HgSO_4 + 2H_2O + SO_2$$

On the other hand, such acids under cold conditions and in limited amounts yield mercury(I) nitrate or mercury(I) sulfate:

$$6Hg + 8HNO_3 \rightarrow 3Hg_2(NO_3)_2 + 2NO + 4H_2O$$

Dilute sulfuric acid has no effect on the metal nor does air-free hydrochloric acid. But dilute nitric acid dissolves the metal; excess mercury in cold dilute acid yields mercury(I) nitrate, the dihydrate $Hg_2(NO_3)_2 \cdot 2H_2O$ separating out on crystallization. Mercury dissolves in aqua regia forming mercury(II) nitrate.

When mercury is rubbed with powdered sulfur or mixed with molten sulfur, black mercury(II) sulfide is formed. When heated with an aqueous solution of potassium pentasulfide, mercury(II) sulfide is obtained as a scarlet product, known as vermillion and used as an artist's pigment.

$$Hg + K_2S_5 \rightarrow HgS + K_2S_4$$

The product on exposure to light gradually converts to black mercury(II) sulfide.

When mercury is rubbed with iodine in the presence of a little ethanol, green mercury(I) iodide forms:

$$2Hg + I_2 \rightarrow Hg_2I_2$$

When the metal is intimately mixed with mercury(II) chloride and heated, mercury(I) chloride is obtained:

$$Hg + HgCl_2 \rightarrow Hg_2Cl_2$$

Mercury does not react with phosphorus but simply dissolves in molten phosphorus.

Water has no effect on mercury, nor does molecular hydrogen. However, atomic hydrogen readily combines with mercury vapors forming hydride, when exposed to radiation from a mercury arc.

Mercury catalytically decomposes hydrogen peroxide. In the presence of acetic acid, the above reaction yields mercury(II) acetate. Mercury reacts with several metals forming their amalgams. Such reactions are exothermic and in the presence of air ignition can occur. The intermetallic compounds obtained from such amalgamation have varying compositions, such as NaHg, $NaHg_2$, $NaHg_4$, Na_3Hg and Na_3Hg_2, etc.

Analysis

Mercury is most accurately determined by the cold vapor atomic absorption spectroscopic method. The instrument is set at the wavelength 253.7 nm. The metal, its salts and organic derivatives in aqueous solution can be measured by this method. The solution or the solid compounds are digested with nitric acid to convert into water-soluble mercury(II) nitrate, followed by treatment with potassium permanganate and potassium persulfate under careful heating. The excess oxidants in the solution are reduced with NaCl-hydroxylamine sulfate. The solution is treated with stannous chloride and aerated. The cold Hg vapor volatilizes into the absorption cell where absorbance is measured.

Mercury and its compounds may also be determined by ICP/AES. The method, however, is less sensitive than the cold vapor–AA technique. The metal also can be measured at low ppb level by colorimetry. Mercury ions react with dithizone in chloroform to show an orange color. Absorbance is measured at 492 nm using a spectrophotometer.

Toxicity

Elemental mercury and all its compounds are highly toxic by all routes of exposure. The element has significant vapor pressure at ambient temperatures (0.0018 torr at 25°C) that can produce severe inhalation hazard. The symptoms from short exposure to high concentration of mercury vapors are bronchitis, coughing, chest pain, respiratory distress, salivation and diarrhea (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed., New York: John Wiley and Sons). Other symptoms are tremor, insomnia and depression. Mercury can cause damage to kidney, liver, lungs and brain. Organomercury compounds and inorganic salt solutions can be absorbed into the body through skin contact and cause severe poisoning. It accumulates as Hg^{2+} in the brain and kidneys. US EPA has classified mercury as one of the priority pollutant metals in environmental matrices.

MERCURY(II) ACETATE

[631-60-7]
Formula: $Hg(C_2H_3O_2)_2$; MW 519.27
Synonym: mercuric acetate

Uses

Mercury(II) acetate is the starting material to prepare many organomercuric compounds.

Physical Properties

Colorless crystals; faint vinegar odor; melts at about 178°C; decomposes at higher temperature or when heated rapidly; soluble in water; the solution decomposes on standing producing a yellow precipitate; soluble in alcohol.

Preparation

Mercury(II) acetate is prepared by dissolving mercury(II) oxide in slight excess of warm 20% acetic acid:

$$HgO + 2CH_3COOH \rightarrow (CH_3COO)_2Hg + H_2O$$

Alternatively, the compound may be made by reacting mercury metal with peracetic acid or hydrogen peroxide (50%) dissolved in acetic acid under careful temperature control.

Reactions

Mercury(II) acetate is the starting material to prepare many organomercury compounds for paints and medicinal use. Such mercuration reactions of organics are discussed briefly below.

Refluxing a mixture of mercury(II) acetate and acetic acid in excess benzene yields phenylmercuric acetate (PMA).

$$C_6H_6 + (CH_3COO)_2Hg \rightarrow (CH_3COOHg)(C_6H_5) + CH_3COOH$$

$$C_6H_6 + 2(CH_3COOHg)_2 \rightarrow (CH_3COOHg)_2(C_6H_4) + 2CH_3COOH$$

Mercury(II) acetate in acetic acid reacts with allyl chloride and methanol to produce 3–chloro–2–methoxypropyl mercuric acetate, $ClCH_2CH(OCH_3)$-$CH_2HgOC(=O)CH_3$. The compound is difficult to isolate from the solution and generally an ammoniacal solution is used for commercial applications.

Reaction with allyl urea and methanol, followed by dilution with water and treatment with sodium chloride, precipitates methoxy(urea)propylmercuric chloride, also known as chloromerodrin, a diuretic agent.

$$(CH_3COOHg)_2 + H_2NC(=O)NHCH_2CH{=}CH_2 + CH_3OH \rightarrow$$

$$H_2NC(=O)NHCH_2CH(OCH_3)CH_2HgOC(=O)CH_3 + CH_3COOH \xrightarrow{NaCl}$$

$$\underset{\text{(chlormerodrin)}}{H_2NC(=O)NHCH_2CH(OCH_3)CH_2HgCl}$$

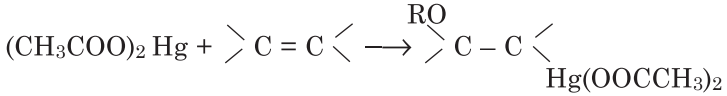
When a mixture of mercury(II) acetate and acetic acid is refluxed with a large excess of phenol and the solution mixture is treated with sodium chloride, a white crystalline product, o-chloromercuriphenol, also known as mercarbolide, precipitates:

$$(CH_3COOHg)_2 + C_6H_5OH \xrightarrow[\text{NaCl}]{\text{reflux}} \underset{\text{(mercarbolide)}}{ClHg(C_6H_4{}_3OH)}$$

Similarly, refluxing a mixture of mercury(II) acetate and acetic acid with *o*–nitrophenol followed by treatment with sodium chloride yields mercurophen:

$$(CH_3COOHg)_2 + C_6H_4(NO_2)(OH) \xrightarrow[\text{NaCl}]{\text{reflux}} \underset{\text{(mercurophen)}}{(ONa)(NO_2)C_6H_3(HgOH)}$$

In general, reactions with olefins carried out in alcohols yield oxomercuration products:



$$(CH_3COO)_2\,Hg + \rangle C = C \langle \longrightarrow \overset{RO}{\rangle} C - C \underset{Hg(OOCCH_3)_2}{\langle}$$

A reversible reaction occurs with carbon monoxide at ordinary temperatures in which CO inserts into Hg—O bond of mercury(II) acetate:

$$CH_3COOHg\text{—}OCH_3 \xleftrightarrow{25^\circ C} CH_3COOHgC(O)OCH_3$$

Reaction with mercury(II) chloride produces methyl mercury chloride:

$$(CH_3COO)_2Hg + HgCl_2 \rightarrow 2CH_3HgCl + 2CO_2$$

The above reaction proceeds via a transition cyclic intermediate.

Reactions with certain metal halides yield their partial methylation products:

$$(CH_3COO)_2Hg + AsCl_3 \rightarrow CH_3HgCl + CH_3AsCl_2 + 2CO_2$$

Analysis

Elemental composition: Hg 62.95%, C 15.07%, H 1.90%, O 20.07%

The compound is analyzed in aqueous phase by cold vapor–AA or ICP/AES method (See Mercury). It also may be derivatized with an olefin or benzene in alcohol to yield the corresponding “mercuration” product that may be identified from physical and spectral properties and elemental analysis. An ether or alcoholic solution of the compound may be analyzed by GC/MS. The characteristic masses should be 259, 257, 256, 202, and 200.

Toxicity

A highly poisonous substance by ingestion, intravenous, intraperitoneal and subcutaneous routes and low-to-moderate toxicity by dermal route. An oral LD_{50} in rats is about 40 mg/kg.

MERCURY(I) CHLORIDE

[10112-91-1]
Formula: Hg_2Cl_2; MW 472.09
Synonyms: mercurous chloride; calomel

Uses

Mercury(I) chloride is used in calomel electrodes; in ceramic painting; as a fungicide; in pyrotechnics for producing dark green light; in agriculture for controlling root maggots; and as an antiseptic and antisyphilitic agent in medicine.

Physical Properties

White tetragonal crystals; refractive index 1.973; hardness 1.5 Mohs; density 7.16 g/cm^3; does not have a normal melting point; triple point 525°C; sublimes at 383°C; insoluble in water, ethanol and ether.

Thermochemical Properties

$\Delta H_f°$	–63.43 kcal/mol
$\Delta G_f°$	–50.36 kcal/mol
S°	45.79 cal/degree mol

Preparation

Mercury(I) chloride is prepared by passing a limited amount of chlorine gas over mercury in a heated silica retort. Excess chlorine should be avoided as it can oxidize mercury(I) chloride to mercury(II) chloride.

$$2Hg + Cl_2 \rightarrow Hg_2Cl_2$$

The product generally contains some mercury(II) chloride which is removed by treating the product mixture with water and filtering out the insoluble mercury(I) salt from the soluble mercury(II) salt.

The compound also can be made by heating mercury(II) chloride with mercury. The product Hg_2Cl_2 sublimes and is collected:

$$HgCl_2 + Hg \rightarrow Hg_2Cl_2$$

Mercury(I) chloride is obtained as a white precipitate by adding a cold acidic solution of sodium chloride or other soluble chloride to a solution of mercurous salt, such as mercury(I) nitrate:

$$[Hg_2]^{2+} (aq) + 2Cl^{-} (aq) \rightarrow Hg_2Cl_2 (s)$$

The precipitation method, however, does not form high-purity product as it contains small amounts of reactant and product ions that stick to the Hg_2Cl_2

precipitate and are difficult to remove by washing with water.

Reactions

Mercury(I) chloride oxidizes to mercury(II) chloride when heated with chlorine:

$$Hg_2Cl_2 + Cl_2 \rightarrow 2HgCl_2$$

Mercury(I) chloride is a reducing agent and, therefore, its reaction with oxidizing substances can oxidize it to Hg(II) compounds.

When heated at elevated temperatures, it partially dissociates to mercury metal and mercury(II) chloride:

$$Hg_2Cl_2 \rightarrow Hg + HgCl_2$$

This disproportionation (or breakdown of a compound into two products containing the same element but in different oxidation states) also occurs to some degree when mercury(I) chloride is heated and sublimed in an open container.

Reaction with ammonia in solution forms an unstable black adduct which slowly converts to mercury(II) amidochloride, NH_2HgCl, releasing mercury:

$$Hg_2Cl_2 + 2NH_3 \rightarrow ClHg\text{—}HgNH_2 + NH_4Cl$$

$$ClHg\text{—}HgNH_2 \rightarrow NH_2HgCl + Hg$$

Analysis

Elemental composition: Hg 84.98%, Cl 15.02%

Mercury(I) chloride may be identified from its physical properties, its reaction with ammonia to form a black product, and it may be measured quantitatively for mercury by cold vapor-AA or ICP/AES.

Toxicity

Mercury(I) chloride is highly toxic by ingestion and other routes of exposure. The symptoms include nausea, vomiting, abdominal pain, diarrhea and kidney damage.

MERCURY(II) CHLORIDE

[7487-94-7]
Formula: $HgCl_2$; MW 271.50; covalent bonding, slightly ionized in water
Synonyms: mercuric chloride; mercury bichloride; corrosive sublimate; mercury perchloride

Uses

Mercury(II) chloride is used in dry batteries; in electroplating aluminum;

for extracting gold; in etching steel; for preserving wood; for tanning leather; in photographic solution; in fabric printing; as an agricultural fungicide; as a disinfectant; and topical antiseptic. The compound also is used as an intermediate in organic syntheses; as a reagent in analytical chemistry; and as a catalyst in the preparation of mercury(II) chloride. A major application of mercury(II) chloride involves preparing several other mercury compounds.

Physical Properties

White orthogonal crystal; density 5.6 g/cm^3; melts at 276°C; vaporizes at 304°C; vapor pressure 5 torr at 166°C and 60 torr at 222°C (the substance is in the solid state at these temperatures); critical temperature 700°C; critical volume 174 cm^3/mol; moderately soluble in water (7.4 g/100 mL at 20°C), solubility increases in the presence of HCl or Cl$^-$ ion in the solution; pH of 0.2M solution 3.2; soluble in alcohol, ether, acetone and ethyl acetate; slightly soluble in benzene and carbon disulfide.

Thermochemical Properties

$\Delta H_f°$	–53.6 kcal/mol
$\Delta G_f°$	–42.7 kcal/mol
S°	34.9 cal/degree mol

Preparation

Mercury(II) chloride, like mercury(I) chloride, is most conveniently made by dry methods that involve either heating a mixture of mercury(II) sulfate and sodium chloride or heating mercury metal with excess chlorine:

$$HgSO_4 + 2NaCl \rightarrow HgCl_2 + Na_2SO_4$$

$$Hg + Cl_2 \rightarrow HgCl_2$$

The product $HgCl_2$ is sublimed off and collected as a white transparent crystalline mass. Very pure product is obtained in these reactions. Excess chlorine in the latter reaction is removed by absorption over sodium hydroxide.

The wet method of preparation involves treating mercury(II) oxide with hydrochloric acid followed by evaporation of the solution and crystallization:

$$HgO + 2HCl \rightarrow HgCl_2 + H_2O$$

Reactions

Mercury(II) chloride is reduced to mercury(I) chloride by heating with mercury; or by treatment with sulfur dioxide, tin(II) chloride, ammonium oxalate and other reducing agents in aqueous solutions:

$$HgCl_2 + Hg \rightarrow Hg + Hg_2Cl_2$$

$$2HgCl_2 + SO_2 + 2H_2O \rightarrow Hg_2Cl_2 + H_2SO_4 + 2HCl$$

$$2HgCl_2 + (NH_4)_2C_2O_4 \rightarrow Hg_2Cl_2 + 2CO_2 + 2NH_4Cl$$

Reaction with tin(II) chloride first forms a white precipitate of mercury(I) chloride which then is further reduced to give a black deposit of mercury:

$$2HgCl_2 + SnCl_2 \rightarrow SnCl_4 + Hg_2Cl_2$$

$$Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg + SnCl_4$$

Mercury(II) chloride is a weakly dissociated salt. When hydrogen sulfide is slowly passed into its solution, a pale yellow precipitate due to $HgCl_2 \cdot 2HgS$ is first formed, which on further treatment with H_2S converts to black amorphous HgS:

$$3HgCl_2 + 2H_2S \rightarrow HgCl_2 \cdot 2HgS + 4HCl$$

Reaction with alkali hydroxides gives a yellow precipitate of mercury(II) oxide, HgO.

When aqueous ammonia is added to mercury(II) chloride, a white precipitate, the so-called "infusible" white precipitate of composition NH_2HgCl forms:

$$HgCl_2 + 2NH_3 \rightarrow H_2N—Hg—Cl + NH_4Cl$$

The product decomposes on sublimation forming mercury(II) chloride, ammonia, and nitrogen. However, in the presence of ammonium chloride, the same reaction with ammonia with $HgCl_2$ in aqueous solution yields "fusible" white precipitate, $(NH_3)_2HgCl_2$. Similar product also is obtained by reaction of gaseous ammonia with solid mercury(II) chloride. However, the solid mercury(II) chloride is more stable than the above "infusible" product and can be melted without decomposition.

$$HgCl_2 + 2NH_3 \xrightarrow{NH_4Cl} (NH_3)_2HgCl_2$$

Mercury(II) chloride reacts with alkali metal chlorides to form water soluble complex salts, such as $KHgCl_3$ or K_2HgCl_4:

$$HgCl_2 + KCl \rightarrow KHgCl_3$$

$$HgCl_2 + 2KCl \rightarrow K_2HgCl_4$$

Action of Grignard reagent on mercury(II) chloride yields mercury alkyls:

$$HgCl_2 + 2C_2H_5MgI \rightarrow \underset{\text{(mercury diethyl)}}{Hg(C_2H_5)_2} + MgI_2 + MgCl_2$$

Analysis

Elemental composition: Hg 73.88%, Cl 26.12%. In an aqueous solution of the salt, mercury may be analyzed by cold vapor–AA technique and chloride measured by ion chromatography.

Toxicity

The compound is a systemic poison by ingestion, skin contact and other routes of exposure. It may produce adverse teratogenic and reproductive effects. There is limited evidence of carcinogenicity in experimental animals.

LD_{50} oral (rat): 1mg/kg

MERCURY(II) CYANIDE

[592-04-1]
Formula: $Hg(CN)_2$; MW 252.63
Synonym: mercuric cyanide

Uses

Mercury(II) cyanide is a topical antiseptic.

Physical Properties

Colorless tetragonal crystal; density 4.0 g/cm^3; decomposes at 320°C; soluble in water and ethanol; slightly soluble in ether.

Preparation

Mercury(II) cyanide is prepared by the action of mercury(II) oxide on aqueous hydrocyanic acid, followed by evaporation:

$$HgO + 2HCN \rightarrow Hg(CN)_2 + H_2O$$

Alternatively, it is produced by the reaction of alkali cyanides with a mercury(II) salt solution.

Analysis

Elemental composition: Hg 79.40%, C 9.51%, N 11.09%. Aqueous solution is analyzed for mercury metal by AA–cold vapor techniques or by ICP/AES (see Mercury). The cyanide ion may be measured by cyanide ion-specific electrode or by ion chromatography after appropriate dilution.

MERCURY DIMETHYL

[593-74-8]
Formula: $(CH_3)_2Hg$; MW 230.67; covalent bonding of methyl radicals to mercury atom; linear shape
Synonyms: dimethylmercury; methylmercury

Occurrence and Uses

Mercury dimethyl is a toxic environmental pollutant. It is found in polluted bottom sediments and in the bodies of fishes and birds. In the bodies of fishes and birds it occurs along with monomethyl mercury. The latter, as CH_3Hg^+ ion, is formed by microorganism-induced biological methylation of elemental mercury or agricultural fungicide mercury compounds that are discharged into the environment.

Mercury dimethyl is used in inorganic synthesis; and as a reference standard for Hg-NMR.

Physical Properties

Colorless liquid; sweet faint odor; refractive index 1.5452; flammable; volatile; density 3.19 g/mL at 20°C; boils at 94°C; solidifies at –43°C; insoluble in water; soluble in ether and alcohols.

Preparation

Mercury alkyls are readily obtained by the actions of Grignard reagents (magnesium alkyl halides) on mercury(II) chloride. Thus, mercury dimethyl is made from magnesium methyl chloride and mercury(II) chloride:

$$2CH_3MgCl + HgCl_2 \rightarrow (CH_3)_2Hg + MgCl_2$$

The above reaction proceeds through the formation of mercury methyl chloride as an intermediate (not shown above).

Alternatively, the compound can be prepared by the reaction of mercury with methyl iodide in the presence of sunlight; or by "mercuration" reaction of organics.

$$Hg + 2CH_3I \xrightarrow{hv} (CH_3)_2Hg + I_2$$

Reactions

Mercury dimethyl, unlike zinc dimethyl, is fairly stable at ordinary temperatures, and is not attacked by air or water.

Mercury dimethyl undergoes single replacement reactions with several metals such as alkali and alkaline earth metals, zinc, aluminum, tin, lead and bismuth forming their corresponding dialkyls.

Such reaction is a synthetic route to prepare many organometallic compounds. Thus, reaction with metallic zinc yields zinc dimethyl:

$$(CH_3)_2Hg + Zn \rightarrow (CH_3)_2Zn + Hg$$

Analysis

Elemental composition: 86.96%, C 10.41%, H 2.62%. The compound can be identified from its physical properties, elemental analyses and infrared spectra. Mercury can be identified by cold-vapor AA or ICP/AES after cautious extraction with nitric acid. In a suitable organic solvent, it may be analyzed by GC/MS. The characteristic ions are 217, 215, 202, 200, 232 and 230.

Toxicity

Mercury dimethyl is a highly toxic substance by all routes of exposure. Several cases of human poisoning are well documented. (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances,* 2nd ed. p. 574, New York: John Wiley & Sons.) The compound can accumulate in the brain and blood of humans. Intake of small quantities can cause death.

MERCURY FULMINATE

[628-86-4]
Formula: $Hg(CNO)_2$; MW 284.63
Synonyms: mercury(II) cyanate; fulminate of mercury

Uses

Mercury fulminate is used in explosives to initiate boosters.

Physical Properties

White or grayish cubic crystals; density 4.42 g/cm^3; explodes on heating; slightly soluble in water; soluble in ethanol and ammonia solution.

Preparation

Mercury fulminate is prepared by the reaction of mercury metal with strong nitric acid and ethanol. The preparative method involves pouring a nitric acid solution of mercury(II) nitrate into ethanol. The reaction is not well understood.

Hazard

The compound is highly sensitive to heat and impact. It detonates when heated at 180°C or struck hard. It also is a toxic substance exhibiting the symptoms of mercury poisoning.

MERCURY(II) IODIDE

[7774-29-0]
Formula: HgI_2; MW 454.40
Synonym: mercuric iodide

Uses

Mercury(II) iodide is used as an analytical reagent, in Nesslers reagent for the analysis of ammonia. The compound also is used in ointments for the treatment of skin diseases.

Physical Properties

Exists in two allotropic forms: red tetragonal allotropic modification (alpha form) and the yellow rhombic modification (beta form).

The red iodide has a density 6.36 g/cm³ at 25°C; transforms to yellow form at 127°C; also converts to yellow form at –180°C; slightly soluble in water (100 mg/L at 25°C); moderately soluble in acetone and alcohol.

The yellow iodide has a density of 6.09 g/cm³ at 27°C; melts at 259°C; vaporizes at 354°C; practically insoluble in water; low-to-moderately soluble in alcohol, benzene and other organic solvents.

Thermochemical Properties

$\Delta H_f°$ (red)	–25.2 kcal/mol
$\Delta H_f°$ (yellow)	–24.6 kcal/mol
$\Delta G_f°$ (red)	–24.3 kcal/mol
S° (red)	43.0 cal/degree mol

Preparation

Mercury(II) iodide is precipitated in its yellow form by adding a stoichiometric amount of potassium iodide to an aqueous solution of mercury(II) salt (e.g., $HgCl_2$):

$$Hg^{2+} + 2I^{-} \rightarrow HgI_2$$

The yellow precipitate rapidly turns red and dissolves in solution when excess potassium iodide is added.

Also, mercury (II) iodide is formed when mercury is rubbed with iodine moistened with ethanol.

Reactions

Mercury(II) iodide reacts with excess iodide ion forming complex tetraiodomercurate(II) ion, $[HgI_4]^{2-}$:

$$HgI_2 + 2I^{-} \rightarrow [HgI_4]^{2-}$$

In caustic soda or caustic potash solution, mercury(II) iodide forms complex salts, Na_2HgI_4 and K_2HgI_4, respectively. Alkaline solution of this complex in excess potassium hydroxide is known as Nessler's reagent, used to analyze ammonia. The reaction of Nessler's reagent with ammonia may be written as:

$$2[HgI_4]^{2-} + NH_3 + 3OH^{-} \rightarrow I\text{—}Hg\text{—}O\text{—}Hg\text{—}NH_3 + 7I^{-} + 2H_2O$$

Similar complexes of silver, copper and other metals are known. Some of them change colors on heating and are used in heat-sensitive paints and applied to machine parts made out of brass or iron:

$$2Cu^{2+} + Hg^{2+} + 6I^{-} \rightarrow \underset{\text{(red)}}{Cu_2HgI_4} + I_2$$

$$2Ag^{+} + Hg^{2+} + 6I^{-} \rightarrow \underset{\text{(yellow)}}{Ag_2HgI_4} + I_2$$

In general, mercury(II) iodide forms neutral complexes of compositions $M_2(HgI_4)$ and $M(HgI_3)$ with alkali and alkaline metal iodides.

When heated with dilute caustic potash solution, a yellow brown powder of composition $HgI_2 \cdot 3HgO$ is obtained.

MERCURY(I) NITRATE

Formula: $Hg_2(NO_3)_2$; MW 525.19; exists as dihydrate, $Hg_2(NO_3)_2 \cdot 2H_2O$ [7782-86-7]
Synonym: mercurous nitrate

Uses

Mercury(I) nitrate is used for preparing calomel and other mercury(I) salts. Other applications are fire gilding and blackening of brass.

Physical Properties

The dihydrate is colorless crystalline substance (the anhydrous salt consists of white monoclinic crystals); density 4.8 g/cm^3; melts at 70°C with partial decomposition; soluble in water (hydrolyzes); soluble in cold dilute nitric acid.

Preparation

Mercury(I) nitrate is prepared by action of metallic mercury with moderately dilute nitric acid. Excess mercury should be used to prevent the formation of mercury(II) nitrate. Hot or concentrated acid must be avoided as it yields the mercury(II) salt.

It also is formed by the reaction of mercury with mercury(II) nitrate solution.

Reactions

Mercury(I) nitrate is acidic in solution. Its aqueous solution hydrolyzes on standing forming a yellow precipitate of the basic nitrate, $Hg_2(NO_3)(OH)$. This precipitation occurs more rapidly when diluted with water and warmed. Sufficient nitric acid in the solution suppresses hydrolysis.

However, if the solution is boiled, mercury(I) nitrate disproportionates to mercury(II) nitrate and mercury:

$$Hg_2(NO_3)_2 \rightarrow Hg(NO_3)_2 + Hg$$

Also, such disproportionation occurs due to light.

Mercury(I) nitrate exhibits reducing properties. It is partially oxidized by atmospheric oxygen at ambient temperatures, forming mercury(II) nitrate and mercury.

On gentle heating, the solid salt yields mercury(II) oxide and nitrogen dioxide:

$$Hg_2(NO_3)_2 \rightarrow 2HgO + 2NO_2$$

Mercury(I) nitrate undergoes double decomposition reactions with anions in aqueous solution, forming corresponding mercury(I) salts. With potassium iodide and sodium bromide, yellow mercury(I) iodide and white mercury(I) bromide precipitate, respectively. Similarly, mercury(I) nitrate in acid medium reacts with dilute sulfuric acid to form mercury(I) sulfate:

$$Hg^{2+}\ (aq) + 2I^{-}(aq) \rightarrow Hg_2I_2\ (s)$$

$$Hg^{2+}\ (aq) + 2Br^{-}(aq) \rightarrow Hg_2Br_2\ (s)$$

$$Hg^{2+}\ (aq) + SO_4{}^{2-}(aq) \rightarrow Hg_2SO_4\ (s)$$

Analysis

Elemental composition: Hg 76.39%, N 5.33%, O 18.28%. The salt is dissolved in dilute nitric acid and analyzed for mercury (see Mercury). The compound is blackened by ammonia and caustic alkali solutions. It may be identified by physical and x-ray properties.

Toxicity

Poison by ingestion and other routes of exposure.

MERCURY(II) NITRATE

[10045-94-0]
Formula: $Hg(NO_3)_2$; MW 324.60; occurs as monohydrate, $Hg(NO_3)_2 \cdot H_2O$ [7783-34-8], and dihydrate, $Hg(NO_3)_2 \cdot 2H_2O$.
Synonym: mercuric nitrate

Uses

Mercury(II) nitrate is used in the preparation of other mercury compounds; in organic synthesis; and as an analytical standard for mercury.

Physical Properties

The monohydrate is a white crystalline or powdery substance; density 4.3g/cm^3; decomposes on heating; soluble in water and nitric acid; insoluble in alcohol.

Preparation

Mercury(II) nitrate is prepared by dissolving mercury in excess hot concentrated nitric acid. Upon evaporation of the solution, large colorless deliquescent crystals of monohydrate, $Hg(NO_3)_2 \cdot H_2O$, form.

It also is obtained by boiling a solution of mercury(I) nitrate or by the action of light on mercury(I) nitrate:

$$Hg_2(NO_3)_2 \rightarrow Hg + 2HgNO_3$$

Reactions

Gentle heating of mercury(II) nitrate gives mercury(II) oxide evolving nitrogen and oxygen:

$$Hg(NO_3)_2 \rightarrow HgO + 2NO_2 + \tfrac{1}{2}\ O_2$$

However, on strong heating, mercury nitrate decomposes to mercury metal:

$$Hg(NO_3)_2 \rightarrow Hg + 2NO_2 + O_2$$

When excess alkali hydroxide is added to a solution of mercury(II) nitrate, a yellow precipitate of HgO is obtained.

Addition of potassium thiocyanate solution forms a white precipitate of mercury(II) thiocyanate:

$$Hg^{2+} + 2SCN^{-} \rightarrow Hg(SCN)_2$$

Addition of a small amount of alkali iodide to mercury(II) nitrate solution precipitates mercury(II) iodide:

$$Hg^{2+} + 2I^{-} \rightarrow HgI_2$$

Similarly, mercury(II) cyanide precipitates upon the addition of potassium cyanide to mercury(II) nitrate solution:

$$Hg^{2+} + 2CN^{-} \rightarrow Hg(CN)_2$$

Analysis

Elemental composition: Hg 61.80%, N 8.63%, O 29.57%. The compound dissolved in dilute hydrochloric acid and the solution diluted appropriately and analyzed for mercury by cold vapor–AA technique. The aqueous solution is analyzed for nitrate ion by nitrate ion-specific electrode or by ion chromatography.

Toxicity

Mercury(II) nitrate is highly toxic by ingestion and possibly other routes of exposure. The LD_{50} oral for the dihydrate in mouse is 25 mg/kg.

MERCURY(II) OXIDE

[21908-53-2]
Formula: HgO; MW 216.59
Synonym: mercuric oxide

Occurrence and Uses

Mercury(II) oxide is found natively in the mineral montroydite. The oxide is used primarily to prepare other mercury salts. The red form of the oxide is used as a depolarizer in a certain type of dry batteries. Other applications are paints and pigments; as a reagent in several wet analyses; and to catalyze in organic reactions. The oxide also is used in ointments as a topical antiseptic.

Physical Properties

Mercury(II) oxide exists in two modifications, red and yellow, differing in particle size—finer particles under 5µm appear red, while particle size greater than 8µm appear reddish. The yellow form converts to red oxide on heating, which reverts back to yellow oxide on cooling. At 400°C, the red oxide becomes black which changes back to red again on cooling. The oxide decomposes at 500°C.

Orthogonal crystalline powder; refractive index (for montroydite) 2.37; density 11.14 g/cm^3; Moh's hardness 2.5; insoluble in water and ethanol; soluble in dilute acids and aqueous solutions of alkali iodides and cyanides.

Thermochemical Properties (Red Modification)

$\Delta H_f°$	–21.70 kcal/mol
$\Delta G_f°$	–13.98 kcal/mol
S°	16.80 cal/degree mol
C_ρ	10.54 cal/degree mol

Preparation

Yellow mercury(II) oxide is precipitated upon the addition of excess caustic soda or caustic potash to an aqueous solution of mercury(II) nitrate or chloride:

$$Hg^{2+} + 2OH^- \rightarrow \underset{\text{(yellow)}}{HgO} + H_2O$$

Most precipitation methods give yellow mercury(II) oxide. However, if barium hydroxide is added to a hot solution of mercury(II) nitrate, the product is red oxide.

Red mercury(II) oxide is obtained by heating mercury in air or oxygen (preferably under pressure) at 450°C:

$$2Hg + O_2 \rightarrow \underset{\text{(red)}}{2HgO}$$

or by thermal decomposition of mercury(II) nitrate or mercury(I) nitrate:

$$Hg(NO_3)_2 \rightarrow HgO + 2NO_2 + ½\ O_2$$

$$Hg_2(NO_3)_2 \rightarrow 2HgO + 2NO_2$$

or by boiling the yellow oxide in a solution of sodium or potassium chloride.

Mercury(II) oxide also is obtained as an intermediate when cinnabar (HgS) is roasted in air in the extraction of mercury.

Reactions

The yellow form of the HgO is more reactive than the red form due to finer particle size.

When heated at 500°C, mercury(II) oxide decomposes to its elements:

$$HgO \rightarrow Hg + \frac{1}{2} O_2$$

Mercury(II) oxide is a basic oxide. It reacts with acids forming their mercury(II) salts:

$$HgO + 2HCl \rightarrow HgCl_2 + 2H_2O$$

$$HgO + H_2SO_4 \rightarrow HgSO_4 + H_2O$$

Mercury(II) oxide dissolves in neutral sodium or potassium sulfite solution forming sulfitomercurate(II) ion:

$$HgO + 2HSO_3^- \rightarrow [Hg(SO_3)_2]^{2-} + H_2O$$

Upon evaporation of the solution, complex salt crystals such as $Na_2[Hg(SO_3)_2]$ or $K_2[Hg(SO_3)_2]$ form.

Mercury(II) oxide reacts with potassium iodide in solution, forming potassium tetraiodomercurate(II):

$$HgO + 4KI + H_2O \rightarrow K_2HgI_4 + 2KOH$$

Reaction with chlorine yields chlorine monoxide, ClO, and in aqueous solution or with chlorine water, the product is hypochlorous acid, HOCl:

$$HgO + Cl \rightarrow Hg + ClO$$

The oxide is reduced to mercury metal when heated with mercury(II) sulfide:

$$2HgO + HgS \rightarrow 3Hg + SO_2$$

Similarly, reaction with zinc and other reducing agents converts the oxide to metallic mercury:

$$HgO + Zn \rightarrow ZnO + Hg$$

Mercury(II) oxide dissolves in a saturated solution of mercury(II) cyanide, forming mercury oxycyanide, $Hg(CN)_2 \cdot HgO$.

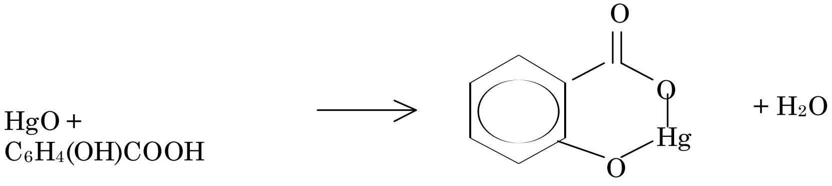
Mercury(II) oxide dissolves in an aqueous solution of acetamide forming mercury(II) acetamide. In this reaction, mercury replaces both the hydrogen atoms of the amide functional group, forming covalent N—Hg bond:

$$HgO + 2CH_3CONH_2 \rightarrow (CH_3CONH)_2Hg + H_2O$$

Similarly, reaction with succinimide yields mercury succinimide [584-43-0].

The yellow oxide reacts with aqueous ammonia to yield a bright yellow crystalline powder, dihydroxymercury(II)–ammonium hydroxide, known as Millon's base, $[(HO–Hg)_2NH_2]OH$ [12529-66-7], a photosensitive unstable product.

Mercury(II) oxide yields mercury(II) salicylate [5970-32-1] when added to an aqueous soution of salicyclic acid:



The product was used medicinally for the treatment of syphilis.

Analysis

Elemental composition: Hg 92.61%, O 7.39%. The compound is digested in nitric acid and mercury in an appropriately diluted acid extract and then is measured by cold-vapor AA or by ICP. The compound may be characterized nondestructively by x-ray methods.

Toxicity

It is highly toxic by ingestion and inhalation as dust. Toxic symptoms are those of mercury (see Mercury). The oral LD_{50} in rodents is between 15 to 20 mg/kg.

MERCURY(II) SULFATE

[7783-35-9]
Formula: $HgSO_4$; MW 296.65
Synonym: mercuric sulfate

Uses

Mercury(II) sulfate is an electrolyte for primary batteries. Other applications are in extraction of gold and silver from roasted pyrites; as a catalyst in organic reactions such as conversion of acetylene to acetaldehyde; and as a reagent for wine coloring.

Physical Properties

White monoclinic crystal; hygroscopic; density 6.47 g/cm^3; decomposes in water; soluble in hot dilute sulfuric acid, hydrochloric acid and concentrated solution of sodium chloride.

Thermochemical Properties

$\Delta H_f°$ –169.1 kcal/mol

Preparation

Mercury(II) sulfate is prepared by heating mercury with an excess of concentrated sulfuric acid; or by dissolving mercury(II) oxide in concentrated sulfuric acid. The solution is evaporated repeatedly to yield anhydrous salt as white leaftlets. However, in the presence of a small amount of water, the monohydrate of the salt, $HgSO_4 \cdot H_2O$ crystallizes as a colorless rhombic prism. Hydrolysis occurs in the presence of a large amount of water, forming a yellow basic sulfate, $HgSO_4 \cdot 2HgO$.

The compound also is prepared by treating alkali sulfate, such as sodium or potassium sulfate with a solution of mercury(II) nitrate.

Reactions

Mercury(II) sulfate on heating first turns yellow and then becomes red-brown. When heated to red heat, it decomposes to mercury, sulfur dioxide, and oxygen.

$$HgSO_4 \rightarrow Hg + SO_4 + O_2$$

Mercury(II) sulfate hydrolyzes in water forming a basic sulfate $HgSO_4 \cdot 2HgO$. It forms double sulfates with alkali metal sulfates, such as $K_2SO_4 \cdot 3HgSO_4 \cdot 2H_2O$.

Analysis

Elemental composition: Hg 67.62%, S 10.81%, O 21.57%. The compound is digested in nitric acid and the acid extract may be analyzed by cold vapor AA or ICP/AES. It also may be characterized by x-ray methods.

MERCURY(II) SULFIDE

[1344-48-5]
Formula: HgS; MW 232.65
Synonyms: mercuric sulfide; cinnabar; vermilion; metacinnabar

Occurrence and Uses

Mercury(II) sulfide occurs in nature as the mineral cinnabar. This is the red sulfide of mercury, which is the principle source of all mercury produced in the world. The black sulfide, known as metacinnabar, occurs rarely in nature, sometimes coexisting with the red form and found as a black deposit over cinnabar.

The most important use of this compound, the principal ore of mercury, is for making mercury metal and its salts. Another major application is pigment. Artificially prepared scarlet product, vermilion, is used as artists' pigment and for coloring plastics. The red form also is used as an antibacterial agent. The black sulfide is used for coloring horns, rubber, and other materials.

Physical Properties

Mercury(II) sulfide has several modifications, the only two stable allotropic forms are:

1. the red hexagonal form known as cinnabar (alpha form), and
2. the black cubic modification (beta form).

Cinnabar is a red crystalline or powdery substance; hexagonal crystal system; refractive index 2.854; density 8.10 g/cm^3; sublimes at 583.5°C; color changes to brown at 250°C and converts to black sulfide at 386°C; reverts to red color on cooling; insoluble in water, alcohol and nitric acid; soluble in aqua regia and solutions of alkali metal sulfides; decomposed by hot concentrated sulfuric acid.

Black sulfide is a black amorphous powder or crystalline substance (beta form); cubic structure; metastable at ordinary temperatures; converts to red sulfide by sublimation at ordinary pressure; density 7.73 g/cm^3; melts at 583.5°C; insoluble in water, alcohol and nitric acid; soluble in aqua regia, alkalies, and solutions of alkali metal sulfides.

Preparation

Red sulfide occurs natively and is mined from mineral cinnabar. Also it can be prepared by heating mercury with a solution of potassium pentasulfide, producing a scarlet cinnabar:

$$Hg + K_2S_5 \rightarrow HgS + K_2S_4$$

The red sulfide also may be made from black sulfide by heating in a concentrated solution of alkaline polysulfide. The shade of pigment varies with temperature, reaction time, and concentration of the black sulfide.

Alternatively, vermilion may be made by grinding sodium sulfide with sulfur and slowly adding mercury. The shades are not bright when prepared at 0°C.

The black mercury(II) sulfide is prepared usually by precipitation from an aqueous solution of mercury(II) salt with hydrogen sulfide. Thus, when H_2S is passed into a solution of $HgCl_2$, a pale yellow precipitate of composition $HgCl_2 \cdot 2HgS$ forms. This converts to amorphous black HgS on further treatment with H_2S.

The black sulfide may also be made by other methods such as adding sodium thiosulfate, $Na_2S_2O_3$ in excess to a dilute solution of sodium mercurichloride, Na_2HgCl_4 and treating mercury with molten or powdered sulfur.

Reactions

When heated in a current of air, mercury(II) sulfide is converted into metallic mercury and sulfur dioxide:

$$HgS + O_2 \rightarrow Hg + SO_2$$

Similar reduction to metallic mercury occurs when the sulfide is heated with several metals or metal oxides:

$$HgS + Fe \rightarrow Hg + FeS$$

$$4HgS + 4CaO \rightarrow 4Hg + 3CaS + CaSO_4$$

Mercury(II) sulfide dissolves in concentrated solutions of alkali or alkaline-earth metal sulfides forming thiosalts, such as $Na_2[HgS_2]\cdot xH_2O$. Such thiosalts are stable in solution only when alkaline hydroxides are present in excess. These salts also are obtained as bright and deliquescent needles when HgS is heated with sulfur and alkaline hydroxides.

Analysis

Elemental composition: Hg 86.22%, S 13.78%. The compound may be identified from its physical properties and also by x-ray methods. The compound may be heated in a current of air and SO_2 formed may be analyzed by GC-FID or GC-FPD. Mercury(II) sulfide may be digested with aqua regia, diluted appropriately, and analyzed for mercury metal by AA using cold vapor method or by ICP-AES (see Mercury).

MOLYBDENUM

[7439-98-7]
Symbol: Mo; atomic number 42; atomic weight 95.94; a Group VIB (Group 6) transition metal element; atomic radius 1.36Å (coordination number 8); ionic radius 0.92Å and 0.62Å for Mo^{3+} and Mo^{6+}, respectively; atomic volume 9.41 cm^3/mol; electron configuration $[Kr]4d^55s^1$; oxidation states 0, +2, +3, +4, +5, and +6; most stable oxidation state +6; seven natural isotopes: Mo-92 (14.84%), Mo-94 (9.25%), Mo-95 (15.92%), Mo-96 (16.68%), Mo-97 (9.55%), Mo-98 (24.13%, Mo-100 (9.63%); several artificial isotopes in the mass range 88-106 are known.

History, Occurrence, and Uses

Molybdenum was first identified as a distinct element by Swedish chemist Karl Wilhelm Scheele in 1778. The metal was isolated by Hjelm in 1782 by reduction of its oxide with carbon. Moissan in 1895 isolated the metal in highly purified form by electrolytic reduction of its oxide and studied many of its physical and chemical properties. The element derived its name in 1816 from the word *molybdos*, meaning a soft mineral that appeared like lead.

Molybdenum does not occur in nature in free elemental form. Its most important ore is molybdenite, MoS_2, from which the metal is obtained commercially. Other ores are powellite (calcium tungstomolybdate), $Ca(MoW)O_4$, and wulfenite (lead molybdate), $PbMoO_4$. The metal is an essential nutrient for plants and is found in trace amounts in some plants such as peas and beans, which absorb it from soil. Also, molybdenum is found in many natural petroleum oils.

The largest quantities of molybdenum produced are consumed in the steel industry. The metal is incorporated to steel to impart high resistance and hardness to the steel and to improve its mechanical properties. In the chemical industry, molybdenum compounds are used widely in coloring agents and solid lubricants. Molybdenum compounds are used also as catalysts in many oxidation-reduction reactions and in petroleum refining for production of high-octane gasoline. The metal also is used as the starting material to prepare many of its salts. Important commercial uses of molybdenum compounds are discussed separately under their individual headings.

Physical Properties

Silvery-white metal or grayish-black powder; cubic crystalline structure; density 10.22 g/cm^3; melts at 2,623°C; vaporizes at 4,639°C; vapor pressure 1 torr at 2,830°C and 5 torr at 3,120°C; compressibility 3.6×10^{-7} cm^2/kg at 20°C; electrical resistivity 5, 15, and 32 microhm–cm at 0°C, 400°C and 1,000°C, respectively; insoluble in water.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	157.3 kcal/mol
$\Delta G_f°$ (gas)	146.4 kcal/mol
S° (cry)	6.86 cal/degree mol
S° gas)	43.5 cal/degree mol
C_ρ (cry)	5.76 cal/degree mol
C_ρ (gas)	4.97 cal/degree mol
ΔH_{fus}	8.96 kcal/mol
Coeff. of linear expansion	4.8×10^{-6}/°C
Thermal conductivity (at 27°C)	1.38 W/cmK

Production

Molybdenum is recovered primarily from its sulfide ore, molybdenite, MoS_2. It also is produced, although to a much lesser extent, from the tungsten ore wulfenite, which yields lead molybdate, $PbMoO_4$. The first phase of the recovery process generally involves concentration of the ore, because ore coming from the mine is very lean and usually contains less than one percent molybdenum. Molybdenite at first is concentrated by flotation which concentrates the MoS_2 over 90%. If wulfenite is used as a source material, concentration is usually done by hydraulic methods.

The concentrated molybdenite ore is then roasted in air, converting molybdenum sulfide to molybdenum trioxide MoO_3. This is harvested in high purity by sublimation. An alternative is to leach molybdenite concentrate with dilute ammonia solution, which converts the metal to ammonium molybdate, $(NH_4)_2MoO_4$. Molybdenum trioxide or ammonium molybdate product is then heated with hydrogen at elevated temperatures from 500 to 1,150°C in a furnace to produce molybdenum powder.

Reactions

At ordinary temperatures molybdenum metal is fairly stable to air, water and most mineral acids. The metal shows high resistance to HCl, H_2SO_4, HF, H_3PO_4 and most other mineral acids in the absence of any oxidizing agent. However, the metal is attacked by nitric acid and aqua regia. The reaction is rapid with dilute nitric acid but slow with concentrated nitric acid due to the formation of a protective oxide film over the metal. With excess nitric acid, the solution becomes colorless due to formation of molybdic acid, H_2MoO_4. Excess molybdenum turns the solution red. Although no reaction occurs with dilute or concentrated H_2SO_4 at ordinary temperatures, when heated above 110°C molybdenum reduces sulfuric acid to sulfur dioxide:

$$2Mo + 2H_2SO_4 \rightarrow 2MoO_2 + SO_2 + 2H_2O$$

Molybdenum is very stable to oxygen at ambient temperatures. However, when heated in air or oxygen to red heat the metal readily converts to its trioxide, MoO_3:

$$2Mo + 3O_2 \rightarrow 2MoO_3$$

Heating the finely divided metal with its trioxide at 750°C makes molybdenum pentoxide, Mo_2O_5:

$$Mo + MoO_3 + O_2 \rightarrow Mo_2O_5$$

When heated in steam at 800°C, the metal is converted to its dioxide, MoO_2:

$$Mo + 2H_2O \rightarrow MoO_2 + 2H_2$$

Molybdenum combines with fluorine gas at ordinary temperatures forming colorless hexafluoride, MoF_6:

$$Mo + 3F_2 \rightarrow MoF_6$$

In the presence of oxygen, an oxyfluoride $MoOF_4$ is obtained:

$$2Mo + O_2 + 4F_2 \rightarrow 2MoOF_4$$

Reactions with chlorine and bromine occur only at elevated temperatures. With chlorine the product is molybdenum pentachloride:

$$2Mo + 5Cl_2 \rightarrow 2MoCl_5$$

When bromine vapor is passed over molybdenum metal at 600 to 700°C in an atmosphere of nitrogen, the product is trimeric molybdenum dibromide (trimolybdenum hexabromide) (Mo_3Br_6):

$$3Mo + 3Br_2 \rightarrow Mo_3Br_6$$

Two other bromides are also obtained from the elements. These are molybdenum tribromide, $MoBr_3$, and molybdenum tetrabromide, $MoBr_4$. $MoBr_3$, a black solid, is obtained by heating the elements at 350 to 400°C.

Molybdenum does not react with iodine even at red heat. It combines with carbon at elevated temperatures forming molybdenum carbide, Mo_2C. When molybdenum powder is heated with ammonia gas, two nitrides, Mo_2N and MoN are formed. The metal does not combine readily with nitrogen even at elevated temperature. The above nitrides are obtained only in small yields. The metal has very little affinity for hydrogen even in finely divided state. Finely divided molybdenum absorbs hydrogen only to a very small extent. Hydrogen desorbs completely at 300°C. Molybdenum reacts with sulfur and hydrogen sulfide at elevated temperatures, forming molybdenum disulfide, MoS_2. The same product also is obtained from hydrogen sulfide alone. The metal combines with tin, zinc, iron and aluminum in molten state.

Finely divided molybdenum reacts with carbon monoxide under pressure to form molybdenum hexacarbonyl:

$$Mo + 6CO \rightarrow Mo(CO)_6$$

However, when heated with carbon monoxide at temperatures above 1,000°C, no carbonyl is obtained but a thin film of molybdenum carbide forms over the metal.

Analysis

Molybdenum may be identified at trace concentrations by flame atomic absorption spectrometry using nitrous oxide-acetylene flame. The metal is digested with nitric acid, diluted and analyzed. Aqueous solution of its compounds alternatively may be chelated with 8–hydroxyquinoline, extracted with methyl isobutyl ketone, and analyzed as above. The metal in solution may also be analyzed by ICP/AES at wavelengths 202.03 or 203.84 nm. Other instrumental techniques to measure molybdenum at trace concentrations include x-ray fluorescence, x-ray diffraction, neutron activation, and ICP-mass spectrometry, this last being most sensitive.

MOLYBDIC ACID AND MOLYBDATES

MOLYBDIC ACID

[7782-91-4]
Formula: H_2MoO_4 (or $MoO_3 \cdot H_2O$); MW 161.95; also forms a monohydrate $H_2MoO_4 \cdot H_2O$ (or $MoO_3 \cdot 2H_2O$); [13462-95-8], MW 179.97; and a dihydrate, $H_2MoO_4 \cdot 2H_2O$ (or $MoO_3 \cdot 3H_2O$), MW 197.99.

The monohydrate is a yellow solid consisting of monoclinic crystals; density 3.124 g/cm^3 at 15°C; loses water of crystallization on heating at 70°C; sparingly soluble in cold water (1.33 g/L at 18°C); moderately soluble in hot water 25.68 g/L at 70°C; soluble in caustic soda and sodium carbonate solution.

The anhydrous acid consists of white hexagonal crystals; density 3.112 g/cm^3; converts to molybdenum trioxide, MoO_3 at 70°C; slightly soluble in water; soluble in alkalies and sulfuric acid.

The monohydrate is prepared by treating a molybdate solution with nitric acid, followed by crystallization which may take several weeks to separate out as a yellow solid. The anhydrous molybdic acid is obtained as a white crystalline substance by careful dehydration of the yellow monohydrate.

MOLYBDATES

Normal isopoly- and peroxymolydates of ammonium and several metals are known. The normal or orthomolybdates may be considered as salts of molybdic acid having formulas $H_2MoO_4 \cdot xH_2O$ or $M_2O \cdot MoO_3 \cdot xH_2O$. They are either of monoclinic or scheelite type crystal structure and obtained as hydrated salts.

Normal molybdates are prepared by two methods: (1) precipitating the insoluble metal molybdates obtained by adding the salt solution of the desired metal to a solution of sodium or potassium molybdate, and (2) neutralizing a slurry or solution of molybdenum trioxide with the hydroxide or carbonate of the desired metal. For example, sodium molybdate, Na_2MoO_4, may be obtained as a dihydrate by evaporating an aqueous solution of molybdenum trioxide and sodium hydroxide. Heating the dihydrate at 100°C converts it to the anhydrous salt. Also, the normal molybdates of certain metals can be prepared by fusion of molybdenum trioxide with the desired metal oxide.

While normal molybdates of alkali metals are all water-soluble, those of other metals are only slightly soluble in water. All these salts have high melting points. Physical properties of some orthomolybdates and their CAS numbers are presented below:

Formula	**CAS No.**	**Color**	**Density, g/cm^3**	**MP °C**
Li_2MoO_4	[13568-40-6]	White	2.66	702
$Na_2 MoO_4$	[7631-95-0]	White	3.28	686
$K_2 MoO_4$	[13446-49-6]	White	2.34	919
$Rb_2 MoO_4$	[13718-22-4]	White	__	958
$Cs_2 MoO_4$	[13597-64-3]	White	__	936
$Ca MoO_4$	[7789-82-4]	White	428	985 (dec)
$Sr MoO_4$	[13470-04-7]	White	4.66	1,040 (dec)
$BaMoO_4$	[7787-37-3]	White	4.97	1,480
$CuMoO_4$	[13767-34-5]	Light green	__	820 (dec)
Ag_2MoO_4	[13765-74-7]	White	__	483
$ZnMoO_4$	[13767-32-3]	White	__	700
$CdMoO_4$	[13972-68-4]	Light yellow	5.35	900 (dec)
Tl_2MoO_4	[34128-09-1]	White	__	Red heat
$PbMoO_4$	[10190-55-3]	White	6.81	1,065
$MnMoO_4$	[14013-15-1]	Yellow	__	__
$FeMoO_4$	[13718-70-2]	Dark brown	__	850

$CoMoO_4$	[13762-14-6]	Violet lilac	3.6	1,040
$NiMoO_4$	[12673-58-4]	Green	__	970

Among molybdate salts, sodium and ammonium molybdates have commercial applications. The normal salt, sodium orthomolybdate, $Na_2 MoO_4$, is used in pigments. It also is used as a corrosion inhibitor and as an additive to soil. Lead molybdate, $Pb MoO_4$, occurs in nature as mineral ulfenite, from which molybdenum metal is recovered.

AMMONIUM MOLYBDATES

Ammonium ion forms several isopolymolybdates, including ammonium di-, tri-, hepta-, and octamolybdates. Among these, ammonium dimolybdate, $(NH_4)_2Mo_2O_7$ [27546-07-2] and ammonium heptamolybdate, $(NH_4)Mo_7O_{24}\cdot 24H_2O$ [12027-67-7], and a tetrahydrate of the latter compound, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ [12054-85-2], have commercial applications. Ammonium heptamolybdate is used as a source of high purity molybdenum metal. All three salts are used for making specialty molybdenum catalysts. Ammonium heptamolybdate is a compound of analytical interest. When added to a solution of orthophosphate in nitric acid, it forms a yellow precipitate of ammonium phosphomolybdate, $(NH_4)_3PO_4\cdot 12MoO_3$. This reaction is used for colorimetric measurement of phosphate ion in water.

MOLYBDENUM BLUE

[1313-29-7]

Molybdenum blue is a mixture of several hydrous molybdenum oxides that have variable and nonstoichiometric compositions in the range $Mo^{V}O_{2.5}$ to $Mo^{VI}O_3$. These compounds are blue solids when isolated. All compounds impart deep blue coloration to the solution. The solids are mostly amorphous and colloidal in nature; that is, they disperse in water as colloidal particles. They are sensitive to oxidation-reduction. There are several molybdenum blue compounds in crystalline state. They may be prepared either as intermediate molybdenum oxides or as their hydrates. Some examples of molybdenum blue compounds are Mo_8O_{23}; $Mo_8O_{23}\cdot 8H_2O$; Mo_9O_{26}; $Mo_2O_5\cdot H_2O$; $Mo_4O_{11}\cdot H_2O$; $Mo_4O_{10}(OH)_2$; $Mo_2O_4(OH)_2$; Mo_3O_8OH.

Molybdenum blue in amorphous form may be made by the reduction of molybdenum trioxide, MoO_3, or molybdate ion, MoO_4^{2-} in sulfuric acid solution with a reducing agent, such as, zinc, hydrazine, sulfur dioxide, hydriodic acid, hydrogen sulfide, or molybdenum metal. The solution turns intense blue and contains colloidal particles. The nature of the product greatly depends on the reducing agent, concentration of H_2SO_4, pH of the medium, and other factors. Metallic tin, copper, or zinc, or the ions Cu^+ or Sn^{2+} effectively reduce MoO_3 only at acid strength between 25% to 75%. The blue color may disappear upon dilution of the solution or on heating (and will reappear on cooling). In neutral solution, Sn^{2+} reduces molybdic acid to form a stable blue product, the color of which does not disappear either on heating or diluting the solution. Several other reducing agents have been used to produce molybdenum blue. They include hydroquinone in sunlight; glucose; atomic hydrogen; and lithium aluminum hydride. Action of atomic hydrogen on MoO_3 yields $Mo_2O_4(OH)_2$ and $Mo_4O_{10}(OH)_2$ in crystalline state. Reaction between MoO_3 and $LiAlH_4$ forms a crystalline compound, $Mo_5O_7(OH)_8$. Electrolytic reduction of ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}\bullet4H_2O$ in sulfuric acid solution may form Mo_3O_8OH, which is readily soluble in water.

Under acid conditions, molybdate reacts with orthophosphate, PO_4^{3-} to form a blue heteropoly acid, molybdophosphoric acid. A similar reaction occurs with arsenate ion, AsO_4^{3-}. In the presence of vanadium, the product is yellow vanadomolybdophosphoric acid. These reactions are used for colorimetric analyses of phosphate, arsenate, and many other substances. Colloidal molybdenum blue has limited applications such as dyeing silk. It readily absorbs onto surface-active materials.

MOLYBDENUM DISULFIDE

[1317-33-5]
Formula: MoS_2; MW 160.07
Synonyms: molybdenite; molybdic sulfide; molybdenum sulfide; molybdenum(IV) sulfide.

Occurrence and Uses

Molybdenum disulfide occurs in nature as mineral molybdenite. It is the principal ore from which molybdenum metal is recovered commercially. The compound is used as a dry lubricant and as an additive to lubricant. It also is used as a catalyst.

Physical Properties

Black powder or hexagonal crystal; density 5.06 g/cm^3; hardness 1.3 Moh's; melts at 2,375°C; insoluble in water and dilute acids; soluble in strong oxidizing acids, such as, aqua regia and boiling sulfuric acid.

Thermochemical Properties

$\Delta H_f°$	–56.19 kcal/mol
$\Delta G_f°$	–53.99 kcal/mol
$S°$	14.96 cal/degree mol
C_ρ	15.20 cal/degree mol

Production

Molybdenum disulfide is mined from natural molybdenite deposits. The compound also can be made by direct combination of elements; i.e., heating molybdenum and sulfur at elevated temperatures and under vacuum. Under such conditions, other sulfides of molybdenum that may have formed convert to the more stable disulfide.

Molybdenum disulfide also may be prepared by treating molybdenum pentachloride with a solution of sodium sulfide:

$$2MoCl_5 + 5Na_2S \rightarrow 2MoS_2 + 10NaCl + S$$

Also, the disulfide is obtained by heating molybdenum trioxide with hydrogen sulfide or sulfur.

Reactions

Molybdenum disulfide is stable in air or oxygen at ordinary temperatures but reacts with oxygen at elevated temperatures forming molybdenum trioxide:

$$2MoS_2 + 9O_2 \rightarrow 2MoO_3 + 4SO_3$$

Chlorine attacks the disulfide at elevated temperatures forming molybdenum pentachloride:

$$2MoS_2 + 7Cl_2 \rightarrow 2MoCl_5 + 2S_2Cl_2$$

Molybdenum disulfide reacts with alkyl lithium under controlled conditions to form compounds of compositions Li_xMoS_2 (intercalation compounds). With butyl lithium, C_4H_9Li, the product is $LiMoS_2$.

Analysis

Elemental composition: Mo 59.94%, S 40.06%. The compound or mineral molybdenite may be identified nondestructively by x-ray and from physical properties. Molybdenum content of the material may be determined by various instrumental techniques after digestion of the solid in concentrated HNO_3 or aqua regia followed by appropriate dilution of acid extract (See Molybdenum.)

MOLYBDENUM HEXACARBONYL

[13939-06-5]
Formula: $Mo(CO)_6$; MW 264.00
Synonym: molybdenum carbonyl

Uses

Molybdenum hexacarbonyl is used for molybdenum plating; for deposition of metallic molybdenum in making molybdenum mirrors; and as a catalyst. It also is used to synthesize many organomolybdenum compounds.

Physical Properties

White, shiny crystals; orthogonal crystal structure; density 1.96 g/cm^3; sublimes at 150°C with decomposition; vapor pressure 0.1 torr at 20°C; insoluble in water; soluble in benzene and paraffin oil; slightly soluble in ether.

Thermochemical Properties

$\Delta H_f°$ (cry)	–234.9 kcal/mol
$\Delta H_f°$ (gas)	–218.0 kcal/mol
$\Delta G_f°$ (cry)	–209.8 kcal/mol
$\Delta G_f°$ (gas)	–204.6 kcal/mol
S° (cry)	77.9 cal/degree mol
S° (gas)	117.1 cal/degree mol
C_ρ (cry)	57.9 cal/degree mol
C_ρ (gas)	49.0 cal/degree mol
ΔH_{vap}	17.3 kcal/mol

Preparation

Molybdenum hexacarbonyl usually is made by treating molybdenum pentachloride with zinc dust in carbon monoxide under high pressure (90 to 120 atm). Also, it can be prepared by direct combination of molybdenum metal powder with carbon monoxide under pressure.

Reactions

Thermal dissociation of molybdenum hexacarbonyl yields molybdenum metal and carbon monoxide.

The carbonyl undergoes a variety of complex formation reactions, involving partial or total replacement of CO groups with other donors. Many reactions have synthetic applications. Such donors include pyridine (py), diglyme, toluene, aniline, cycloheptatriene, alkyl disulfide and metal cyctopentadiene. A few examples are given below:

$$Mo(CO)_6 \xrightarrow[UV \text{ or heat}]{pyridine} (py)Mo(CO)_5,\ (py)_2Mo(CO)_4, (py)_3Mo(CO)_3$$

$$Mo(CO)_6 \xrightarrow{diglyme} (diglyme)Mo(CO)_5$$

$$Mo(CO)_6 \xrightarrow{aniline} (aniline)Mo(CO)_3$$

$$Mo(CO)_6 \xrightarrow{toluene} (toluene)Mo(CO)_3$$

$$Mo(CO)_6 \xrightarrow{C_5H_5Na} n^5 - C_5H_5Mo(CO)_3Na$$

$$Mo(CO)_6 \xrightarrow{cycloheptatriene} n^6 - C_7H_8Mo(CO)_3$$

Molybdenum hexacarbonyl also forms carbonylate anions, $Mo(CO)_5^{2-}$, carbonyl halide anions, $Mo(CO)_5^{x-}$ and carbonyl hydride anions, $Mo(CO)_5H^-$ in solution under controlled conditions. These species are unstable and have not been isolated.

Reaction with a carboxylic acid, RCOOH, forms the corresponding carboxylate complex $[Mo(OCOR)_2]_2$.

Reaction with mild reducing agents, such as sodium borohydride, $NaBH_4$, yields dimolybdenum decacarbonylate anion $[Mo_2(CO)_{10}]^{2-}$ in solution.

Analysis

Elemental composition: Mo 36.34%, C 27.30%, O 36.36%. A benzene solution of the hexacarbonyl may be analyzed by GC/MS. Molybdenum metal digested in nitric acid solution may be analyzed by various instrumental techniques. Also, the compound may be thermally dissociated and the liberated CO may be identified by GC using a TCD or by GC/MS using an appropriate capillary column.

Toxicity

Molybdenum hexacarbonyl is toxic by ingestion, inhalation and other routes of exposure. It decomposes, giving toxic carbon monoxide.

MOLYBDENUM HEXAFLUORIDE

[7783-77-9]
Formula: MoF_6; MW 209.93
Synonym: molybdenum(VI) fluoride

Uses

Molybdenum hexafluoride is used for separation of molybdenum isotopes.

Physical Properties

White cubic crystals or colorless volatile liquid; hygroscopic; density 2.54 g/cm^3; melts at 17.5°C; boils at 34°C; critical temperature 200°C; critical pressure 46.88 atm; critical volume 226 cm^3/mol; reacts with water (hydrolyzed).

Thermochemical Properties

$\Delta H_f°$ (l)	–378.9 kcal/mol
$\Delta H_f°$ (g)	–372.3 kcal/mol
$\Delta G_f°$ (l)	–352.1 kcal/mol
$\Delta G_f°$ (g)	–351.9 kcal/mol
S° (l)	62.1 cal/degree mol
S° (g)	83.8 cal/degree mol
C_ρ (l)	40.6 cal/degree mol
C_ρ (g)	28.7 cal/degree mol
ΔH_{fus}	1.03 kcal/mol
ΔH_{vap}	6.50 kcal/mol

Preparation

Molybdenum hexafluoride is prepared by passing fluorine over molybdenum powder:

$$Mo + 3F_2 \rightarrow MoF_6$$

Analysis

Elemental composition: Mo 45.70%, F 54.30%. The compound may be identified from its physical properties. Molybdenum may be analyzed by AA or ICP in an acid extract of the compound following digestion with nitric acid.

Toxicity

The compound is toxic by ingestion and is an irritant to skin.

MOLYBDENUM ORANGE

[12656-85-8]
Synonyms: molybdate orange; molybdate chrome orange; moly orange; molybdate red; chrome vermilion

Molybdenum orange is a solid solution of lead molybdate, lead chromate and often lead sulfate. It is used as a pigment in paints, plastics and printing inks. The pigment is used for red hues in automobile and appliance paints.

Molybdenum orange is precipitated by adding solutions of sodium chromate, sodium molybdate, and sodium sulfate to a solution of lead nitrate. The solid mixture is filtered and the precipitate is slowly dried under controlled conditions. Molybdenum orange is obtained as a fine powder of dark orange or light red color.

The compound is toxic by inhalation. There is sufficient evidence of its carcinogencity in humans.

MOLYBDENUM(IV) OXIDE

[18868-43-4]
Formula: MoO_2; MW 127.94
Synonym: molybdenum dioxide

Physical Properties

Greyish tetragonal or monoclinic crystals; density 6.47 g/cm^3; insoluble in water; slightly soluble in hot concentrated sulfuric acid; insoluble in alkalies, hydrochloric acid and hydrofluoric acid.

Thermochemical Properties

$\Delta H_f°$	–140.75 kcal/mol
$\Delta G_f°$	–127.39 kcal/mol
S°	11.07 cal/degree mol
C_ρ	13.38 cal/degree mol

Preparation

Molybdenum(IV) oxide is obtained by passing steam over red hot molybdenum:

$$Mo + 2H_2O \rightarrow MoO_2 + 2H_2$$

Alternatively, the oxide may be prepared by heating a molybdate salt, such as ammonium molybdate, with a reducing agent such as zinc. The dioxide also may be obtained along with other oxides of molybdenum when molybdenum metal is heated in air.

A brown-black suspension of MoO_2 in hydrate form may be obtained by reducing a solution of ammonium molybdate with hydrogen in the presence of colloidal palladium.

Reactions

The dioxide readily oxidizes to trioxide when heated in air. It also is oxidized to MoO_3 by nitric acid. When heated with hydrogen above 470°C, the oxide is reduced to molybdenum metal.

Unlike the trioxide, molybdenum dioxide is stable towards nonoxidizing acids, alkalies or fused salts.

Molybdenum(IV) oxide combines with chlorine at 300°C to form dioxydichloride, MoO_2Cl_2:

$$MoO_2 + Cl_2 \rightarrow MoO_2Cl_2$$

When heated above 1775°C in the absence of air, the dioxide dissociates to trioxide and metallic molybdenum:

$$3MoO_2 \rightarrow 2MoO_3 + Mo$$

When heated with carbon tetrachloride at elevated temperatures, the dioxide converts to molybdenum tetrachloride, $MoCl_4$:

$$MoO_2 + CCl_4 \rightarrow MoCl_4 + CO_2$$

Reactions with chlorinated hydrocarbons at elevated temperatures also yield the tetrachloride.

Analysis

Elemental composition: Mo 74.99%, O 25.01%. Molybdenum oxide is identified by x-ray crystallography. Molybdenum content in the oxide can be determined by AA, ICP, or x-ray fluorescence analysis.

MOLYBDENUM(VI) OXIDE

[1313-27-5]
Formula: MoO_3; MW 143.94
Synonyms: molybdenum trioxide; molybdic acid anhydride; molybdic anhydride; molybdic oxide

Uses

Molybdenum(VI) oxide is used in catalyst compositions to carry out desulfurization of petroleum feedstocks and to remove nitrogen-containing compounds from petroleum fractions. Other uses of this oxide include preparation of various molybdate salts and as reagents for chemical analyses.

Physical Properties

Soft white powder; orthorhombic crystals; turns yellow on heating; density 4.69 g/cm^3 at 21°C; melts at 795°C without decomposition to a dark yellow liquid; vapor pressure 20 torr at 851°C and 200 torr at 1,014°C; boils at 1,155°C; sparingly soluble in cold water (1.066 g/L at 18°C) and moderately soluble in hot water (20.55 g/L at 70°C); dissolves in acids and alkalies.

Thermochemical Properties

$\Delta H_f°$	–178.08 kcal/mol
$\Delta G_f°$	–159.66 kcal/mol
S°	18.58 cal/degree mol
C_ρ	17.92 cal/degree mol

Preparation

Molybdenum(VI) oxide is obtained by igniting molybdenum or its compounds in air:

$$2Mo + 3O_2 \rightarrow 2MoO_3$$

$$2MoS_2 + 7O_2 \rightarrow 2MoO_3 + 4SO_2$$

$$MoS_2 + 4O_2 \rightarrow MoO_3 + SO_2 + SO_3$$

Roasting the sulfide is carried out in a multiple-hearth roaster under controlled temperature and airflow. The product mixture is sublimed to obtain high purity oxide.

Purified molybdenum(VI) oxide also is made by prolonged heating of ammonium molybdate in air:

$$(NH_4)_2Mo_2O_7 \rightarrow 2MoO_3 + 2NH_3 + H_2O$$

An alternative method involves repeatedly evaporating a mixture of ammonium molybdate and nitric acid. Ammonium nitrate so formed is separated from the product molybdenum(VI) oxide by extraction with water:

$$(NH_4)_2Mo_2O_7 + 2HNO_3 \rightarrow 2MoO_3 + 2NH_4NO_3 + H_2O$$

Reactions

Molybdenum(VI) oxide is the most stable oxide of molybdenum. It reacts with alkali solutions, forming molybdates:

$$2MoO_3 + 2NaOH \rightarrow Na_2Mo_2O_7 + H_2O$$

Similarly, ammonium dimolybdate, $(NH_4)_2Mo_2O_7$, crystallizes when aqueous solutions of MoO_3 containing excess ammonia are evaporated at 100°C. Crystallization at low temperatures, however, forms ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, instead of dimolybdate.

Molybdenum(VI) oxide combines with several metal oxides forming their orthomolybdates. Such products are obtained as hydrated salts upon neutralization of slurries of MoO_3 and the metal oxides with alkalies:

$$MoO_3 + ZnO + nH_2O \rightarrow ZnMoO_4\cdot nH_2O$$

$$MoO_3 + Ag_2O + nH_2O \rightarrow Ag_2MoO_4\cdot nH_2O$$

When heated with sulfur vapor, molybdenum disulfide, MoS_2, is obtained.

Reaction with alkali fluorides (except LiF) yields double salts, such as $K_3[MoO_3F_3]$, formed as colorless cubic crystals.

When heated in dry hydrogen chloride, MoO_3 forms a hydrochloride adduct, $MoO_3\cdot 2HCl$, obtained as a sublimate of pale yellow needles.

A sulfuric acid solution of the oxide (25-75% solution) can be reduced with tin, copper, zinc, and other reducing agents forming a blue solution of "molybdenum blue" which are hydrous oxides of non-stoichiometric compositions (see Molybdenum Blue). Reduction with atomic hydrogen under carefully controlled conditions yields colloidal dispersion of compounds that have probable compositions $Mo_2O_4(OH)_2$ and $Mo_4O_{10}(OH)_2$. Reduction with lithium aluminum hydride yields a red compound of probable composition $Mo_5O_7(OH)_8$. Molybdenum(VI) oxide suspension in water also can be reduced to molybdenum blue by hydriodic acid, hydrazine, sulfur dioxide, and other reductants.

Molybdenum(VI) oxide behaves as a basic oxide in reactions with strong acids. Thus it forms an oxychloride, $MoO(OH)_2Cl_2$, with hydrochloric acid. Sulfuric acid forms an oxysulfate, MoO_2SO_4.

Heating with chlorine at 500°C yields MoO_2Cl_2 and with bromine vapor the products are MoO_2Br_2 and $Mo_2O_3Br_4$.

When heated with finely divided molybdenum at 750°C, molybdenum trioxide converts to pentaoxide, Mo_2O_5.

Analysis

Elemental composition: Mo 66.66%, O 33.34%. Molybdenum(VI) oxide may be identified from its physical and chemical properties and by x-ray analysis. Molybdenum content in the oxide can be measured by various instrumental techniques (see Molybdenum).

Toxicity

Molybdenum trioxide has been found to be toxic in experimental animals by oral, dermal, and intraperitoneal routes.

LD_{50} oral (rat): 125mg/kg
LD_{50} subcutaneous (mouse): 94 mg/kg

MOLYBDENUM PENTACHLORIDE

[10241-05-1]
Formula: $MoCl_5$; MW 273.20; monomeric in vapor phase but occurs as dimeric Mo_2Cl_{10} in solid phase (Mo—Mo bond 3.84 Å)
Synonym: molybdenum(V) chloride

Uses

Molybdenum pentachloride is used as a catalyst in chlorination reactions. It also is used in fire-retardant resins; for soldering of flux; for deposition of molybdenum coating; and to prepare several other molybdenum compounds, including molybdenum oxychlorides and hexacarbonyl.

Physical Properties

Greenish-black monoclinic crystals or dark red as liquid or vapor; paramagnetic; hygroscopic; density 2.93 g/cm^3; melts at 194°C; boils at 268°C; vapor density 9.5 (air=1) at 350°C; critical temperature 577°C; critical volume 369 cm^3/mol; soluble in dry ether, dry alcohol and many other organic solvents; reacts with water.

Thermochemical Properties

ΔH_{vap}	15.0 kcal/mol
ΔH_{fus}	4.54 kcal/mol

Preparation

Molybdenum pentachloride may be prepared by heating molybdenite in chlorine. Sulfur chloride formed in the reaction is removed by distillation:

$$2MoS_2 + 7Cl_2 \rightarrow 2MoCl_5 + 2S_2Cl_2$$

Also, the compound may be prepared by the action of chlorine on molybdenum metal at elevated temperatures (500°C):

$$2Mo + 5Cl_2 \rightarrow 2MoCl_5$$

The pentachloride may be obtained from the tetrachloride, $MoCl_4$. The latter, when heated in a sealed tube sublimes, and upon cooling, disproportionates to $MoCl_5$ and the trichloride, $MoCl_3$:

$$2MoCl_4 \rightarrow MoCl_5 + MoCl_3$$

Reactions

Molybdenum pentachloride is hydrolyzed readily in water forming an oxychloride, $MoOCl_3$. The reaction proceeds with hissing noise and evolution of heat.

$$MoCl_5 + H_2O \rightarrow MoOCl_3 + 2HCl$$

It forms the oxychlorides $MoOCl_3$ and MoO_2Cl_2 in contact with air or oxygen. $MoOCl_3$ is thermodynamically the most stable oxychloride.

When heated with hydrogen at 400°C or the vapors passed over heated molybdenum metal, the pentachloride converts to trichloride:

$$MoCl_5 + H_2 \rightarrow MoCl_3 + 2HCl$$

When refluxed in benzene, the pentachloride converts to tetrachloride, $MoCl_4$.

Reaction with potassium chloride in fused state or in the presence of iodine monochloride forms molybdenum hexachloride anion, $MoCl_6^{2-}$, which forms salts such as K_2MoCl_6:

$$MoCl_5 \xrightarrow{\text{fused KCl or KCl in ICl}} MoCl_6^{-}$$

Reaction with tetrachloroethylene forms molybdenum tetrachloride (an alpha-isomer of $MoCl_4$ that is isomorphous with $NbCl_4$.)

$$MoCl_3 + C_2Cl_4 \rightarrow \text{alpha-}MoCl_4$$

However, when the pentachloride is heated with hydrocarbons, a beta-form of $MoCl_4$ forms. The product always is contaminated with carbon. Heating the pentachloride with molybdenum metal forms the same beta-$MoCl_4$. Reaction with hydrogen bromide yields molybdenum tetrabromide.

Molybdenum pentachloride forms mixed complexes and oxychloride adducts with several donors. Thus, the adducts with pyridine, bipyridyl and alkyl nitriles are $MoCl_4(py)_2$, $MoCl_4(bipy)$ and $MoCl_4(RCN)_2$, respectively.

Combination with bipyridyl ligand in carbon tetrachloride followed by hydrolysis yields a molybdenum oxychloride bipyridyl complex of formula $MoOCl_3(bipy)$. When mixed with ammonium chloride in acetonitrile and water, an oxychloride-acetonitrile complex, $NH_4[MoOCl_4CH_3CN]$, is obtained.

Reactions with triphenylphosphine oxide, $(C_6H_5)_3P{=}O$, forms two products, an orange complex $MoO_2Cl_2[O(C_6H_5)_3]_2$ and a green complex, $MoOCl_3[O(C_6H_5)_3]_2$ (Cotton, F. A., Wilkinson, G., Murillo, C. A. and M. Bochmann. 1999. *Advanced Inorganic Chemistry*, 6th ed. p. 936: New York: John Wiley & Sons).

Analysis

Elemental composition: Mo 35.12%, Cl 64.88%. Molybdenum pentachloride may be identified from its physical properties and the products it forms in various reactions. The molybdenum content may be measured by flame or furnace-AA or ICP/AES measurement following digestion with nitric acid and appropriate dilution.

Toxicity

The compound is toxic by all routes of exposure and is corrosive to skin and eyes. The vapors irritate mucous membranes.

NEODYMIUM

[7440-00-8]
Symbol Nd; atomic number 60; atomic weight 144.24; a rare earth lanthanide element; a light rare earth metal of cerium group; an inner transition metal characterized by partially filled 4*f* subshell; electron configuration $[Xe]4f^35d^16s^2$; most common valence state +3; other oxidation state +2; standard electrode potential, $Nd^{3+} + 3e^- \leftrightarrow -2.323$ V; atomic radius 1.821Å (for CN 12); ionic radius, Nd^{3+} 0.995Å; atomic volume 20.60 cc/mol; ionization potential 6.31 eV; seven stable isotopes: Nd-142 (27.13%), Nd-143 (12.20%), Nd-144 (23.87%), Nd-145 (8.29%), Nd-146 (17.18%), Nd-148 (5.72%), Nd-150 (5.60%); twenty-three radioisotopes are known in the mass range 127-141, 147, 149, 151-156.

History, Occurrence, and Uses

The element was discovered by von Welsbach in 1885 after he succeeded in fractionating ammonium didymium nitrate, thus splitting didymia into two new rare earths. Earlier, in 1841, Mosander extracted a rose-colored oxide from cerite, which he named didymium and which actually was a mixture of two rare earth elements. These two new elements were named by von Welsbach as *praseodymia* (green twin) and *neodymia* (new twin).

Neodymium occurs in nature in the minerals bastnasite, monazite, cerite and allanite. The element always is associated with other rare earths, especially cerium group elements. Its abundance in the earth's crust is about 0.0024%.

The pure metal has very little commercial application. However, in the form of alloys neodymium has found some important but limited applications in metallurgy. It is added to cast iron, magnesium, aluminum, zirconium and titanium alloys. It imparts high temperature strength and creep resistance to these alloys. It acts as a "getter" for oxygen, sulfur, hydrogen, nitrogen and other elements. Small quantities of neodymium salts are used as a coloring agent for glass and porcelain, imparting red color. Neodymium oxide, Nd_2O_3, incorporated into glass is used as a laser material to produce coherent light. Its mixture with praseodymium, commonly known as didymium [8006-73-3] is used in making glass-blowing and welding goggles to protect eyes from sodium light. Such glass also is used in astronomy to produce sharp bands and calibrate spectral lines.

Physical Properties

Silvery-white, soft malleable metal; exists in two allotropic forms: an alpha hexagonal from and a beta form that has body-centered cubic crystal structure; the alpha allotrope converts to beta modification at 868°C; paramagnetic; density 7.004 g/cm^3; compressibility 3.0x10^{-6} cm^3/kg; melts at 1024°C; vaporizes at 3027°C; vapor pressure 400 torr at 2870°C; electrical resistivity 65x10^{-6} ohm-cm (as measured on polycrystalline wire at 25°C); Young's modulus 3.79x10^{-11} dynes/cm^2; Poisson's ratio 0.306; thermal neutron cross section 46 barns.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	78.3 kcal/mol
$\Delta G_f°$ (cry)	0.0
$\Delta G_f°$ (gas)	69.9 kcal/mol
S° (cry)	17.1 cal/degree mol
S° (gas)	45.2 cal/degree mol
C_ρ (cry)	6.56 cal/degree mol
C_ρ (gas)	5.28 cal/degree mol
ΔH_{fus}	1.70 kcal/mol
ΔH_{vap}	78.5 kcal/mol
Thermal conductivity (at 28°C)	0.031 cal/cm^2/sec/°C

Reactions

Neodymium corrodes slowly in dry atmosphere at ambient temperature. However, in moist air, the rate of oxidation is faster, forming a hydrated oxide. At elevated temperatures, the metal combines with oxygen, forming neodymium sesquioxide. Above 200°C the metal burns in halogens forming halides. Neodymium combines with many nonmetallic elements including hydrogen, nitrogen, carbon, phosphorus, and sulfur at elevated temperatures forming their binary compounds. With hydrogen, products are interstitial hydrides, NdH_2 and NdH_3. It combines with metalloid elements boron, selenium, and arsenic at elevated temperatures forming the corresponding boride, selenide, and arsenide respectively.

The metal dissolves in dilute mineral acids, but concentrated sulfuric acid has little action on it. Its surface passivates when immersed in 2 to 5% solution of nitric acid in ethanol. A protective oxide layer forms over the metal surface, which prevents any further contact.

Neodymium is a moderately strong reducing agent. It reduces several metal oxides, such as magnesia, alumina, silica, and zirconia at elevated temperatures, converting these oxides to their metals.

Production

Neodymium is recovered mostly from mineral monazite and bastnasite, the two most abundant rare-earth minerals. Monazite is a rare earth-thorium phosphate usually containing between 9 to 20% neodymium. Bastnasite is a rare earth fluocarbonate ore containing 2 to 15% neodymium. Both ores are first cracked by heating with concentrated sulfuric acid or sodium hydroxide. The recovery process from monazite ore using sulfuric acid is described below:

Heating the ore with sulfuric acid converts neodymium to its water soluble sulfate. The product mixture is treated with excess water to separate neodymium as soluble sulfate from the water-insoluble sulfates of other metals, as well as from other residues. If monazite is the starting material, thorium is separated from neodymium and other soluble rare earth sulfates by treating the solution with sodium pyrophosphate. This precipitates thorium pyrophosphate. Alternatively, thorium may be selectively precipitated as thorium hydroxide by partially neutralizing the solution with caustic soda at pH 3 to 4. The solution then is treated with ammonium oxalate to precipitate rare earth metals as their insoluble oxalates. The rare earth oxalates obtained are decomposed to oxides by calcining in the presence of air. Composition of individual oxides in such rare earth oxide mixture may vary with the source of ore and may contain neodymium oxide, as much as 18%.

The oxalates obtained above, alternatively, are digested with sodium hydroxide converting the rare earth metals to hydroxides. Cerium forms a tetravalent hydroxide, $Ce(OH)_4$, which is insoluble in dilute nitric acid. When dilute nitric acid is added to this rare earth hydroxide mixture, cerium(IV) hydroxide forms an insoluble basic nitrate, which is filtered out from the solution. Cerium also may be removed by several other procedures. One such method involves calcining rare earth hydroxides at 500°C in air. Cerium converts to tetravalent oxide, CeO_2, while other lanthanides are oxidized to trivalent oxides. The oxides are dissolved in moderately concentrated nitric acid. Ceric nitrate so formed and any remaining thorium nitrate present is now removed from the nitrate solution by contact with tributyl phosphate in a countercurrent.

After removing cerium (and thorium), the nitric acid solution of rare earths is treated with ammonium nitrate. Lanthanum forms the least soluble double salt with ammonium nitrate, which may be removed from the solution by repeated crystallization. Neodymium is recovered from this solution as the double magnesium nitrate by continued fractionation.

Three alternative methods may be mentioned here, which give high purity material and are less tedious than the one described above. These are (1) ion exchange, (2) metallothermic reduction, and (3) electrolysis.

In the ion exchange process, the nitric acid solution of the rare earth oxides obtained above is passed through a sulfonated styrene-divinylbenzene copolymer or other cation exchange resin in the hydrogen form. The rare earths are selectively eluted by flowing down a chelating solution of ethylenediamine tetraacetic acid (EDTA), or citric acid, or nitrilotriacetate (NTA) through the loaded column. The most stable complexes are eluted first. Metal ions are selectively stripped out in successive stages.

In the metallothermal reduction, the mixture of rare earth oxides obtained above is first converted to their halide salts. This is done by heating the oxides at 300 to 400°C with dry and purified hydrogen fluoride, or preferably, by allowing dry hydrogen fluoride to pass over rare earth oxides and ammonium fluoride at 300-400°C. If chloride salt is desired, the oxides must be heated with ammonium chloride. For example, neodymium oxide may be converted to its fluoride or chloride:

$$Nd_2O_3 + 6NH_4F \cdot HF \rightarrow 2NdF_3 + 6NH_4F\uparrow + 3H_2O\uparrow$$

$$Nd_2O_3 + 6NH_4Cl \rightarrow 2NdCl_3 + 6NH_3\uparrow + 3H_2O\uparrow$$

Neodymium, along with lanthanum, cerium and praseodymium, has low melting points and high boiling points. The fluorides of these and other rare earth metals are placed under highly purified helium or argon atmosphere in a platinum, tantalum or tungsten crucible in a furnace. They are heated under this inert atmosphere or under vacuum at 1000 to 1500°C with an alkali or alkaline earth metal. The halides are reduced to their metals:

$$2NdF_3 + Ca \rightarrow 2Nd + 3CaF_2$$

$$NdCl_3 + 3Li \rightarrow Nd + 3LiCl$$

The crucible is allowed to cool and is held at a temperature slightly above the melting point of neodymium for a sufficient time to allow separation of the metal.

In the electrolytic process, a fused mixture of anhydrous rare earth chlorides (obtained above) and sodium or potassium chloride is electrolyzed in an electrolytic cell at 800 to 900°C using graphite rods as the anode. The cell is constructed of iron, carbon or refractory linings. Molten metal settles to the bottom and is removed periodically.

Analysis

Neodymium may be analyzed by x-ray diffraction, x-ray fluorescence, atomic absorption, or atomic emission spectrometry. Also, the metal may be identified and measured by neutron activation analysis.

NEODYMIUM OXIDE

[1313-97-9]
Formula: Nd_2O_3; MW 336.48
Synonyms: neodymia; neodymium sesquioxide

Uses

Neodymium oxide is incorporated into glass to impart a bright purple color. It also is used in protective filter lenses for welding and glass-blowing goggles; and for polishing glasses. The compound is applied as a doping material for yttrium aluminum microwave devices; and to activate calcium tungstate, calcium silicate, and other host crystals for their applications in room temperature lasers. The oxide also is used as a catalyst for dehydrogenation of alcohol.

Physical Properties

Blue powder; hexagonal crystals; fluoresces red; density 7.24 g/cm^3; melts around 1,900°C; practically insoluble in water, 30 mg/L at 75°C; dissolves in acids.

Thermochemical Properties

$\Delta H_f°$	–432.1 kcal/mol
$\Delta G_f°$	–411.3 kcal/mol
$S°$	37.9 cal/degree mol
C_ρ	26.6 cal/degree mol

Production

Neodymium oxide is produced from the two principal rare earth minerals, monazite, and bastnasite. The oxide is obtained as an intermediate in the recovery of neodymium metal (See Neodymium).

The oxide also may be formed by thermal dissociation of neodymium oxalate, hydroxide or carbonate:

$$Nd_2(C_2O_4)_3 \rightarrow Nd_2O_3 + 6CO_2$$

$$2Nd(OH)_3 \rightarrow Nd_2O_3 + 3H_2O$$

$$Nd_2(CO_3)_3 \rightarrow Nd_2O_3 + 3CO_2$$

Reactions

The anhydrous oxide absorbs moisture from the air at ambient temperatures forming hydrated oxide. The oxide also absorbs carbon dioxide from air, forming neodymium carbonate.

Neodymium oxide dissolves in strong mineral acids forming corresponding neodymium salts:

$$Nd_2O_3 + 3H_2SO_4 \rightarrow Nd_2(SO_4)_3 + 3H_2O$$

Reactions with acetic and other organic acids produce corresponding salts.

When heated with ammonium chloride at 300 to 400°C, the oxide converts to chloride liberating ammonia and water:

$$Nd_2O_3 + 6NH_4Cl \rightarrow 2NdCl_3 + 6NH_3 + 3H_2O$$

When heated with hydrogen fluoride, the product is neodymium fluoride:

$$Nd_2O_3 + 6HF \rightarrow 2NdF_3 + 3H_2O$$

The oxide is reduced to neodymium metal when heated with hydrogen, carbon monoxide, or other reducing agents.

Analysis

Elemental composition: Nd 85.73%, O 14.27%. The oxide may be characterized by x-ray diffraction and fluorescent properties. Neodymium may be analyzed in an acid extract of the oxide by ICP-AES or ICP-MS techniques under appropriate dilution of the extract.

NEON

[7440-01-9]
Symbol Ne; atomic number 10; atomic weight 20.179; an inert gas; a Group VIII or Group 0 (Group 18) noble gas element; electron configuration $1s^22s^22p^6$; valence 0; atomic radius 0.71Å; three stable isotopes, Ne-20 (90.48%), Ne-21 (0.27%), Ne-22 (9.25%); ten short-lived artificial isotopes are known in the mass range 17-19, 23-29; half-life of longest radioactive isotope Ne-24 is 3.34 min.

History, Occurrence, and Uses

Neon was discovered by Ramsay and Travers in 1898.Its name comes from the Greek word *neos*, which means new. It is present in the atmosphere at a concentration of 0.00182% by volume (dry atmosphere). This element also is found in stars and interstellar gas clouds. Earth's earliest crust probably contained neon occluded in minerals. The gas later escaped into the atmosphere.

The most important use of this gas is in the 'neon' lights and fluorescent signs for advertisements. Neon contained in glow discharge lamps or high voltage discharge tubes at low pressure emits red light. In the presence of mercury vapors, the color of the glow turns blue. Neon also is used in sodium vapor lamps for street lighting and in various pilot lamps for electronic equipments. In most types of fluorescent lights neon is used in combination with other inert gases, usually argon, krypton, and xenon.

Neon is also used in scintillation counters, neutron fission counters, proportional counters, and ionization chambers for detection of charged particles. Its mixtures with bromine vapors or chlorine are used in Geiger tubes for counting nuclear particles. Helium-neon mixture is used in gas lasers. Some other applications of neon are in antifog devices, electrical current detectors, and lightning arrestors. The gas is also used in welding and preparative reactions. In preparative reactions it provides an inert atmosphere to shield the reaction from air contact.

Physical Properties

Colorless, odorless, tasteless gas; gas density 0.9002 g/L at 0°C; liquid density 1.206 g/mL at its boiling point; liquefies at –245.9°C; solidifies at –248.67°C; forming face-centered cubic crystals; critical temperature –228.75°C; critical pressure 26.9 atm; solubility in water at 20°C, 10.5 mL/L.

Production

Neon is derived commercially from the atmosphere. It is recovered from air after separation of oxygen and nitrogen in air separation plants. The recovery process is based on liquefaction of air. Neon and helium have boiling points below that of liquid air. Thus, at liquid air temperature, nitrogen, oxygen, argon, krypton, and xenon remain in the liquid form, while a gas stream consisting of neon, helium, and some nitrogen is collected as gaseous mixture. The composition of this mixture can vary with the condenser and rate of withdrawal. Nitrogen is removed further by passing the gaseous mixture at 5 to 6 atm through a condenser maintained at liquid nitrogen temperatures. The residue after this step contains neon as the major component, with significant amounts of helium, hydrogen, and nitrogen.

Such crude neon mixture is purified by various chemical and physical processes. Hydrogen is separated by chemically oxidizing it to water, which is removed by drying. Remaining nitrogen from the crude neon is removed by adsorption over charcoal at the liquid nitrogen temperature. After the removal of nitrogen and hydrogen, the technical grade neon may contain about 75% neon and 25% helium. Such neon-helium mixtures may be further separated into their individual components either by differential absorption on charcoal at cold temperatures or by fractional distillation of their liquefied mixture. Fractional distillation, based on the difference of boiling points between helium (–269°C) and neon (–223°C), is the more expensive process. Neon also may be obtained in liquid form if the charcoal in the adsorption process is maintained at its liquefaction temperature. Process conditions may vary depending on purity of the product desired.

Compounds

Being a zero valent element and having a highly stable octet configuration, neon is inert to practically all chemicals. However, unlike some other inert gases such as xenon which forms fluorides, oxides, or oxofluorides or argon, which forms clatharates, no such compounds are known for neon. Neon forms an unstable hydrate at low temperature under high pressure. It does ionize, however, under high vacuum as in the electric discharge tube, forming ions such as Ne_2^+, $(HeNe)^+$, NeH^+, and $(NeAr)^+$. Such ions have been identified from optical and mass spectroscopic studies.

Analysis

Neon may be analyzed by GC using a thermal conductivity or a flame ionization detector. The gas may be measured by GC/MS using a capillary column. Characteristic masses for its GC/MS identification are 20 and 22.

NEPTUNIUM

[7439-99-8]

Symbol Np; atomic number 93; atomic weight 237 (most stable isotope); a man-made transuranium radioactive element; actinide series; electron configuration $[Rn]5f^46d^17s^2$; oxidation states +3, +4, +5 and +6; most stable valence state +3; the longest-lived isotope Np-237 has a half-life of 2.14x10^6 year; seventeen isotopes are known in the mass range 226-242.

History, Occurrence, and Uses

Neptunium, the first transuranium element, was discovered by E. M. McMillan and P. H. Abelson in 1940 in Berkeley, California. It was produced in the cyclotron in a nuclear reaction by bombarding uranium-238 with neutrons. An isotope of mass 239 and atomic number 93 and $t_{1/2}$ of 2.4 days was produced in this reaction. Neptunium-237, the longest-lived alpha-emitter with half-life 2.14x10^6 years, was discovered two years later in 1942 by Wahl and Seaborg. The new element was named after the planet Neptune, the planet next to Uranus in the solar system.

Neptunium is not found in nature in any extractable quantities. However, it occurs in uranium ores in exceedingly small concentrations resulting from neutron capture of uranium isotopes. No major application is known for this element. Its isotope, Np-237, is used in neutron detection instruments.

Physical Properties

Silvery-white metal; exhibits three crystalline modifications: an orthorhombic alpha form, stable at ordinary temperatures and density 20.45 g/cm^3; the alpha-form transforms to a tetragonal beta allotrope of density 19.36 g/cm^3 when heated at 280°C; the beta form converts to a body-centered cubic crystalline gamma modification at 577°C, having a density 18.0 g/cm^3.

The metal melts at 644°C; boils at 3,902°C (estimated); dissolves in hydrochloric acid.

Production

Neptunium-237 is obtained as a by-product of making plutonium from uranium isotopes in nuclear reactors. Significant amounts of this element may be recovered from plutonium plant nuclear wastes. Both the recovery and purification of neptunium can be carried out by various chemical processes, including precipitation, solvent extraction and ion exchange.

Neptunium-237 may be synthesized by bombarding uranium-235 or uranium-238 with neutrons:

$$^{235}_{92}U \xrightarrow{n} {}^{236}_{92}U + \gamma \xrightarrow{n} {}^{237}_{92}U + \gamma \xrightarrow{\beta^-} {}^{237}_{93}Np$$

Neptunium-239 may be obtained from uranium-238 by neutron bombardment as it was first produced:

$$^{238}_{92}U \xrightarrow{n} {}^{239}_{92}U + \gamma \xrightarrow{\beta^-} {}^{239}_{93}Np$$

Neptunium may be prepared in the metallic state by the reduction of its trifluoride with barium vapor at 1,200°C followed by rapid cooling. Its tetrafluoride may be reduced with excess calcium metal at about 750°C under argon atmosphere.

Neptunium Compounds

Neptunium is a reactive metal. Some of its chemical properties are similar to uranium and plutonium. Neptunium exists in several oxidation states, both in solutions and solid crystals. Several compounds have been well characterized by x-ray crystallography. Among its oxides, the green dioxide, NpO_2 may be obtained by thermal decomposition of its nitrate, hydroxide, or oxalate at 700 to 800°C. Two other oxides, a dark brown Np_2O_5 and a brown Np_3O_8, also are known. All these oxides may be prepared by several methods, including heating the hydroxide $Np(OH)_5$ in air above 275°C, or by treating neptunium metal with molten lithium perchlorate in the presence of ozone.

Neptunium forms a number of halides in various oxidation states. These include tri-, tetra- and hexafluorides of compositions NpF_3, NpF_4, and NpF_6, respectively; trichloride, $NpCl_3$ and tetrachloride, $NpCl_4$; tribromide, $NpBr_3$; and the triiodide NpI_3. Neptunium fluorides are formed by heating neptunium dioxide at elevated temperatures with fluorine in the presence of hydrogen fluoride. The tetrachloride, $NpCl_4$ is obtained similarly by heating the dioxide with carbon tetrachloride vapor at temperatures above 500°C. Neptunium tribromide and triiodide are prepared by heating the dioxide in a sealed vessel at 400°C with aluminum bromide and aluminum iodide, respectively.

Neptunium metal reacts with hydrogen under milder conditions at 50°C and one atmospheric pressure, forming hydrides of varying stoichiometric compositions. The metal combines with carbon at 1,200°C, forming two carbides, NpC and Np_2C_3. Heating the trifluoride, NpF_3 with silicon at 1,500°C forms neptunium silicide, $NpSi_2$. Many other neptunium compounds have been prepared and their crystal structures determined. These include the black orthorhombic sulfide, Np_2S_3, and the tetragonal oxysulfide, NpOS, and the pink hexagonal oxofluoride, NpO_2F_2. Neptunium also is known to form many intermetallic compounds with aluminum, beryllium and other metals.

In solution, neptunium oxidizes to Np^{3+} and Np^{4+} ions, the salts of which are pink and greenish-yellow, respectively. Unlike its rare earth analog promethium, neptunium also forms oxoions, such as, NpO^+ (blue green) and NpO^{2+} (light pink).

NICKEL

[7440-02-0]
Symbol: Ni; atomic number 28; atomic weight 58.693; a transition metal element in the first triad of Group VIII(Group 10) after iron and cobalt; electron configuration $[Ar]3d^84s^2$; valence states 0, +1, +2, and +3; most common oxidation state +2; the standard electrode potential, $Ni^{2+} + 2e^- \leftrightarrow Ni$ –0.237 V; atomic radius 1.24Å; ionic radius (Ni^{2+}) 0.70Å; five natural isotopes: Ni-58 (68.08%), Ni-60 (26.22%), Ni-61 (1.14%), Ni-62 (3.63%), Ni-64 (0.93%); nineteen radioactive isotopes are known in the mass range 51-57, 59, 63, 65-74; the longest-lived radioisotope Ni-59 has a half-life $7.6x10^4$ years.

History, Occurrence, and Uses

Nickel was isolated first and recognized as an element by Cronstedt in 1751. The metal was derived in pure form by Richter in 1804. The metal takes its name from two German words 'Nickel' and 'kupfernickel', which mean Old Nick's (or Satan) and Old Nick's copper, respectively.

The abundance of nickel in the earth's crust is only 84 mg/kg, the 24th most abundant element. It is found in most meteorites, particularly in the iron meteorites or siderites, alloyed with iron. Its average concentration in seawater is 0.56 µg/mL. Nickel is one of the major components of the earth's core, comprising about 7%.

The most common nickel ores are pentlandite, $(Ni,Fe)_9S_{16}$, limonite, $(Fe,Ni)O(OH) \cdot nH_2O$, and garnierite, $(Ni,Mg)_6Si_4O_{10}(OH)_8$. Other ores that are of rare occurrence are the sulfide ores, millerite, NiS, polydymite Ni_3S_4 and siegenite, $(Co,Ni)_3S_4$; the arsenide ores niccolite, NiAs, gersdorffite, NiAsS, and annabergite, $Ni_3As_2O_8 \cdot 8H_2O$; and the antimonide ore, NiSb.

The most important applications of nickel metal involve its use in numerous alloys. Such alloys are used to construct various equipment, reaction vessels, plumbing parts, missile, and aerospace components. Such nickel-based alloys include Monel, Inconel, Hastelloy, Nichrome, Duranickel, Udinet, Incoloy and many other alloys under various other trade names. The metal itself has some major uses. Nickel anodes are used for nickel plating of many base metals to enhance their resistance to corrosion. Nickel-plated metals are used in various equipment, machine parts, printing plates, and many household items such as scissors, keys, clips, pins, and decorative pieces. Nickel powder is used as porous electrodes in storage batteries and fuel cells.

Another major industrial use of nickel is in catalysis. Nickel and raney nickel are used in catalytic hydrogenation or dehydrogenation of organic compounds including olefins, fats, and oils.

Physical Properties

Silvery-white lustrous metal; face-centered cubic crystal structure; ductile; ferromagnetic; density 8.908 g/cm^3 at 20°C; hardness 3.8 Mohs; melts at 1,455°C; vaporizes at 2,730°C; electrical resistivity 6.97 microhm-cm at 20°C; total emissivity 0.045, 0.060 and 0.190 erg/s.cm^2 at 25, 100 and 1,000°C, respectively; modulus of elasticity (tension) 206.0x10^3 MPa, modulus of elasticity (shear) 73.6x10^3 MPa; Poisson's ratio 0.30; thermal neutron cross section (for neutron velocity of 2,200 m/s): absorption 4.5 barns, reaction cross section 17.5 barns; insoluble in water; dissolves in dilute nitric acid; slightly soluble in dilute HCl and H_2SO_4; insoluble in ammonia solution.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	102.7 kcal/mol
$\Delta G_f°$ (cry)	0.0
$\Delta G_f°$ (gas)	91.9 kcal/mol
S° (cry)	7.14 cal/degree mol
S° (gas)	43.52 cal/degree mol
C_ρ (cry)	6.23 cal/degree mol

C_p (gas)	5.58 cal/degree mol
Co-efficient of thermal expansion	13.3×10^{-6}/°C (at 0-100°C)
Thermal conductivity (at 100°C)	82.8 W/m.K

Production

Nickel usually is recovered from its sulfide ore, pentlandite $(Ni,Fe)_9S_{16}$. Although laterite type oxide ores sometimes are used as starting materials, pentlandite is used in many commercial operations. Pentlandite often is found in nature associated with other sulfide minerals, such as pyrrhotite, Fe_7S_8,and chalcopyrite, $CuFeS_2$.

The ores are crushed and powdered. Sulfides are separated from gangue by froth flotation or magnetic separation processes. After this, the ore is subjected to roasting and smelting. These steps are carried out initially in rotary kilns or multihearth furnaces and then smelting is done in either blast furnaces or reverberatory, or arc furnaces. Most sulfur is removed as sulfur dioxide. Iron and other oxides produced in roasting are also removed along with siliceous slag during smelting. A matte obtained after smelting usually contains impure nickel-iron-copper sulfides and sulfur. The molten matte is treated with silica and an air blower in a converter in the Bessemerizing stage to remove all remaining iron and sulfur.

Copper-nickel matte obtained in this stage is allowed to cool slowly over a few days to separate mineral crystals of copper sulfide, nickel sulfide and nickel-copper alloy. The cool matte is pulverized to isolate sulfides of nickel and copper by froth flotation. Nickel-copper alloy is extracted by magnetic separation. Nickel metal is obtained from the nickel sulfide by electrolysis using crude nickel sulfide cast into anodes and nickel-plated stainless steel cathodes.

Alternatively, nickel sulfide is roasted to nickel oxide, which then is reduced to crude nickel and is electrorefined as above.

Two other refining processes are also frequently employed. One involves hydrometallurgical refining in which sulfide concentrates are leached with ammonia solution to convert the copper, nickel, and cobalt sulfides into their complex amines. Copper is precipitated from this solution upon heating. Under such conditions, the sulfide-amine mixture of nickel and cobalt are oxidized to their sulfates. The sulfates then are reduced to metallic nickel and cobalt by heating with hydrogen at elevated temperatures under pressure. The metals are obtained in their powder form.

The more common carbonyl refining process involves reaction of crude nickel with carbon monoxide under pressure at 100°C to form nickel tetracarbonyl, $Ni(CO)_4$. The liquid tetracarbonyl upon heating at 300°C decomposes to nickel metal and carbon monoxide. Very pure nickel can be obtained by the carbonyl refining processes, as no other metal forms a similar carbonyl under these conditions.

Reactions

At ordinary temperatures, bulk nickel in compact form has no perceptible reactivity with air or water. However, in finely-divided state, the metal reacts readily and can be pyrophoric under certain conditions. When heated in air at 400°C or with steam, nickel converts to its oxide, NiO.

When heated with bromine vapors or chlorine gas, nickel catches fire forming nickel bromide, $NiBr_2$, and yellow nickel chloride, $NiCl_2$, respectively.

Finely divided nickel combines with carbon monoxide to form zero valent nickel tetracarbonyl, $Ni(CO)_4$. The reaction occurs at 50°C and one atmosphere, although it is usually carried out at 200°C under high CO pressure between 100 to 400 atm for high yield of carbonyl, and to prevent product decomposition. Carbon monoxide at ordinary pressure may be passed over freshly reduced metal to form the tetracarbonyl.

Finely divided nickel absorbs a large volume of hydrogen at high temperatures. Even at ordinary temperatures, considerable occlusion of hydrogen occurs on to the metal surface and no definite composition of any hydride formed is known. The metal activates molecular hydrogen to its atomic state, contributing to its catalytic action in hydrogenation of unsaturated compounds.

Dilute mineral acids attack nickel to a varying extent. The metal dissolves readily in dilute nitric acid. Evaporation of the solution forms emerald green crystals of nickel nitrate hexahydrate, $Ni(NO_3)_2 \cdot 6H_2O$.

Actions of dilute hydrochloric and sulfuric acid on nickel are relatively slow: slower than on iron. Concentrated nitric acid passivates the metal, oxidizing it and forming a protective film on its surface which prevents any further reaction.

Nickel is stable in caustic alkalies. At moderate temperatures, it decomposes gaseous ammonia into hydrogen and nitrogen. Nickel combines with sulfur, phosphorus, carbon, arsenic, antimony, and aluminum at elevated temperatures. Fusion of nickel powder with molten sulfur yields nickel sulfide, NiS. Reaction with aluminum can be explosive at 1,300°C, forming nickel-aluminum intermetallic products of varying compositions.

Nickel powder combines with carbon dioxide in ammonia solution forming nickel carbonate. Boiling the solution to expel ammonia precipitates pure carbonate, $NiCO_3$.

Fine nickel powder reacts with sulfamic acid in hot aqueous solution under controlled conditions, forming nickel sulfamate tetrahydrate, $Ni(SO_3NH_2)_2 \cdot 4H_2O$, used in electroplating baths.

Analysis

Nickel may be measured quantitatively by several microanalytical gravimetric methods that include: (1)formation of a red precipitate with dimethylglyoxime, (2) precipitation as a black sulfide with ammonium sulfide, (3) precipitating as a complex cyanide by treating with alkali cyanide and bromine, and (4) precipitation as a yellow complex by treating an ammoniacal solution of nickel with dicyandiamide sulfate (Grossman's reagent), followed by the addition of potassium hydroxide. All of these methods can separate nickel from cobalt in solution.

Nickel, however, may be measured more accurately and rapidly at trace concentrations by various instrumental techniques including flame and furnace AA, ICP/AES, ICP-MS, and x-ray fluorescence. The wavelength at which nickel is measured by AA is 232.0 nm. For flame AA measurement, air-acetylene is recommended as a flame gas. The wavelength for ICP/AES measurement should be 231.60 nm. If there is any interference from other elements, an alternative wavelength of 221.65 nm can be used.

ICP-MS is the most sensitive method to detect nickel at low ppt. X-ray methods are relatively less sensitive to AA or ICP/AES spectrometry but they do not require any acid digestion of the metal or its salts. They can be applied to solid powder for nondestructive measurement of the metal.

Toxicity

Skin contact can cause dermatitis and a type of chronic eczema, known as "nickel itch", caused by hypersensitivity reactions of nickel on the skin (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. pp. 621-622, New York: John Wiley & Sons.) Although oral toxicity of the metal is very low, ingestion may cause hyperglycemia and depression of the central nervous system. Chronic inhalation of nickel dust can cause lung and sinus cancers in humans. Nickel and certain of its compounds are listed by IARC under Group 2B carcinogens as "possibly carcinogenic to humans" (*International Agency for Research on Cancer*. 1990. IARC Monograph, Vol. 49: Geneva.)

NICKEL ACETATE

[373-02-4]
Formula $(CH_3COO)_2Ni$; MW 176.80; forms a stable tetrahydrate, $Ni(CH_3COO)_2 \cdot 4H_2O$ [6018-89-9].

Uses

Nickel acetate is used as a catalyst. It also is used as a dye mordant in textiles. Other applications are in electroplating nickel and as a sealer for anodizing aluminum.

Physical Properties

The tetrahydrate is a green crystalline solid; sweet taste; odor of acetic acid; density 1.744 g/cm^3; loses water on heating to form a yellow-green powder of anhydrous nickel acetate; decomposes above 250°C; soluble in water, 17g/100mL at 20°C; sparingly soluble in alcohol.

Preparation

Nickel acetate is prepared by reacting nickel hydroxide or nickel carbonate with dilute acetic acid. The tetrahydrate is crystallized from solution.

$$Ni(OH)_2 + 2CH_3COOH \rightarrow (CH_3COO)_2Ni + 2H_2O$$

$$NiCO_3 + 2CH_3COOH \rightarrow (CH_3COO)_2Ni + CO_2 + 2H_2O$$

On heating, the solution hydrolyzes depositing nickel hydroxide.

Analysis

Elemental composition (of anhydrous acetate): Ni 33.21%, C 27.17%, H 3.42%, O 36.20%. The water of crystallization of the tetrahydrate may be determined by TGA and DTA methods. Nickel content of the salt may be determined by AA, ICP-AES and other instrumental techniques.

NICKEL ACETYLACETONATE

[3264-82-2]
Formula: $(CH_3COCHCOCH_3)_2Ni$; MW 256.93; monomeric in vapor phase but trimeric in solid phase; forms a dihydrate
Synonyms: bis(acetylacetonato)nickel(II); bis(2,4-pentanediono)nickel(II); bis(2,4-pentanedionato-O,O')nickel

Uses

Nickel acetylacetonate is used as a catalyst in hydrogenation and other organic reactions.

Physical Properties

Emerald-green crystals; orthorhombic structure; density 1.455 g/cm^3 at 17°C; melts at 230°C; soluble in water, alcohol, chloroform, benzene and toluene; insoluble in ether.

Preparation

Nickel acetylacetonate is prepared by the reaction of acetylacetone with nickel chloride hexahydrate or nickel hydroxide, followed by crystallization:

$$2CH_3C(=O)CH_2C(=O)CH_3 + Ni(OH)_2 \rightarrow Ni(CH_3C(=O)CHC(=O)CH_3)_2 + 2H_2O$$

Analysis

Elemental composition: Ni 22.85%, C 46.75%, H 5.49%, O 24.91%. The compound may be characterized by its physical properties, elemental analysis, and by IR, UV and NMR spectra and x-ray diffraction data. A benzene or chloroform solution may be injected directly into a GC column and may be identified from its mass spectra. The characteristic mass ions for its identification by GC/MS are 58, 60, 100, 257. The aqueous solution or the nitric acid extract may be analyzed either by flame or furnace AA, or by ICP-AES to determine nickel content.

NICKEL CARBONATE

[3333-67-3]
Formula: $NiCO_3$; MW 118.72
Two basic carbonates are known. They are $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$ [29863-10-3], and $NiCO_3 \cdot 2Ni(OH)_2$ [12607-70-4], MW 304.17. The second form occurs in nature as a tetrahydrate, mineral, zaratite. Commercial nickel carbonate is usually the basic salt, $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$.

Uses

Nickel carbonate is used to prepare nickel catalysts and several specialty compounds of nickel. It also is used as a neutralizing agent in nickel plating solutions. Other applications are in coloring glass and in the manufacture of ceramic pigments.

Physical Properties

$NiCO_3$: Light green rhombohedral crystals; decomposes on heating; practically insoluble in water, 93 mg/L at 25°C; dissolves in acids.

$2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$: Light green crystals or brown powder; decomposes on heating; insoluble in water; decomposes in hot water; soluble in acids and in ammonium salts solutions.

Zaratite: Emerald greed cubic crystals; density 2.6 g/cm^3; insoluble in water; soluble in ammonia and dilute acids.

Thermochemical Properties

$\Delta H_f°$ ($NiCO_3$)	–140.6 kcal/mol

Preparation

Anhydrous nickel carbonate is produced as a precipitate when calcium carbonate is heated with a solution of nickel chloride in a sealed tube at 150°C. Alternatively, treating nickel powder with ammonia and carbon dioxide followed by boiling off ammonia yields pure carbonate.

When sodium carbonate is added to a solution of Ni(II) salts, basic nickel carbonate precipitates out in impure form.

Reactions

Nickel carbonate is the starting material for preparing many nickel salts. It reacts with dilute acids evolving carbon dioxide, and upon evaporation of the solution corresponding nickel salts are formed. The nitrate, sulfate and phosphate salts are prepared from carbonate. Similarly, reactions with hydrofluoric, hydrochloric, hydrobromic, or hydriodic acids yield hydrated nickel halides: namely $NiF_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$, $NiBr_2 \cdot 6H_2O$, and $NiI_2 \cdot 6H_2O$, respectively:

$$NiCO_3 + HCl \rightarrow NiCl_2 \cdot 6H_2O + CO_2$$

Nickel carbonate decomposes to nickel oxide when strongly ignited:

$$NiCO_3 \rightarrow NiO + CO_2$$

Nickel carbonate, when dissolved in aqueous thiocyanic acid, yields a yellow brown precipitate of hydrated nickel thiocyanate:

$$2\ NiCO_3 + 2HSCN \rightarrow Ni(SCN)_2 + CO_2 + H_2O$$

Nickel carbonate forms many double salts, such as, $Na_2CO_3 \cdot NiCO_3 \cdot 10H_2O$ with alkali metal carbonates. However, such double carbonates usually are prepared by mixing an alkali metal or ammonium bicarbonate solution with a nickel salt solution, followed by crystallization.

Analysis

Anhydrous and basic nickel carbonates may be determined from x-ray diffraction measurements. The degree of hydration can be measured by DTA and TGA methods. Additionally nickel content in the carbonate may be determined by analyzing an acid solution of the salt using various instrumental methods (See Nickel).

NICKEL CHLORIDE

[7718-54-9]
Formula: $NiCl_2$; MW 129.60; forms a stable hexahydrate, $NiCl_2 \cdot 6H_2O$ [7791-20-0], MW 237.69 at ordinary temperatures.
Synonyms: nickel dichloride; nickel(II) chloride

Uses

Nickel chloride is used in nickel electroplating baths. It also is used to prepare various nickel salts and nickel catalysts; and in industrial gas masks to protect from ammonia.

Physical Properties

The anhydrous salt forms yellow crystal scales; deliquesces; density 3.55 g/cm^3; melts at 1,001°C; sublimes at 973°C; highly soluble in water, 64 g/100mL at 20°C; soluble in alcohol.

The hexahydrate forms green monoclinic crystals; deliquesces; extremely soluble in water, 254 g/100mL at 20°C, and about 600 g/100 ml at 100°C; also very soluble in alcohol.

Thermochemical Properties

$\Delta H_f°$ ($NiCl_2$)	–72.98 kcal/mol
$\Delta H_f°$ ($NiCl_2 \cdot 6H_2O$)	–502.67 kcal/mol
$\Delta G_f°$ ($NiCl_2$)	–61.92 kcal/mol

$\Delta G_f°$ ($NiCl_2 \cdot 6H_2O$)	–409.54 kcal/mol
S° ($NiCl_2$)	23.34 cal/degree mol
S° ($NiCl_2 \cdot 6H_2O$)	82.30 cal/degree mol
C_p ($NiCl_2$)	17.13 cal/degree mol

Preparation

Anhydrous nickel chloride is prepared by burning nickel in chlorine gas. Some other methods of preparation involve
(1) the action of acetyl chloride on nickel acetate in a nonaqueous solvent such as benzene:

$$(CH_3COO)_2Ni + 2CH_3COCl \xrightarrow{benzene} NiCl_2 + 2CH_3COOCOCH_3$$

(2) the action of thionyl chloride on nickel chloride hexahydrate:

$$NiCl_2 \cdot 6H_2O + 6SOCl_2 \rightarrow NiCl_2 + 12HCl + 6SO_2$$

(3) heating nickel chloride hexahydrate or nickel chloride ammoniate:

$$NiCl_2 \cdot 6H_2O \rightarrow NiCl_2 + 6H_2O$$

$$NiCl_2 \cdot 6NH_3 \rightarrow NiCl_2 + 6NH_3$$

The hexahydrate is prepared either by the action of hot dilute hydrochloric acid on nickel powder or by dissolving nickel oxide in dilute hydrochloric acid followed by crystallization. For the preparation of ammoniate, see Reactions below.

Reactions

When ammonia gas is passed over anhydrous nickel chloride the product is an ammoniate, hexamine nickel chloride, $NiCl_2 \cdot 6NH_3$. Ammoniate also can be prepared in solution by dissolving nickel chloride hexahydrate in an aqueous solution of ammonia.

Nickel chloride forms double salts with alkali metal chlorides or ammonium chloride. Such double salts, $NH_4Cl \cdot NiCl_2 \cdot 6H_2O$, are obtained as hexahydrate when crystallized from a mixed solution of nickel chloride and ammonium chloride in equimolar amounts..

Warming a solution of nickel chloride and sodium hydroxide at moderate concentrations may partially precipitate a basic salt of indefinite composition. The average composition of this salt is $NiCl_2 \cdot 3Ni(OH)_2$. Salt composition may vary depending on reaction conditions.

When hydrogen sulfide is passed through a buffered solution of nickel chloride, nickel sulfide, NiS, precipitates.

An alcoholic solution of nickel chloride, when treated with an ethereal solution of dithiobenzoic acid, C_6H_5CSSH, blue nickel(II) dithiobenzoate, $(C_6H_5CSS)_2Ni$, is formed:

$$NiCl_2 + 2C_6H_5CSSH \rightarrow Ni\ (C_6H_5CSS)_2 + 2HCl$$

The product oxidizes readily to a violet dimeric nickel(IV) complex.

Analysis

Elemental composition (for anhydrous $NiCl_2$): Ni 45.30%, Cl 54.70%

Percent composition of $NiCl_2 \cdot 6H_2O$: Ni 24.69%, Cl 29.83%, H_2O 45.48%. Nickel may be analyzed in an aqueous solution of salt by various instrumental techniques (See Nickel). Chloride ion in the aqueous solution may be determined by titration with silver nitrate using potassium chromate indicator; or preferably by ion-chromatography. The solutions must be appropriately diluted for all analyses.

NICKEL COMPLEXES

Nickel forms a large number of complexes with various anions (monodentate, bidentate, and polydentate) and many neutral ligands. The most common coordination numbers of the metal in these complexes are six and four while the metal is usually in +2 oxidation state, Ni^{2+}. Also, some complexes of three and five coordinations exist. Several zero valent nickel complexes, such as nickel tetracarbonyl, and a number of substituted carbonyl complexes are well known.

The most common Ni^{2+}complexes of monodentate neutral ligands are octahedral ammine and aqua complexes $[Ni(NH_3)_6]^{2+}$ and $[Ni(H_2O)_6]^{2+}$, respectively, which form salts such as $Ni(NH_3)_6Cl_2$, $[Ni(H_2O)_2(NH_3)_4](NO_3)_2$, $Ni(NH_3)_6Br_2$, and $Ni(NH_3)_6SO_4$. Such complex salts are stable at ordinary to moderate temperatures depending on size of the anion. The hexaaqua nickel ion is bright green while hexamine complex ion imparts blue to purple color to the solution.

Some other common ligands are pyridine (py), ethylenediamine (en), cyanide ion (CN^-), thiocyanate ion (SCN^-), acetylacetonate (acac), salicylaldehyde (sal), triphenylphosphine (PPh_3) and various trihalophosphines. Ethylenediame and acetylacetonate are examples of two common bidentate ligands.

Nickel(0) complexes are obtained by substitution of CO molecules in nickel tetracarbonyl, $Ni(CO)_4$. They contain ligands, such as CO, NO, PF_3, PCl_3 and $P(C_6H_5)_3$ and their mixed combinations coordinated to nickel. Some examples of such zero valent complexes are $Ni(PF_3)_4$, $Ni(PCl_3)_4$, $Ni(CH_3PCl_4)_4$, $(CO)Ni(PF_3)_3$, $(CO)_3Ni(PF_3)$, and $(PPh_3)_2Ni(NO)_2$.

A formal oxidation state of –1 for nickel also exists as, for example, in the nickel hydrocarbonyl, $H_2Ni_2(CO)_6$.

Nickel(II) complexes of simple anions, such as F^-, Cl^-, SCN^-, NO_2^-, readily combine with alkali metal or ammonium ions forming their complex salts. For example, action of fluorine on a mixture of $NiCl_2$ and KCl yields diamagnetic dipotassium hexafluoronickelate(IV), $K_2[NiF_6]$. Similarly, many complex nitrites of the type hexanitronickelates, $[Ni(NO_2)_6]^{4-}$ can be crystallized from solutions containing alkali and alkaline earth nitrites. An example is tetrapotassium hexanitronickelate(II), $K_4[Ni(NO_2)_6]$, a brownish red octahedral complex that can be crystallized from water. Similar cyanonickelate complex salts of alkali metals can be prepared by dissolving nickel cyanide in excess alkali cyanide solution followed by evaporation. An example of such four coordinated nickel(II) cyanide complex is yellow disodium tetracyanonickelate(II), $Na_2[Ni(CN)_4] \cdot 3H_2O$. A bridged binuclear nickel(I) cyano complex, potassium tetracyano-μ-dicyanonickelate(I), $K_4[(CN)_2Ni(CN)_2Ni(CN)_2]$ is an example of nickel's formal oxidation state being +1. Nickel forms both four and six coordinated thiocyanatonickelates with thiocyanate anions. Such complexes may be prepared by evaporation of solutions of nickel thiocyanate, $Ni(SCN)_2$ and alkali metal thiocyanates. They are usually recrystallized from alcohol and may be fairly stable in aqueous solutions without decomposition. Such complexes include green disodium tetrathiocyanatonickelate(II), $Na_2[Ni(SCN)_4] \cdot 8H_2O$ and the blue tetrapotassium hexathiocyanatonickelate(II), $K_4[Ni(SCN)_6] \cdot 4H_2O$.

The π-cyclopentadienyl nickel complex, π-$(C_5H_5)_2Ni$, known as nickelocene is analogous to similar sandwich complexes of iron and cobalt, ferrocene and cobalocene, respectively. This emerald-green paramagnetic complex, having a density of 1.47 g/cm^3, melts at 173°C and oxidizes slowly in air. It is prepared by reacting sodium cyclopentadienide with nickel bromide dimethoxyethane. Many nickelocene derivatives have been prepared. They include green methylnickelocene; red cyclopentadienylnickel nitrosyl, $(\pi\text{-}C_5H_5)Ni(NO)$; the violet-red diamagnetic dimeric complex cyclopentadienylnickel carbonyl, $(\pi\text{-}C_5H_5NiCO)_2$ prepared by the action of nickelocene on nickel tetracarbonyl; the red complex bis(π-indenyl)nickel; and the greenish-brown tri-n-butylphosphine π-cyclopentadienyl methylnickel, $P(C_4H_9)_3(\pi\text{-}C_5H_5)NiCH_3$.

Many organonickel complexes of arene, aryl, allyl and other systems are known. They may be prepared by different methods from nickel tetracarbonyl or nickel halides using Grignard reagent or other organometallics. Arenenickel complexes are made by the reaction of nickel bromide or nickel tetracarbonyl with aromatics. π-Allyl complexes of nickel, such as bis(π-allyl)nickel, $(\pi\text{-}C_3H_5)_2Ni$ can be made by the reaction of the Grignard reagent, allylmagnesium bromide, $CH_2{=}CH{-}CH_2MgBr$ with anhydrous nickel bromide. Alternatively, this compound or related complexes can be prepared by the reaction of allyl bromide, $CH_2{=}CH{-}CH_2Br$ with nickel tetracarbonyl. The violet nickel aryl complex bis(triphenylmethyl)nickel, $[(C_6H_5)_3C]_2Ni$ can be prepared by the reduction of nickel chloride in the presence of hexaphenylethane, $(C_6H_5)_3C{-}C(C_6H_5)_3$.

Several five-coordinate nickel(II) complexes having both the trigonal bipyramidal and square pyramidal geometry are known. Such complexes are of the type $[NiL_5]^{2+}$, $[NiL_3X_2]$ and $[NiL_4X]^+$, where L is a phosphine or arsine ligand and X is typically a halide ion but also can be a hydride or other anion. Such complexes in many cases contain unidentate ligands and their trigonal bipyramidal structure may change to square pyramidal geometry. Some typical examples of such nickel(II) five-coordinate complexes include $[Ni(CN)_5]^{3-}$, $NiCl_2(SbMe_3)_3$, $[NiMe(PMe_3)_4]^+$, $[NiBr(PMe_3)_4]^+$, $[Ni(SbMe_3)_5]^{2+}$, and $[Ni(Me_3AsO)_5]^{2+}$.

Four-coordinate nickel(II) complexes have both tetrahedral and square planar geometry. Square planar geometry that forms more stable complexes is preferred because the d^8 configuration of Ni^{2+} with eight electrons can occupy the four planar bonding orbitals more readily than the higher energy antibonding orbitals in tetrahedral coordination. The small number of tetrahedral complexes that are known are of the type $[NiX_4]^{2-}$, $[NiX_3L]^-$, and NiL_2X_2, where X is a halide ion and L is a neutral ligand usually trialkyl arsine, AsR_3; triphenyl phosphine, PPh_3; or triphenyl phosphine oxide, $O{=}PPh_3$. Some examples are $[NiCl_4]^{2-}$, $[NiBr_3(OPh_3)]^-$, and $NiCl_2(AsMe_3)_2$.

Most four-coordinate nickel(II) complexes are square planar. They are of red, brown and yellow color and practically all are diamagnetic. Some examples are red bis(dimethylglyoximato)nickel(II) and the yellow tetracyanonickelate(II) ion, $[Ni(CN)_4]^{2-}$.

NICKEL CYANIDE

[557-19-7]
Formula: $Ni(CN)_2$; MW 110.74; forms a stable tetrahydrate, $Ni(CN)_2 \cdot 4H_2O$ [13477-95-7], MW 182.79

Uses

Nickel cyanide is used for nickel plating. It also is used to synthesize butadiene from acetylene.

Physical Properties

The tetrahydrate, $Ni(CN)_2 \cdot 4H_2O$ constitutes apple green plates or powder; loses water of crystallization on heating at 200°C; decomposes on further heating; insoluble in water; slightly soluble in dilute acids; soluble in potassium cyanide solution and in ammonia, caustic soda, caustic potash and other bases.

Preparation

Nickel cyanide is prepared by treating a soluble nickel salt, such as nickel chloride or nickel sulfate, with potassium cyanide solution:

$$Ni^{2+} + 2CN^- \rightarrow Ni(CN)_2$$

The product is a tetrahydrate, $Ni(CN)_2 \cdot 4H_2O$, which on heating at 200°C yields yellow-brown anhydrous salt, $Ni(CN)_2$.

Reactions

Nickel cyanide is practically stable in dilute acids at ordinary temperatures. Although the compound is water insoluble, it reacts with excess cyanide ions in solution to form yellow tetracyanonickelate(II), $[Ni(CN)_4]^{2-}$anion:

$$Ni(CN)_2 + 2CN^- \rightarrow [Ni(CN)_4]^{2-}$$

Alkali metal salts of such tetracyanonickelate(II) anion may be crystallized from such solutions as hydrates, $K_2[Ni(CN)_4 \cdot 3H_2O$ upon evaporation of the solution. In strong cyanide solution, a pentacyano complex anion, red pentacyanonickelate(II), $[Ni(CN)_5]^{3-}$ forms. Strong acids decompose cyanonickelate salts, precipitating nickel cyanide.

Cyanonickelate(II) may be reduced to red cyanonickelate(I) ion in solution by nascent hydrogen. Red potassium cyanonickelate(I), $K_2[Ni(CN)_3]$ has been isolated. X-ray structure indicates that this compound is a binuclear complex, potassium tetracyano-μ-dicyanonickelate(I), $K_4[(CN)_2Ni(CN)_2Ni(CN)_2]$.

Analysis

Elemental composition: Ni 53.00%, C 21.69%, N 25.30%. The compound may be identified by x-ray and selective chemical reactions with cyanide ions. Nickel may be analyzed in an acidified aqueous solution after it is solubilized with concentrated nitric acid or aqua regia (See Nickel).

Toxicity

The compound is toxic by ingestion.

NICKEL HYDROXIDE

[12054-48-7]
Formula: $Ni(OH)_2$; MW 92.708; also forms a stable monohydrate, $Ni(OH)_2 \cdot H_2O$ [36897-37-7], MW 110.72

Uses

Nickel hydroxide is used to prepare nickel salts and nickel catalysts; and in the manufacture of nickel-cadmium batteries.

Physical Properties

Green hexagonal crystal; density 4.10 g/cm³; decomposes to NiO on heating at 230°C; insoluble in water; K_{SP} 5.47×10^{-16}; monohydrate is insoluble in water but soluble in dilute acids and ammonia.

Thermochemical Properties

$\Delta H_f°$	–126.60 kcal/mol
$\Delta G_f°$	–106.88 kcal/mol
S°	21.03 cal/degree mol

Preparation

Nickel hydroxide is prepared by various methods, mostly involving reaction of caustic soda or caustic potash with a soluble nickel salt. Thus, treating nickel sulfate solution with sodium hydroxide forms a voluminous green gel. The gel crystallizes on prolonged storage. Alternatively, the solution on neutralization forms a fine precipitate of nickel hydroxide. Nickel nitrate also is used as starting material to prepare nickel hydroxide. Its aqueous solution, on treatment with sodium or potassium hydroxide, yields a gelatinous precipitate of nickel hydroxide which may be extracted with hot alcohol to form high purity product.

Nickel hydroxide in high purity is prepared by an electrolytic process using metallic nickel as the anode and nickel nitrate solution as the electrolyte. Nickel hydroxide is electrodeposited at an inert cathode.

Analysis

Elemental composition: Ni 63.32%, H 2.17%, O 34.51%. The hydroxide may be digested with nitric acid, diluted appropriately, and analyzed for nickel by various instrumental methods (See Nickel). Also, water content may be measured by TGA or DTA method after decomposing the hydroxide at 230°C. The residue NiO may be characterized by x-ray and other methods (See Nickel Oxide).

NICKEL NITRATE

[13138-45-9]
Formula: $Ni(NO_3)_2$; MW 182.72; occurs as hexahydrate at ordinary temperatures, $Ni(NO_3)_2 \cdot 6H_2O$ [13478-00-7], MW 290.79
Synonyms: nickel(II) nitrate; nickelaus nitrate

Uses

Nickel nitrate is used in the preparation of nickel-impregnated catalysts. It also is used to make nickel plates in nickel-cadmium batteries. Other applications are in ceramics to produce brown colors and in preparing nickel oxide.

Physical Properties

The hexahydrate forms emerald green monoclinic crystals; hygroscopic; density 2.05 g/cm^3; isomorphous with corresponding cobalt salt; melts at 56.7°C; loses water on heating, decomposing to nickel oxide; very soluble in water; aqueous solution acidic; soluble in ethanol.

Preparation

Nickel nitrate hexahydrate may be prepared by several methods based on the reaction of dilute nitric acid on nickel powder, nickel oxide or nickel carbonate. The reaction is exothermic and requires controlled cooling during production. The hexahydrate can be dehydrated to anhydrous salt by treatment with fuming nitric acid.

Analysis

Elemental composition (anhydrous $Ni(NO_3)_2$): Ni 32.13%, N 15.33%, O 52.54%. The percent composition of Ni, NO_3^-, and H_2O in the hexahydrate $Ni(NO_3)_2 \cdot 6H_2O$ is 20.18%, 42.65% and 37.17%, respectively. The hexahydrate may be identified by TGA, DTA and x-ray techniques. Nickel may be measured in an appropriately diluted aqueous solution by AA, ICP and other instrumental techniques. Nitrate ion, NO_3^- may be measured in an appropriately diluted solution by ion chromatography or with a nitrate ion-selective electrode.

NICKEL OXIDE

[1313-99-1]
Formula: NiO; MW 74.692
Synonyms: nickel(II) oxide; nickelous oxide; green nickel oxide; nickel protoxide.

Occurrence

The oxide occurs in nature in the mineral, bunsenite.

Uses

Nickel oxide is used in the ceramic industry for making frit, ferrites, and coloring porcelain. The oxide in sinter form is used in the production of nickel-steel alloys. It supplies oxygen to the melt for removal of carbon as carbon dioxide. Some other important uses of nickel oxide include preparation of many nickel salts, specialty chemicals, and nickel catalysts. It also is used as an electrode in fuel cells.

Physical Properties

Green cubic crystals; transforms to a grayish black octahedral form, known as black oxide, when strongly ignited; black oxide has a metallic luster; density of green oxide is 6.72 g/cm^3; Mohs hardness 5.5; melts at 1955°C; insoluble in water; soluble in acids at ordinary temperatures; black form dissolves in hot acids.

Preparation

Nickel oxide is prepared by heating pure nickel powder with oxygen at a temperature above 400°C. In some commercial processes, green nickel oxide is made by heating a mixture of nickel powder and water in air at 1,000°C. Adding some nickel oxide to the above mixture enhances the rate of reaction. An alternative method of preparation of the green oxide involves thermal decomposition of an oxo acid salt of nickel at elevated temperatures. Thus, nickel nitrate, nickel sulfate or, more conveniently, nickel carbonate when heated at 1,000°C, yields the green oxide. The black oxide, on the other hand, is produced at a lower temperature from incomplete calcination of the carbonate or nitrate salt at 600°C. The oxygen content of the black form is slightly greater than its green counterpart.

Reactions

Several nickel salts are obtained by reactions of nickel oxide with mineral acids. Thus, the reaction of black nickel oxide with hot dilute sulfuric acid forms nickel sulfate, $NiSO_4 \cdot 6H_2O$. Similarly, dilute nitric acid, hydrochloric, and hydrobromic acids when heated react with the black form of nickel oxide to yield corresponding nickel salts as hexahydrates.

Heating nickel oxide with hydrogen, carbon, or carbon monoxide reduces it to metallic nickel.

Nickel oxide combines with sodium or potassium hydroxide at elevated temperatures (>700°C), forming sodium or potassium nickelate; i.e., K_2NiO_2:

$$NiO + 2NaOH \rightarrow Na_2NiO_2 + H_2O$$

Analysis

Elemental composition: Ni 78.58%, O 21.42%. Nickel may be analyzed in a diluted solution of the oxide in nitric acid by AA, ICP and other instrumental methods. The oxide may be identified from its physical properties and by x-ray diffraction.

NICKEL PHOSPHATE

[10381-36-9]
Formula: $Ni_3(PO_4)_2$; MW 366.07; forms a stable heptahydrate, $Ni_3(PO_4)_2 \cdot 7H_2O$ [14396-43-1]
Synonyms: nickel orthophosphate, trinickel orthophosphate

Uses

Nickel phosphate is used in coating steel and in treatment of metal surfaces. It also is used to prepare the pigment, nickel yellow for oil and water colors. The compound is used in electroplating also.

Physical Properties

The heptahydrate is a light apple green powder; decomposes on heating; insoluble in water; soluble in acids and ammonia solution.

Preparation

Nickel phosphate heptahydrate is obtained as a pale green flocculent precipitate when disodium hydrogen phosphate, Na_2HPO_4 is added to a nickel salt solution. The precipitate is air-dried.

Analysis

Elemental composition (of anhydrous $Ni_3(PO_4)_2$): Ni 48.11%, P 16.92%, O 34.97%.The water of crystallization in the hydrated salt is determined by DTA and TGA methods. Nickel content may be determined by AA or ICP-AES analysis of the nitric acid extract of nickel phosphate.

NICKEL SULFAMATE

[13770-89-3]
Formula: $Ni(SO_3NH_2)_2 \cdot 4H_2O$; MW 322.93; occurs as a tetrahydrate.

Uses

Nickel sulfamate is used as an electrolyte in nickel electroplating systems.

Preparation

Nickel sulfamate is prepared by heating an aqueous solution of sulfamic acid, H_2NSO_3H, with fine nickel powder or black nickel oxide under controlled conditions:

$$2H_2NSO_3H + NiO \rightarrow Ni(SO_3NH_2)_2 + H_2O$$

At ordinary temperatures, sulfamic acid hydrolyzes slowly forming ammonium bisulfite. However, when heated it hydrolyzes rapidly forming sulfuric acid. Therefore nickel sulfamate should be prepared rapidly before any sulfamic acid hydrolysis occurs due to longer contact time with water.

Nickel sulfamate also can be prepared by the action of sodium sulfamate on nickel carbonate:

$$2H_2NSO_3Na + NiCO_3 \rightarrow Ni(SO_3NH_2)_2 + Na_2CO_3$$

Nickel sulfamate is usually not isolated from its product mixtures. The product solution is sold for commercial applications.

Analysis

Elemental composition: Ni 18.16%, S 19.86%, H 3.75%, N 8.67%, O 49.54%. The composition of water in nickel sulfamate tetrahydrate is 22.31%. Nickel content in solution may be determined by AA, ICP and other instrumental techniques.

NICKEL SULFATE

[7786-81-4]
Formula: $NiSO_4$; MW 154.75; occurs as hexahydrate, $NiSO_4 \cdot 6H_2O$ [10101-97-0], MW 262.85 and the heptahydrate, $NiSO_4 \cdot 7H_2O$ [10101-98-1], MW 280.86

Occurrence and Uses

Nickel sulfate heptahydrate occurs in nature as the mineral morenosite.

Probably, the most important uses of nickel sulfate are as an electrolyte in nickel plating and electrorefining. Nickel sulfate also is used as a mordant in dyeing and printing textiles. Other uses are in the preparation of many nickel compounds and nickel catalysts; as a reducing agent; for imparting nickel coating or flashing on steel surface; and for blackening zinc and brass.

Physical Properties

The anhydrous salt is a yellow cubic crystalline solid; density 3.68 g/cm^3; decomposes at 848°C; readily dissolves in water; insoluble in ethanol, ether and acetone.

The hexahydrate, $NiSO_4 \cdot 6H_2O$ occurs in two crystalline forms, a blue tetragonal alpha-allotrope and an emerald green monoclinic beta form. The blue alpha form converts to green beta above 53.3°C. The beta form is isomorphous with magnesium sulfate hexahydrate, $MgSO_4 \cdot 6H_2O$. Density of hexahydrate is 2.07 g/cm^3; refractive index 1.511; loses water on heating; very soluble in water; also very soluble in ethanol and ammonia solution.

The heptahydrate, $NiSO_4 \cdot 7H_2O$, forms green rhombohedral crystals; refractive index 1.467; density 1.948 g/cm^3; loses water on heating; highly soluble in water (about 75 g/100mL at 15°C); soluble in alcohol.

Thermochemical Properties

$\Delta H_f°$ (anhydrous $NiSO_4$)	–208.6 kcal/mol
$\Delta H_f°$ (alpha-$NiSO_4 \cdot 6H_2O$)	–641.2 kcal/mol
$\Delta H_f°$ (beta-$NiSO_4 \cdot 6H_2O$)	–638.7 kcal/mol
$\Delta H_f°$ ($NiSO_4 \cdot 7H_2O$)	–711.4 kcal/mol
$\Delta G_f°$ (anhydrous $NiSO_4$)	–181.6 kcal/mol
$\Delta G_f°$ (alpha-$NiSO_4 \cdot 6H_2O$)	–531.8 kcal/mol
$\Delta G_f°$ ($NiSO_4 \cdot 7H_2O$)	–588.8 kcal/mol
S° (anhydrous $NiSO_4$)	22.0 cal/degree mol
S° (alpha-$NiSO_4 \cdot 6H_2O$)	79.9 cal/degree mol
S° ($NiSO_4 \cdot 7H_2O$)	90.6 cal/degree mol
C_ρ (anhydrous $NiSO_4$)	33.0 cal/degree mol
C_ρ (alpha-$NiSO_4 \cdot 6H_2O$)	78.4 cal/degree mol
C_ρ ($NiSO_4 \cdot 7H_2O$)	87.1 cal/degree mol

Preparation

Nickel sulfate can be made by several methods. It is prepared by dissolving nickel metal, its oxide, or its carbonate in sulfuric acid. In such methods, powdered metal or black nickel oxide is added to hot dilute sulfuric acid, or nickel carbonate is added to dilute sulfuric acid at ambient temperature:

$$NiO + H_2SO_4 \rightarrow NiSO_4 + H_2O$$

$$NiCO_3 + H_2SO_4 \rightarrow NiSO_4 + CO_2 + H_2O$$

Impurities may be precipitated by treating the diluted solution with barium carbonate. Evaporation followed by cooling crystallizes hexahydrate in two modifications: blue tetragonal crystals obtained between 31.5 and 53.3°C, and above 53.3°C green monoclinic crystals form. The heptahydrate, $NiSO_4 \cdot 7H_2O$, crystallizes at ordinary temperatures from pure aqueous solutions.

Nickel sulfate also can be produced in large-scale by gas phase reaction of nickel tetracarbonyl, sulfur dioxide, and oxygen at 100°C:

$$Ni(CO)_4 + SO_2 + O_2 \rightarrow NiSO_4 + 4CO$$

Reactions

Hydrated nickel sulfate on heating at 103°C loses all of its water molecules. At 848°C, the anhydrous sulfate decomposes to nickel oxide and sulfur trioxide:

$$NiSO_4 \rightarrow NiO + SO_3$$

Nickel sulfate is used in preparing many insoluble nickel salts. In aqueous solutions, such insoluble nickel compounds precipitate; e.g.,

$$3Ni^{2+} + 3PO_4^{3-} \rightarrow Ni_3(PO_4)_2$$

Nickel sulfate forms double salts with ammonium or alkali metal sulfates. For example, blue-green hydrated ammonium nickel sulfate, $(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6H_2O$, crystallizes from a mixed solution of nickel sulfate and ammonium sulfate. Such double sulfates are isomorphous to corresponding alkali metal or ammonium double sulfates of iron, cobalt, magnesium, zinc, and other bivalent metals.

Analysis

Elemental composition (in anhydrous $NiSO_4$): Ni 37.93%, S 20.72%, O 41.35%. The water content in hexahydrate, $NiSO_4 \cdot 6H_2O$, and heptahydrate, $NiSO_4 \cdot 7H_2O$, are 41.12% and 47.98%, respectively. Nickel may be analyzed in aqueous solution by AA, ICP, and other instrumental methods (see Nickel). Sulfate may be analyzed in aqueous solution by ion chromatography. The compound may be characterized by x-ray methods.

NICKEL SULFIDE

[1314-04-1]
Formula: NiS; MW 90.75; the compound may have nonstoichiometric compositions.
Synonyms: nickel monosulfide; nickel(II) sulfide; millerite.

Occurrence and Uses

Nickel sulfide occurs in nature as mineral millerite. Its principal use is as a source material for making nickel metal.

Physical Properties

Trigonal crystalline solid or amorphous powder; mineral millerite has a yellow metallic luster; color varies from yellow to brownish black; density 5.30 to 6.65 g/cm^3; exhibits three allotropic modifications: (1) the acid-soluble amorphous alpha form obtained from nickel salt solution by precipitation with ammonium sulfide, (2) the alpha form rapidly transforms to a crystalline beta form as a brown colloidal dispersion upon exposure to air, and (3) a rhombohedral gamma modification found native as mineral millerite, which also can be prepared artificially under certain conditions.

Gamma-NiS slowly converts to beta-NiS in solution. Beta form probably is richer in sulfur than alpha and gamma modifications and therefore they could have varying stoichiometric compositions.

Nickel sulfide melts at 797°C and is insoluble in water (3.6 mg/L at 18°C; soluble in concentrated nitric acid and potassium hydrogen sulfide solution; slightly soluble in alcohol.

Thermochemical Properties

$\Delta H_f°$	–19.6 kcal/mol
$\Delta H_f°$ (precipitated NiS)	–18.5 kcal/mol
$\Delta G_f°$	–19.0 kcal/mol
S°	12.66 cal/degree mol
C_ρ	11.26 cal/degree mol

Preparation

Nickel sulfide is mined directly from natural deposits. Also, it can be prepared in the laboratory by precipitation from an aqueous solution of a nickel salt with ammonium sulfide, $(NH_4)_2S$, or by precipitation from an acetic acid solution with hydrogen sulfide. While the aqueous solution method yields an amorphous product (alpha-NiS) which rapidly changes on exposure to air and contact with the solution to a brown crystalline sulfide (beta-NiS), the acid solution method forms only crystalline beta-NiS.

Nickel sulfide also can be prepared by reacting nickel powder with molten sulfur.

Analysis

Elemental composition: Ni 64.68%, S 35.33%. The compound may be identified by x-ray crystallographic and physical properties. Nickel may be measured in nitric acid extract by AA or ICP methods (See Nickel).

NICKEL TETRACARBONYL

[13463-39-3]
Formula: $Ni(CO)_4$; MW 170.73; a zerovalent nickel compound
Synonym: nickel carbonyl

History and Uses

Nickel tetracarbonyl was prepared first in 1888 by Mond and Langer by passing carbon monoxide over finely divided nickel. It is the most important zero valent compound of nickel and is used industrially to make high-purity nickel powder and pellets and to produce nickel coatings on steel.

Physical Properties

Colorless volatile liquid; diamagnetic; flammable; burns with a bright luminous flame; density 1.319 g/mL; freezes at –25°C; boils at 43°C; vapor pressure 320.6 torr at 20°C; vapor density 5.89 (air=1); critical temperature about 200°C; critical pressure 30 atm; practically insoluble in water, 180 mg/L at 10°C; miscible with most organic solvents including ethanol, acetone, and benzene; soluble in nitric acid and aqua regia.

Thermochemical Properties

$\Delta H_f°$ (liq)	–151.3 kcal/mol
$\Delta H_f°$ (gas)	–144.1 kcal/mol
$\Delta G_f°$ (liq)	–140.6 kcal/mol
$\Delta G_f°$ (gas)	–140.4 kcal/mol
S° (liq)	74.9 cal/degree mol
S° (gas)	98.1 cal/degree mol
C_ρ (liq)	48.9 cal/degree mol
C_ρ (gas)	34.7 cal/degree mol

Preparation

Nickel tetracarbonyl is made by passing carbon monoxide over finely divided nickel at 50 to 100°C. (The finely divided nickel is obtained from reduction of nickel oxide by hydrogen below 400°C.)

$$Ni + 4CO \rightarrow Ni(CO)_4$$

In several commercial processes the reaction is carried out at a temperature of 200°C under 400 atm carbon monoxide pressure for obtaining high yield of nickel tetracarbonyl and also to prevent thermal dissociation.

Nickel tetracarbonyl may be prepared in the laboratory by the Hieber process, a disproportion reaction of several nickel compounds of organic thio acids, such as nickel(II) phenyldithiocarbamate, $(C_6H_5—NH—C(=S)—S)_2Ni$, with carbon monoxide under controlled conditions. In such disproportionation reactions, the divalent nickel ion converts to a tetravalent nickel complex (Hieber. H. 1952. *Z.anorg.Chem.*, 269, pp. 28). The overall reaction is:

$$2Ni^{II} + 4CO \rightarrow Ni^{IV}(complex) + Ni^{o}(CO)_4$$

Reactions

Nickel tetracarbonyl decomposes to metallic nickel and carbon monoxide when heated at 180 to 200°C. Thus, when its vapors are passed through a tube heated at 180 to 200°C, a brilliant mirror of metallic nickel is deposited on the tube:

$$Ni(CO)_4 \rightarrow Ni + 4CO$$

Reaction with chlorine yields phosgene (carbonyl chloride) and nickel chloride:

$$Ni(CO)_4 + 4Cl_2 \rightarrow NiCl_2 + 4COCl_2$$

Concentrated nitric acid and other oxidizing agents decompose nickel tetracarbonyl forming their nickel salts, carbon dioxide and water:

$$2Ni(CO)_4 + 4HNO_3 + 5O_2 \rightarrow 2Ni(NO_3)_2 + 8CO_2 + 2H_2O$$

Nickel tetracarbonyl reacts with nitric oxide in the presence of moisture, forming a deep blue compound, nickel nitrosyl hydroxide, $Ni(NO)OH$.

Analysis

Elemental composition: Ni 34.38%, C 28.13%, O 37.48%. The compound may be identified and measured quantitatively by GC/MS. An appropriately diluted solution in benzene, acetone, or a suitable organic solvent may be analyzed. Alternatively, nickel tetracarbonyl may be decomposed thermally at 200°C, the liberated carbon monoxide purged with an inert gas, and transported onto the cryogenically cooled injector port of a GC followed by analysis with GC-TCD on a temperature-programmed column. Nickel may be analyzed by various instrumental techniques following digestion of the compound with nitric acid and diluting appropriately (See Nickel).

Hazard

Nickel tetracarbonyl is both a fire and explosion hazard and is a highly toxic compound. It is a volatile flammable liquid with a flash point (closed cup) –4°F (–18°C) and forms explosive mixtures with air. It explodes when heated in oxygen or air or when it is dry and shaken vigorously with oxygen in the presence of mercury or mercuric oxide.

The carbonyl is toxic by all routes of exposure, manifesting both immediate and delayed effects. Symptoms from breathing its vapors are headache, dizziness, giddiness, nausea, vomiting, and hallucinations. Prolonged inhalation can cause rapid breathing, congestion of the lungs, and brain and liver injury. Ingestion can be fatal. It induces tumors in lungs and livers of experimental animals.

Inhalation LC_{50} in mice over a 30-minute exposure period is 0.067 mg/L and the oral LD_{50} in rats is about 60 mg/kg.

NIOBIUM

[7440-03-1]

Symbol: Nb; atomic number 41; atomic weight 92.906; a Group VB (Group 5) element; a transition metal in the triad of vanadium and tantalum; also, known as columbium; electron configuration $[Kr]4d^45s^1$; valence states +3, +4 and +5; the most common oxidation state +5; atomic radius 1.47Å; ionic radius, Nb^{5+} 0.68Å; atomic volume 10.8 cm^3/mol; ionization potential 6.77 eV; one stable natural isotope, Nb-93; several radioactive isotopes are known in the mass range 88-92 and 94-101.

History and Occurrence

The element was discovered in 1801 by British chemist Charles Hatchett during analysis of a black mineral sample from the British Museum, originally sent in 1753 from Connecticut. He named the element *columbium*, after the country of its origin, Columbia (United States). In 1844, Rose announced the discovery of a new element which he named as *niobium*, in honor of Niobe, the daughter of Tantalus, the mythological Goddess of Tears. Later, it was established that Hatchett's columbium and Roses' niobium were the same element. Both names remained in use for more than one hundred years. In 1949 at the Fifteenth International Union of Chemistry Congress held at Amsterdam, the name niobium was officially adopted as the international name.

Niobium was prepared in the metallic state for the first time by Blomstrand in 1866, later by Moissan, and still later, by Goldschmidt. While Blomstrand reduced niobium chloride with hydrogen to form niobium, Moissan and Goldschmidt reduced the oxide with carbon (in an electrical furnace) and aluminum powder, respectively.

Niobium occurs naturally in several minerals, mostly associated with tantalum and many rare earth elements. The metal is never found in free elemental form. It occurs mostly as hydroxide, silicate, or borate or as its oxy salt, niobate, which is mostly associated with isomorphous tantalate. The principal niobium minerals are pyrochlore, loparite, and koppite all of which contain titanium together with calcium and other metals, such as cerium. They are complex hydroxide minerals and their composition may vary with place. Another type of niobium mineral is the niobates-tantalates mixed ores of Nb_2O_6—Ta_2O_6 or of compositions $(Nb,Ta)_2O_6$. Such ores usually contain iron and sometimes manganese which partially replaces iron. A typical example is an isomorphous admixture of $Fe(NbO_3)_2$—$Fe(TaO_2)_2$. Many impurity metals, such as tungsten, titanium, and tin are also found in these ores.

The abundance of niobium in the earth's crust is estimated to be in the range 20 mg/kg and its average concentration in sea water is 0.01 mg/L. The metal also is found in the solar system including the lunar surface. Radionucleides niobium-94 and -95 occur in the fission products of uranium-235.

Uses

Niobium is a very important metal in both ferrous and nonferrous metallurgy. As an additive to alloys or when alloyed with other metals niobium imparts high mechanical strength, high electrical conductivity, and ductility to alloys. It enhances corrosion resistance of most alloys. The metal and several of its alloys exhibit superconductivity. Nobium is used as an additive in the manufacture of most high strength, low alloy carbon steels and microalloyed steels that are used in the construction of oil and gas pipelines, bridges, buildings, concrete bars, and automobiles.

Nobium also is added to nickel- and cobalt-based superalloys and is a component of zirconium, titanium and tungsten alloys.

Other applications of niobium are in electronic and propulsion devices, in electrodes; in catalysis; and in vacuum tubes and high-pressure sodium vapor lamps.

Physical Properties

Grayish, soft metal with a white luster on polished surfaces; ductile and very malleable at room temperature; also highly ductile at cryogenic temperatures; body-centered cubic crystals; density 8.66 g/cm^3 at 20°C; melts at 2,468±10°C; vaporizes at 5,127°C; electrical resistivity 13.2 microhm-cm at 20°C; becomes superconducting at 9.15K; thermal neutron-capture cross section 1.1 barns; insoluble in water; insoluble in hydrochloric acid, nitric acid and aquaregia; soluble in hydrofluoric acid; soluble in fused alkali hydroxide.

Thermochemical Properties

$\Delta H_f°$	0.0
$\Delta H_f°$ (gas)	172.76 kcal/mol
$\Delta G_f°$	0.0
$\Delta G_f°$ (gas)	173.50 kcal/mol
S°	8.70 cal/degree mol
S° (gas)	44.49 cal/degree mol
C_p	5.88 cal/degree mol
C_p (gas)	7.21 cal/degree mol
ΔH_{fus}	6.318 kcal/mol
ΔH_{vap}	166.6 kcal/mol
Thermal conductivity	0.52 watts/cm°C
Coeff. linear expansion	0.064×10^{-6}/°C at 25°C
$\Delta H_{combstn}$	226.8 kcal/mol

Production

There are several processes for extracting and refining niobium from its ores. (Payton, P.H. 1981. Niobium and Niobium Compounds. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd. ed., Vol, 15, pp. 820-827. New York: Wiley Interscience). The process of choice depends on nature of the ore and end use intended for the metal. Some common steps in these recovery processes involve ore preconcentration, breaking or opening the ore, obtaining pure niobium compounds, reduction of niobium compounds to niobium metal, purification or refining metal and fabrication. If niobium is extracted from a niobium-tantalum ore, the most important step is separation of niobium from tantalum, both of which are chemically very similar.

Ferroniobium can be produced from the ore pyrochlore in batch process by thermal reduction in a refractory-lined steel or preferably an electric furnace reactor. Aluminum powder is used as a reducing agent. A mixture of niobium ore, iron oxide, aluminum powder, lime, and an oxidizer such as sodium chlorate, is fed into the reactor. The mixture is ignited electrically. Molten ferroniobium formed is collected at the reactor bottom and low density slags containing impurities float on top of the molten alloy. Some other metal oxides present in the ore or in the reactant feed are also reduced by aluminum under ignition. Such metals generated in small amounts may incorporate into ferroniobium and include silicon, tantalum, titanium, tin and lead. This fused mass also contains minor quantities of aluminum.

Ore-opening, a key step in the recovery of niobium is carried out by several methods. Some major methods are: (1) Heating the ore, niobates, or niobates-tantalates with hydrofluoric acid (70-80% by weight) and nitric acid. This method is not economical for pyrochlore-type ores that have high contents of alkali and alkaline earth oxides for which they require high acid consumption. (2) Fusion with sodium hydroxide at elevated temperatures is another common method of ore opening. Fusion is carried out in an iron retort at a temperature between 500 to 800°C. Pyrochlore and columbites are converted to insoluble niobates. Fusion products are leached with water and filtered to separate insoluble niobates. Niobates are then converted to niobic acid by treatment with hydrochloric acid and separated by filtration. (3) Pyrochlore and columbites alternatively may be digested with concentrated sulfuric acid at 300 to 400°C in an iron crucible. Sulfate complexes of niobium formed are hydrolyzed by boiling with water to yield white colloidal precipitate of niobic acid. (4) Ore crushed to finely ground state may be heated with carbon at high temperatures to produce metal carbides. This method is applicable to pyrochlore type ores. The reaction is initiated at 950°C and carried out at 1,800°C for completion. The product mixture containing carbides of niobium, tantalum and titanium is leached with hydrochloric acid to separate most acid-soluble materials. Carbide mixture is then dissolved in hydrofluoric acid converting them to respective fluorides. Carbides alternatively may be ignited in air or oxygen to convert them to oxides. (5) Another ore-opening process usually applied to columbites involves chlorination. For this method, ore is crushed and mixed with carbon and heated with chlorine gas at 500 to 1,000°C. Niobium and other metals form their chlorides, which are volatile and can be separated by fractional condensation. Niobium, aluminum and iron form niobium pentachloride, aluminum chloride and iron(II)– and iron(III) chlorides, respectively. These chlorides and the chlorides of impurity metals that are formed are transported over a column of sodium chloride pellets at 400°C for separation. While more volatile chlorides pass through the condenser, iron and aluminum form low melting eutectic compounds and drain from the bottom of the column. Niobium pentachloride is selectively condensed.

Separation of niobium from tantalum and impurity metals is the most important step in its extraction from the ore. It may be achieved by several methods that include solvent extraction, ion exchange, fractional crystallization, fractional sublimation, and other techniques. Solvent extraction is applied mostly in several large-scale commercial processes. Although the classical fractional crystallization method forms effective separation, it is a tedious process. Ion exchange techniques provide more effective removal of impurities than the solvent extraction methods. They are applied most often to produce high purity niobium and tantalum in small quantities. In solvent extraction methods, various acids are used in combination with hydrofluoric acid. An effective organic solvent for such solvent extraction is methyl isobutyl ketone (MIBK). Extraction is based on the principle that solubility of niobium and other metals varies with acid strength. Thus, in such extractions, pH is adjusted to obtain proper acidic conditions. There are also several variations in solvent extraction processes. Often ammonia is added to the niobium-bearing extract to precipitate niobium as oxyfluoride. The precipitate is then filtered, dried, and calcined to obtain high-purity niobium oxide. Another method involves addition of potassium fluoride to the extract to obtain a niobium potassium double fluoride. Recovery processes based on chlorination of the ore also utilize solvent extraction techniques. Chlorination at elevated temperatures yields anhydrous chlorides of niobium together with tantalum and iron. The chloride mixture is dissolved in MIBK and/or other suitable organic solvents and extracted with hydrochloric acid. While tantalum partitions into HCl, niobium and iron remain in the organic phase. Boiling with 20% H_2SO_4 precipitates niobic acid, thus separating niobium from iron, which remains in solution.

Many earlier commercial processes were based on separating niobium from tantalum and other metals by fractional crystallization. This method involves adding excess potassium fluoride to a solution of niobium ores in hydrofluoric acid. This forms complex fluorides and oxyfluorides of niobium, tantalum, and titanium of compositions $K_2NbOF_5 \cdot H_2O$, K_2TaF_6 and $K_2TiF_6 \cdot H_2O$, respectively. These complex salts are dissolved in 3% HF. Increasing concentrations of HF converts niobium oxyfluoride to K_2NbF_7 and $KNbF_6$. Out of these three complex salts, niobium complex is most soluble in HF, while that of tantalum is least soluble. Thus, by appropriate control of temperatures and concentrations of HF and potassium fluoride (which suppresses solubility of these complexes), less soluble tantalum complex may be crystallized, leaving behind niobium complex in solution.

High purity grade metal may be produced by reduction of niobium pentaoxide, Nb_2O_5 or pentachloride, $NbCl_5$ at elevated temperatures ranging from 1400 to 2000°C and often under vacuum using various reducing agents, such as carbon, hydrogen, sodium and other substances:

$$Nb_2O_5 + 7C \rightarrow 2NbC + 5CO$$

$$Nb_2O_5 + 5NbC \rightarrow 7Nb + 5CO$$

$$2NbCl_5 + 5H_2 \rightarrow 2Nb + 10HCl$$

$$NbCl_5 + 5Na \rightarrow Nb + 5NaCl$$

Reactions

At ordinary temperatures niobium does not react with most chemicals.

However, the metal is slowly attacked by hydrofluoric acid and dissolves. Also, at ordinary temperatures, it is attacked by hydrogen fluoride and fluorine gases, forming niobium petafluoride, NbF_5.

The metal reacts with chlorine at 300°C forming niobium pentachloride, $NbCl_5$. It reacts with hot concentrated hydrochloric acid, also forming the pentachloride. Niobium dissolves in hot concentrated sulfuric acid at 170°C. Fused alkalies such as caustic soda and caustic potash attack niobium, embrittling the metal.

Niobium is oxidized by air at 350°C, first forming pale yellow oxide film of increasing thickness, which changes its color to blue. On further heating to 400°C, it converts to a black film of niobium dioxide, NbO_2 [12034-59-2]. Niobium forms three oxides: the cubic monoxide, NbO [12034-57-0]; the tetragonal dioxide, NbO_2 [12034-59-2]; and the monoclinic pentoxide, Nb_2O_5 [1313-96-8]. These oxides are obtained by heating Nb metal powder at very high temperatures. Reaction of niobium powder with niobium dioxide in compressed argon at 1,700°C yields grayish niobium monoxide:

$$Nb + NbO_2 \rightarrow 2NbO$$

Similarly, heating the metal powder with pentoxide at 1,100°C forms bluish-black dioxide:

$$Nb + 2Nb_2O_5 \rightarrow 5NbO_2$$

Niobium absorbs hydrogen at 250°C, forming a stable interstitial solid solution. The reaction is exothermic. X-ray studies indicate a hydride, $NbH_{0.85}$. The hydride decomposes when heated at 500°C.

Niobium metal absorbs nitrogen, similar to hydrogen, forming interstitial solid solution. The absorption occurs at 300°C and the solubility of nitrogen in the metal is directly proportional to the square root of the partial pressure of nitrogen. The reaction is exothermic and the composition of such interstitial solid solution varies with the temperature. When the metal is heated with nitrogen at temperatures between 700 to 1,100°C, the product is niobium nitride, Nb_2N or ($NbN_{0.5}$) [12033-43-1]. When heated with ammonia at these temperatures, niobium forms this nitride. Another niobium nitride exists, NbN [24621-21-4], with a face-centered cubic crystalline structure.

Niobium combines with carbon, boron, silicon and other elements at very high temperatures, forming interstitial binary compounds of varying compositions. With carbon, it forms niobium carbide having compositions varying from $NbC_{0.7}$ to NbC [12069-94-2]. With boron, the products are orthorhombic niobium boride, NbB [12045-19-1], and the hexagonal diniobium diboride, Nb_2B_2[12007-29-3].

Analysis

Niobium content in its ores, alloys or compounds may be measured quantitatively by dissolving the solid samples into aqueous phase followed by x-ray fluorescence, colorimetry, or gravimetry measurement. Samples may be dissolved in hydrofluoric acid or in its combination with nitric acid. Alternatively, niobium may be extracted into aqueous phase by fusion with caustic soda, caustic potash, or potassium pyrosulfate after which the fused mass is leached with water. Niobium may be separated from tantalum and other interfering substances by solvent extraction or ion exchange techniques. The metal forms water-soluble colored complexes with ascorbic acid and 5-nitrosalicylic acid or water-insoluble colored complexes with tannin, pyrocatechol, Cupferron, and other complexing agents for colorimetric measurements.

NIOBIUM PENTACHLORIDE

[10026-12-7]
Formula: $NbCl_5$; MW 270.17
Synonyms: columbium pentachloride; niobium(V) chloride

Uses

Niobium pentachloride is used in making niobium metal and several niobium compounds.

Physical Properties

Yellow monoclinic crystals; deliquesces; density 2.75 g/cm^3; decomposes in moist air with the evolution of HCl; melts at 204.7°C; vaporizes at 254°C; decomposes in water; soluble in alcohol, hydrochloric acid, chloroform and carbon tetrachloride.

Thermochemical Properties

$\Delta H_f°$	–190.6 kcal/mol
$\Delta G_f°$	–163.3 kcal/mol
S°	50.3 cal/degree mol
C_ρ	35.4 cal/degree mol

Preparation

Niobium pentachloride is obtained as an intermediate during extraction of niobium from its ores (see Niobium). Also, the pentachloride is obtained readily by direct chlorination of niobium metal at 300 to 350°C:

$$2Nb + 5Cl_2 \rightarrow 2NbCl_5$$

The pentachloride also may be made by chlorination of niobium pentoxide in the presence of carbon at 300°C. The products, however, contain small amounts of niobium oxide trichloride, $NbOCl_3$.

Analysis

Elemental composition: Nb 34.39%, Cl 65.61%. The compound may be decomposed in water carefully and the aqueous solution appropriately diluted and measured for niobium by x-ray fluorescence or colorimetry (See Niobium). Chloride ion may be measured by ion chromatography or titration with a standard solution of silver nitrate using potassium chromate as an indicator. An appropriately diluted carbon tetrachloride solution of niobium pentachloride may be analyzed by GC/MS. The solution may be injected directly onto a semipolar capillary GC column and identified from the mass spectra. The characteristic mass ions for compound identification are 93 and 270.

NIOBIUM PENTAFLUORIDE

[7783-68-8]
Formula: NbF_5; MW 187.90
Synonyms: columbium pentafluoride; niobium(V) fluoride

Uses

Niobium pentafluoride is used in making other fluoro compounds of niobium.

Physical Properties

Colorless monoclinic crystals; hygroscopic; density 3.293 g/cm^3; melts at 72°C; vaporizes at 236°C; hydrolyzes in water forming hydrofluoric acid and fluoroniobic acid, H_2NbOF_5; soluble in alcohol, slightly soluble in chloroform, carbon disulfide and sulfuric acid.

Thermochemical Properties

$\Delta H_f°$	–433.5 kcal/mol
$\Delta G_f°$	–406.1 kcal/mol
S°	38.3 cal/degree mol
C_ρ	32.3 cal/degree mol

Preparation

Niobium pentafluoride is obtained as an intermediate during the recovery of niobium metal from its ores (See Niobium). It also can be prepared by direct fluorination of niobium metal at 250 to 300°C, either by fluorine gas or anhydrous hydrofluoric acid. The pentafluoride vapors are condensed in a pyrex or quartz tube from which it is sublimed at 120°C under vacuum and collected as colorless crystals.

Also, niobium pentafluroide can be prepared by the reaction of fluorine with niobium pentachloride:

$$2NbCl_5 + 5F_2 \rightarrow 2NbF_5 + 5Cl_2$$

Analysis

Elemental composition: Nb 49.44%, F 50.56%. The compound is dissolved in water cautiously. The solution is diluted appropriately and analyzed for niobium by x-ray fluorescence or colorimetry (see Niobium). The fluoride ion in aqueous solution may be measured by ion chromatography or a fluoride ion-selective electrode.

NIOBIUM PENTOXIDE

[1313-96-8]
Formula: Nb_2O5; MW 265.81
Synonyms: niobium(V) oxide; diniobium pentaoxide; columbium pentaoxide

Uses

Niobium pentaoxide is used for preparing many niobium salts, including niobium carbide (Balke process). It also is used in the aluminothermic process in the production of niobium metal.

Physical Properties

White orthogonal crystals; density 4.60 g/cm^3; melts at 1,512°C; insoluble in water; soluble in hydrofluoric acid.

Thermochemical Properties

$\Delta Hf°$	–454.0 kcal/mol
$\Delta Gf°$	–422.1 kcal/mol
S°	32.8 cal/degree mol
Cρ	31.6 cal/degree mol
ΔH_{fus}	24.9 kcal/mol

Preparation

Niobium pentoxide is produced as an intermediate during recovery of Nb metal from ores (See niobium).

Also, the pentoxide may be produced by igniting niobium metal powder, niobium carbide, or niobium fluoride in oxygen.

Reactions

Niobium pentaoxide undergoes two important types of reactions, one is reduction to niobium metal or to lower oxides, and the other involves conversion of pentoxide to oxide trihalides when treated with halogens or halides. These reactions occur mostly at elevated temperatures. Reductions may be carried out by carbon, hydrogen, niobium carbide, niobium metal, and other reducing agents at elevated temperatures and often in vacuum:

$$Nb_2O_5 + 7C \rightarrow 2NbC + 5CO$$

$$2Nb_2O_5 + Nb \rightarrow 5NbO_2$$

When treated with aqueous hydrofluoric acid followed by evaporation to dryness, niobium dioxide fluoride, NbO_2F [15195-33-2] is formed:

$$Nb_2O_5 + 2HF \rightarrow 2Nb_2O_5 + H_2O$$

Niobium pentoxide reacts with hydrogen chloride gas at 400 to 700°C to form niobium oxide trichloride, $NbOCl_3$ [13597-20-1]:

$$Nb_2O_5 + 6HCl \rightarrow 2NbOCl_3 + 3H_2O$$

Reaction with carbon tetrachloride at elevated temperatures also yields the same product:

$$2Nb_2O_5 + 3CCl_4 \rightarrow 4NbOCl_3 + 3CO_2$$

Pentaoxide also reacts with niobium pentachloride at elevated temperatures, forming the oxide trichloride:

$$Nb_2O_5 + 3NbCl_3 \rightarrow 5NbOCl_3$$

Yellow-brown oxide called tribromide of niobium, $NbOBr_3$ [14459-75-7], is produced by reacting niobium pentoxide with bromine and carbon at 550°C:

$$Nb_2O_5 + 3Br_2 + 3C \rightarrow 2NbOBr_3 + 3CO$$

Analysis

Elemental composition: Nb 69.90%, O 30.10%. The oxide is dissolved in HF—HNO_3 mixture and diluted appropriately. The solution is analyzed for niobium by x-ray fluorescence or colorimetry (See Niobium).

NITRIC ACID

[7697-37-2]
Formula: HNO_3; MW 63.01

History and Uses

Nitric acid was known to alchemists in ancient times. Cavendish in 1784 synthesized the acid by applying an electric spark to humid air. Earlier in 1776, Lavoisier determined that the acid contained oxygen. In 1798, Milner prepared nitric acid from ammonia along with nitrogen oxides by oxidation of ammonia vapor over red-hot manganese dioxide. In 1816, Gay-Lussac and Berthollet established its composition.

Nitric acid is one of the most important industrial chemicals in the world. Its largest use is in the fertilizer industry for producing various nitrate fertilizers. Such fertilizers include ammonium-, sodium-, potassium-, and calcium nitrates. Other major applications of nitric acid are in making nitrates and nitrooganics for use in explosives, gunpowder, and fireworks. Ammonium nitrate, nitroglycerine, nitrocellulose, and trinitrotoluenes are examples of such explosives, while barium and strontium nitrates are used in fireworks.

Another major application is in producing cyclohexanone, a raw material for adipic acid and caprolactam to produce nylon.

Nitric acid is a common laboratory reagent. It also is one of the most used oxidizing agents, applied in several organic and inorganic syntheses. Some synthetic applications of nitric acid include the production of diazo dyes, varnishes, lacquers, plastics, polyurethanes, and detergents. Other applications are in metal etching, ore extractions, pickling of stainless steel, rocket propellant, for processing nuclear fuel, as a solvent in aqua regia, for sample digestion in metal analysis by AA or ICP, and in preparing analytical standards.

Concentrated nitric acid used in commerce is not 100% pure nitric acid. It is the constant boiling mixture containing 68% pure acid.

Physical Properties

Colorless liquid; highly corrosive; refractive index 1.397 at 16.5°C; density 1.503 g/L; freezes at –42°C; boils at 83°C; completely miscible with water; forms a constant boiling azeotrope with water at 68.8 wt% nitric acid; the azeotrope has density 1.41 g/mL and boils at 121°C.

Thermochemical Properties

$\Delta Hf°$ (liq)	–41.61 kcal/mol
$\Delta Hf°$ (gas)	–32.28 kcal/mol
$\Delta Hf°$ (molar aq.)	–49.56 kcal/mol
$\Delta Hf°$ (liq)	–19.31 kcal/mol
$\Delta Gf°$ (gas)	–17.87 kcal/mol
$\Delta Gf°$ (molar aq.)	–26.61 kcal/mol
$S°$ (liq)	37.19 cal/degree mol
$S°$ (gas)	63.64 cal/degree mol
C_ρ (liq)	26.26 cal/degree mol
C_ρ (gas)	12.75 cal/degree mol
ΔH_{fus}	2.51 kcal/mol

Production

Nitric acid may be produced by several methods. In the laboratory, it is prepared by distilling a solution of potassium nitrate in concentrated sulfuric acid containing equal amounts (by weight) of each..

$$KNO_3 + H_2SO_4 \rightarrow KHSO_4 + HNO_3$$

Nitric acid decomposes to nitrogen dioxide. Therefore, the temperature must be kept as low as possible. During this preparation, nitric acid condenses as a fuming liquid. The pure acid may be obtained when it is collected at –42°C, its freezing point. When nitric acid is collected by condensation at room temperature, it may decompose partially to nitrogen pentaoxide, N_2O_5, which fumes in moist air. Early commercial processes were based on reaction of Chile saltpeter ($NaNO_3$) with sulfuric acid. Concentrated nitric acid was obtained by distilling the reaction mixture.

Nitric acid also may be obtained by rapid passage of air through an electric arc. The method is based on Cavendish's first preparation of nitric acid. In this method, nitrogen and oxygen first combine to form nitric oxide. The gaseous product mixture usually containing about 2% nitric oxide is combined with excess oxygen to form nitrogen dioxide and nitrogen pentoxide. Dissolution of these gases in water forms nitric acid. The process, however, is expensive and unsuitable for commercial application.

Currently, nitric acid is manufactured exclusively by catalytic oxidation of ammonia. Platinum or platinum-rhodium is an effective catalyst of this oxidation (Ostwald process). Three basic steps in such ammonia oxidation process are: (1) oxidation of ammonia to form nitric oxide:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

The above reaction is rapid and shifts almost fully to the product side. (2) oxidation of nitric oxide to form nitrogen dioxide:

$$2NO + O_2 \rightarrow 2NO_2$$

The above reaction also is rapid and goes almost to completion below 150°C. (3) dissolution of nitrogen dioxide in water:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

This reaction is moderately exothermic, releasing 32.4 kcal/mol.

Several mechanisms have been proposed for absorption of nitrogen dioxide in water. Nitrogen dioxide readily dimerizes to tetroxide, N_2O_4, at low temperatures and increasing pressure.

$$2NO_2 \leftrightarrow N_2O_4 \qquad \Delta H_{rxn} = -13.7 \text{ kcal/mol}$$

Absorption of tetroxide in water also could form nitric acid and nitric oxide:

$$3N_2O_4 + 2H_2O \rightarrow 4HNO_3 + 2NO$$

Several modifications in plant design and process conditions for ammonia oxidation processes have taken place in recent years. These variations are more or less based on operating pressures and temperatures, reduction of NO_x emission and other environmental regulations, and the desired plant production capacity.

Nitric acid obtained in standard ammonia oxidation is usually 50 to 70% by weight aqueous solution. Pure nitric acid of 98-99% may be obtained either by extractive distillation or by direct strong nitric (DSN) processes. In the distillation method, concentrated nitric acid of 50-70% is distilled with 93% sulfuric acid in a steam-heated tower. Sulfuric acid acts as a dehydrating agent. The distilled nitric acid vapor is condensed to pure nitric acid, while sulfuric acid absorbing water from 50-70% nitric acid loses its strength to about 70% and collects at the bottom. The 70% sulfuric acid is concentrated back to 93%

for reuse by removal of water in a sulfuric acid concentrator.

In the DSN process, nitrogen tetroxide, N_2O_4 obtained from ammonia oxidation is absorbed by concentrated nitric acid in the presence of air or oxygen to yield pure nitric acid. Alternatively, N_2O_4 may be separated from the product gases of the ammonia oxidation process by refrigeration and then is treated with dilute nitric acid in air or oxygen.

Reactions

Reactions of nitric acid are of three types. First, those of a strong monobasic acid. When dissolved in water, it readily forms hydronium, H_3O^+, and nitrate NO_3^- ions:

$$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$$

Second, it reacts vigorously with bases:

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

The ionic species that would be present in an aqueous solution when mixed with caustic soda solution are:

$$H^+ + NO_3^- + Na^+ + OH^- \rightarrow Na^+ + NO_3^- + H_2O$$

Evaporation of the solution will yield the salt sodium nitrate, $NaNO_3$.

Third, the most important reactions of nitric acid are the oxidation reactions in solution, attributed to the NO_3^- ion in the presence of hydrogen ions. Such oxidation depends on the pH of the medium and the nature of the substance oxidized.

Nitric acid reacts with practically all common metals. Such reactions, however, can vary, forming different products depending on the position of the metal in electrochemical series, the concentration of nitric acid, temperature, and pH. Very weakly electropositive metals such as arsenic, antimony, or tin are oxidized to oxides in higher valence states; e.g.,

$$2HNO_3 + 2Sb \rightarrow Sb_2O_3 + 2NO + H_2O$$

Metal oxides are formed as hydrates, like $Sb_2O_3 \cdot nH_2O$. Nitric acid reacts with more electropositive metals forming nitrates and one of the oxides of nitrogen. The nature of NO_x formed depends on the position of the metal in the electrochemical series and temperature. Those metals that do not liberate hydrogen from dilute acids generally form nitric oxide and metal nitrates under cold or dilute conditions. While under warm or concentrated conditions of nitric acid, the same metals yield nitrogen dioxide and nitrates. An example is copper, which can generate nitric oxide or nitrogen dioxide from nitric acid. Its reaction with nitric acid under cold and warm conditions are shown below:

$$3Cu + 8HNO_3 \xrightarrow[\text{dilute acid (1:1)}]{\text{cold}} 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + 4HNO_3 \xrightarrow[\text{concentrated acid}]{\text{warm}} Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

On the other hand, metals that are more electropositive than hydrogen, such as zinc and magnesium which liberate hydrogen from dilute acids, react with nitric acid to give nitrous oxide and the metal nitrates:

$$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

$$4\ Mg + 10HNO_3 \rightarrow 4Mg(NO_3)_2 + N_2O + 5H_2O$$

Magnesium may react with very dilute nitric acid liberating some hydrogen.

Nitric acid oxidizes most metal ions to their higher oxidation states:

$$3Fe^{2+} + NO_3^- + 4H^+ \rightarrow 3Fe^{3+} + NO + 2H_2O$$

$$3Cu_2O + 14HNO_3 \rightarrow 6Cu(NO_3)_2 + 2NO + 7H_2O$$

Concentrated nitric acid passivates many metals, such as, iron, cobalt, nickel, aluminum and chromium, forming a protective film of oxides on their surfaces, thus preventing any further reaction. Very dilute nitric acid is reduced by a strong reducing agents, such as metallic zinc, to form ammonia and hydroxylamine, NH_2OH.

Noble metals, such as gold, platinum, palladium, rhodium and iridium are not attacked by nitric acid at ordinary temperatures. These metals, however, dissolve in aqua regia (3:1 HCl—HNO_3 mixture). Nitric acid in aqua regia oxidizes gold to Au^{3+}, which readily combines with Cl^- to form soluble chlorocomplex, $AuCl_4^-$.

Except silicon, all other carbon group metals, namely, germanium, tin, and lead, are oxidized by concentrated nitric acid. While germanium and tin form their dioxides, lead forms nitrate.

$$3Ge + 4HNO_3 \rightarrow 3GeO_2 + 4NO + 4H_2O$$

$$3Sn + 4HNO_3 \rightarrow 3SnO_2 + 4NO + 4H_2O$$

$$3Pb + 8HNO_3 \rightarrow 3Pb(NO_3)_2 + 4H_2O$$

Concentrated nitric acid oxidizes nonmetals, such as sulfur, phosphorus, and iodine forming their oxyacids with liberation of nitric oxide. For example, cold concentrated nitric acid reacts with sulfur to form sulfuric acid:

$$S + 2HNO_3 \rightarrow H_2SO_4 + 2NO$$

Hot concentrated nitric acid reacts with iodine forming iodic acid:

$$3I_2 + 10HNO_3 \rightarrow 6HIO_3 + 10NO + 2H_2O$$

Similarly, phosphoric acid, H_3PO_4, is obtained from reaction of nitric acid with violet phosphorus.

Among the oxygen group elements, while sulfur is oxidized to +6 oxidation state (in H_2SO_4), selenium and tellurium are oxidized to +4 oxyacids with the liberation of nitrogen dioxide:

$$Se + 4HNO_3 \rightarrow H_2SeO_4 + 4NO_2 + H_2O$$

Reaction with fluorine forms an unstable compound, 'fluorine nitrate', NO_3F:

$$HNO_3 + F_2 \rightarrow HNO_3F + HF$$

Nitric acid undergoes decomposition when heated above its boiling point or when exposed to light:

$$4HNO_3 \xrightarrow{light} 4NO_2 + 2H_2O + O_2$$

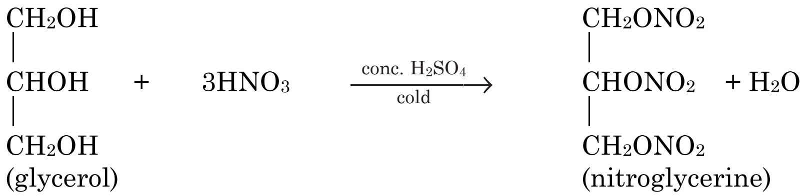
Nitric acid is used for nitration of many organic compounds. Many nitro derivatives are made by such reactions. Pure nitric acid or often its combination with concentrated sulfuric acid is employed in these syntheses. When pure nitric acid is dissolved in concentrated sulfuric acid, it forms nitronium ion, NO_2^+, the active species in nitration reactions:

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

Nitration reactions are mostly substitution type, forming a wide variety of products including nitrobenzene, nitrotoluenes, nitroglycerine, nitrocellulose, trinitrotoluene, nitrophenols and nitroparaffins, many of which are known chemical explosives. Some examples are:

$$\underset{\text{(benzene)}}{C_6H_6} + \underset{\text{(nitric acid)}}{HONO_2} \xrightarrow{\text{conc. } H_2SO_4} \underset{\text{(nitrobenzene)}}{C_6H_5NO_2} + H_2O$$

$$\underset{\text{(}n\text{-propane)}}{CH_3CH_2CH_3} + \underset{\text{(nitric acid)}}{HONO_2} \xrightarrow{\text{conc. } H_2SO_4} \underset{\text{(nitropropane)}}{CH_3CH_2CH_2NO_2}$$



$$\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{(glycerol)} \end{matrix} \quad + \quad 3HNO_3 \quad \xrightarrow[\text{cold}]{\text{conc. } H_2SO_4} \quad \begin{matrix} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2ONO_2 \\ \text{(nitroglycerine)} \end{matrix} \quad + H_2O$$

Cotton reacts with nitric acid to form a polymeric explosive material, nitrocellulose. Nitric acid reacts with hexamethylenetetramine, ammonium nitrate, and acetic anhydride to form cyclotrimethylenetrinitramine, a high explosive known as cyclonite, used to make plastic bombs:

$$\underset{\text{(hexamethylenetetramine)}}{\text{Cyclo-}[C_3H_6(NH)_2N\text{—}CH_2\text{—}N(CH_3)_2]} + 4HNO_3 + 2NH_4NO_3 + \underset{\text{(acetic anhydride)}}{6CH_3C(=O)\text{—}O\text{—}C(=O)CH_3}$$

$$\longrightarrow \underset{\text{(cyclonite)}}{\text{cyclo-}[N(NO_2)CH_2N(NO_2)CH_2N(NO_2)CH_2]} + \underset{\text{(acetic acid)}}{12CH_3COOH}$$

Analysis

The strength of nitric acid can be determined by acid-base titration against a standard solution of a strong base such as NaOH using a color indicator, or by potentiometric titration using a pH meter. Nitrate ion, NO_3^- in its aqueous solution, may be measured with a nitrate ion-selective electrode or by ion chromatography following appropriate dilution.

Hazard

Because it is a strong oxidizing agent, nitric acid may undergo violent reactions with powerful reducing agents. Many nitration reactions of organics yield explosive products. Pure nitric acid is highly corrosive to skin causing severe injury. Concentrated acid (68.8 wt %) is moderately corrosive to skin. The acid may decompose under heating or photochemically, liberating toxic nitrogen dioxide gas.

NITRIC OXIDE

[10101-43-9]
Formula: NO; MW 30.006
Synonym: nitrogen monoxide

History, Occurrence, and Uses

Nitric oxide was discovered by Van Helmont in 1620. It occurs in the exhaust gases from automobiles along with other oxides of nitrogen, at trace concentrations. It also is found in minute quantities in the upper atmosphere, resulting from the oxidation of nitrogen in the presence of ionizing radiation or by electric discharge. Nitric oxide is the most stable oxide of nitrogen. It is used as an intermediate or as a starting reactant in the production of many nitrogen compounds, including nitrogen dioxide, nitric acid and nitrosyl chloride.

Physical Properties

Colorless gas; paramagnetic; density 1.3402 g/L; slightly heavier than air, air density 1.04 (air=1); liquefies at –151.8°C to a blue liquid; the refractive index of the liquid 1.330 at –90°C; the density of the liquid 1.269 g/mL at –150.2°C; solidifies at –163.6°C to a bluish-white snow-like solid; critical temperature –94°C; critical pressure 65 atm; slightly soluble in water, 4.6 mL gas dissolves in 100 mL water at 20°C while 7.34 mL and 2.37 mL dissolve in the same volume of water at 0 and 60°C, respectively; more soluble in alcohol than water; soluble in carbon disulfide, and in ferrous sulfate solution (reacts).

Thermochemical Properties

$\Delta H_f°$	21.57 kcal/mol
$\Delta G_f°$	20.69 kcal/mol
S°	50.35 cal/degree mol
C_ρ	7.13 cal/degree mol

Production

Nitric oxide is produced from nitrogen and oxygen by passing an electric spark through air or by bringing oxygen and nitrogen together at high temperatures. In either method, only small quantities of nitric oxide are generated.

Nitric oxide also can be made by reactions of nitric acid, nitrate, or nitrite salts with metals, metal oxides, or sulfates. Several metals react with nitric acid liberating nitric oxide. (See Nitric Acid, Reactions). For example, action of 1:1 nitric acid on copper turnings forms nitric oxide:

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO\uparrow$$

The above method does not yield pure nitric oxide.

In the laboratory pure nitric oxide may be prepared by warming a mixture of a nitrate salt with ferrous sulfate and concentrated sulfuric acid. The overall reaction may be written as:

$$2NaNO_3 + 5H_2SO_4 + 6FeSO_4 \rightarrow NaHSO_4 + 3Fe_2(SO_4)_3 + 4H_2O + 2NO\uparrow$$

Nitric acid formed as an intermediate by the action of sulfuric acid on nitrate is reduced by ferrous sulfate to produce nitric oxide. The reaction must be carried out under only mild heating. Otherwise, under prolonged heating, nitric oxide may combine with any unreacted ferrous sulfate to form a brown ring derivative.

Another method of preparing pure nitric oxide is to heat nitrate-nitrite mixture with a metal oxide in a lower oxidation state:

$$KNO_3 + 3KNO_2 + Cr_2O_3 \rightarrow 2K_2CrO_4 + 4NO\uparrow$$

Reactions

Although nitric oxide is the most stable of all the oxides of nitrogen, it reacts spontaneously with oxygen forming nitrogen dioxide:

$$2NO + O_2 \rightarrow 2NO_2$$

The above reaction is exothermic.

Reactions with chlorine and bromine form nitrosyl chloride and nitrosyl bromide, respectively:

$$2NO + Cl_2 \rightarrow 2NOCl$$

$$2NO + Br_2 \rightarrow 2NOBr$$

Nitric oxide readily loses an electron to form nitrosyl or nitrosonium ion, NO^+, which is known to form salts, such as nitrosyl hydrogen sulfate, $(NO)^+(HSO_4)^-$ or nitrosyl tetrafluoroborate, $(NO)^+(BF_4)^-$.

Nitric oxide is reduced to nitrous oxide by sulfurous acid:

$$2NO + H_2SO_3 \rightarrow N_2O + H_2SO_4$$

Also, it is reduced by several other reducing agents, forming a wide variety of products. For example, when nitric oxide is passed over a heated metal, such as copper or iron, it is reduced to nitrogen gas:

$$2NO + 2Cu \rightarrow N_2 + 2CuO$$

Tin, in the presence of hydrochloric acid, reduces nitric oxide to hydroxylamine. The overall molecular equation may be as follows:

$$2NO + 3Sn + 6HCl \rightarrow 2NH_2OH + 3SnCl_2$$

Chromium(II) salts in acid medium can reduce nitric oxide to ammonia:

$$NO + 5Cr^{2+} + 5H^+ \rightarrow NH_3 + 5Cr^{3+} + H_2O$$

Nitric oxide is oxidized to nitrate ion by permanganate ion. In acid medium, the products are nitric acid and manganese dioxide:

$$NO + MnO_4^- \rightarrow NO_3^- + MnO_2$$

$$NO + MnO_4^- + H^+ \rightarrow HNO_3 + MnO_2$$

Nitric oxide forms a brown ring in cold ferrous sulfate solution (brown ring test for nitrates). The reaction involves the replacement of a water molecule by nitric oxide in hydrated ferrous ion:

$$[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O$$

A similar replacement reaction occurs with cyanide ion in the complex hexacyanoferrate(III):

$$[Fe^{III}(CN)_6]^{3-} + NO \rightarrow [Fe^{III}(CN)_5(NO)]^{2-} + CN^-$$

Nitric oxide reacts with sodium in liquid ammonia forming sodium hyponitrite, an ionic compound of composition $Na_2^{2+}(NO^-)_2$:

$$2NO + 2Na \xrightarrow{\text{liquid } NH_3} Na_2N_2O_2$$

Analysis

Nitric oxide is analyzed with GC using a TCD or by mass spectrometer using helium as a diluent and carrier gas. The characteristic mass for NO ion is 30. Also, it can be identified by the brown ring test in cold $FeSO_4$ solution (see Reactions). In contact with air it oxidizes to NO_2, which is then identified from color, odor, and chemical properties.

Toxicity

Nitric oxide gas is moderately toxic. Exposure can cause severe irritation of the eyes, nose, and throat. Chronic inhalation produces pulmonary edema, irritation of the respiratory tract and corrosion of teeth.

NITROGEN

[7727-37-9]

Symbol: N; atomic number 7; atomic weight 14.0067; a Group V A (Group 15) nonmetallic element; occurs as diatomic gas; covalent molecule; Lewis structure :N≡N: ; bond length 1.10 Å; bond energy 226 kcal/mol; first ionization energy 335.4 kcal/mol; electronegativity 3.0; valence states –3, –2, –1, 0, +1, +2, +3, +4 and +5; more common valence states –3, + 5, +4, +3, +2, +1; two stable isotopes, N-14 (99.63%) and N-15 (0.37%); six radioactive isotopes that have the mass numbers, 12, 13, 16, 17, 18, and 19; longest-lived radioisotope, N-13, $t_{1/2}$ 9.97 min.

History, Occurrence, and Uses

Nitrogen was discovered independently in 1772 by Swedish chemist Carl Scheele and Scottish botanist Daniel Rutherford. Priestly, Cavendish, and Lavoisier also obtained nitrogen independently more or less around the same time. Nitrogen was recognized first as an element by Lavoisier, who named it "azote", meaning "without life." The element was named nitrogen in 1790 by Chaptal. The name derived from the Greek name 'nitre' for potassium nitrate which contains nitrogen.

Nitrogen is the principal component of air. The earth's atmosphere constitutes about 78% nitrogen by volume. Nitrogen also occurs as nitrates in several minerals such as Chile saltpeter (sodium nitrate), niter or saltpeter (potassium nitrate) and minerals containing ammonium salts. Nitrogen is contained in many complex organic molecules including proteins and amino acids that occur in all living organisms. Nitrogen occurs ubiquitously all over the earth from the upper stratosphere and thermosphere to deep down in the crust from which it is outgassed continuously along with other deep earth gases. It is found in volcanic gases, mines, spring water, and absorbed in rocks. The concentration of nitrogen in the earth's crust is estimated to be 20 mg/kg. Its average concentration in seawater is about 0.5 mg/L. Nitrogen also is found in other planets. Its concentration in Mars' atmosphere is 2.6%.

Molecular nitrogen as a constituent of atmosphere serves as a diluent of oxygen in the air needed for breathing. Gaseous nitrogen has numerous uses in chemical, food, metal, and electrical industries. Nitrogen is needed in commercial production of ammonia (Haber process) and in preparation of many nitrides. It also is the starting material in making cyanamide salts, cyanides, and nitrogen oxides for producing nitric acid. Other applications are in gas chromatrography, as a carrier gas, to provide an inert atmosphere in chemical reactions, to prevent oxidation reactions, to reduce fire or explosion hazards, and to dilute a reacting gas.

In the food industry nitrogen is used to prevent mold growth, spoilage from oxidation, and insect infestation.

Other miscellaneous applications of nitrogen gas include pressurizing cable jackets, preventing carburization in welding and soldering, inflating balloons, agitating liquid baths, and cooling catalytic reactors in petroleum refining.

Liquid nitrogen is used in rapid freezing of food and in its packaging, storage and transportation, for preserving blood, tissues, and bone marrow, for cryopulverizing plastics, resins, waxes, spices, and scrap rubber to achieve small particle size, and for deforming stainless steel to make high strength wires for springs.

Physical Properties

Colorless, odorless and tasteless gas; diamagnetic; density 1.229 g/L; converts to a colorless liquid at –195.79°C; specific gravity of the liquid N_2 0.808; solidifies at –210°C; solid nitrogen exists in two allotropic forms, a cubic alpha form and a hexagonal beta form; alpha allotrope changes to beta form at –237.5°C; critical temperature –146.94°C; critical pressure 33.46 atm; vapor pressure of the fluid at –203°C 5.1 torr; the gas is slightly soluble in water, 2.4

parts by volume dissolving in 100 parts water at 0°C; soluble in liquid ammonia; insoluble in alcohol.

Thermochemical Properties

$\Delta H_f°$ (N_2)	0.0
$\Delta H_f°$ (N)	112.78 kcal/mol
$\Delta G_f°$ (N_2)	0.0
$\Delta G_f°$ (N)	108.89 kcal/mol
S° (N_2)	45.77 cal/degree mol
S° (N)	36.61 cal/degree mol
C_ρ (N_2)	6.961 cal/degree mol
C_ρ (N)	4.968 cal/degree mol

Production

All commercial processes involve either separation of nitrogen from air by cryogenic distillation or combustion of air with natural gas to remove oxygen. In the former process, air is liquefied and the liquid air is subjected to fractional distillation to separate its components.

In the combustion process, natural gas (methane), or propane or carbon is burned in air for the removal of oxygen:

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2O$$

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

The above reactions are exothermic and proceed to complete combustion. The gaseous mixture from combustion consists of nitrogen, carbon dioxide, water vapor and trace amounts of carbon monoxide and hydrogen. The mixture is cooled and the water vapor is condensed to liquid water, carbon dioxide and residual water is removed by adsorbing over molecular sieve.

Many nitrogen generator devices are commercially available to produce high purity gas in small amounts. In these, nitrogen is obtained from compressed air. It is separated from other air components by selective permeation through polymeric hollow fiber membranes after prefiltration.

In the laboratory, nitrogen may be generated by several methods, such as: thermal decomposition of ammonium dichromate:

$$(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O;$$

reaction of ammonia with bromine water:

$$8NH_3 + 3Br_2 \rightarrow N_2 + 6NH_4^+ + 6Br^-;$$

decomposition of ammonia with copper(II) oxide at elevated temperatures:

$$2NH_3 + 3CuO \rightarrow N_2 + 3Cu + 3H_2O;$$

decomposition of ammonium nitrite in hot aqueous solution:

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O;$$

and carefully decomposing sodium azide:

$$2NaN_3 \rightarrow 2Na + 3N_2$$

Reactions

At ordinary temperatures, nitrogen is very stable and chemically inert to most substances. However, at elevated temperatures and pressures or in the presence of an electric spark or ionization radiation, nitrogen can combine with many substances.

Nitrogen reacts with hydrogen at 400°C and 200 to 300 atm pressure in the presence of a catalyst, such as iron oxide, to form ammonia (the Haber process):

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Nitrogen combines with oxygen at elevated temperatures, or when an electric spark is passed through its mixture with oxygen, nitrogen oxides are formed:

$$N_2 + O_2 \rightarrow 2NO$$

Ionization radiations also cause such combination, a process that occurs in the upper atmosphere forming oxides of nitrogen in low yields.

Nitrogen reacts with a mixture of red hot charcoal and sodium metal to form sodium cyanide:

$$N_2 + 2Na + 2C \rightarrow 2NaCN$$

The cyanide salt also is obtained by heating nitrogen with a mixture of graphite and sodium carbonate at 900°C:

$$N_2 + Na_2CO_3 + 4C \rightarrow 2NaCN + 3CO$$

When nitrogen mixed with methane is passed through an electric arc, the products are hydrogen cyanide and acetylene:

$$N_2 + 4CH_4 \rightarrow 2HCN + C_2H_2$$

Nitrogen reacts with acetylene at 1,500°C forming hydrogen cyanide:

$$N_2 + C_2H_2 \rightarrow 2HCN$$

Nitrogen reacts with calcium carbide at high temperature to form calcium cyanamide:

$$N_2 + CaC_2 \rightarrow CaCN_2 + C$$

Carbides of certain metals, such as cerium and uranium, react with nitrogen at very high temperatures forming their nitrides:

$$2CeC_2 + N_2 \xrightarrow{>1200°C} 2CeN + 4C$$

Nitrogen combines with alkali and alkaline earth elements at ordinary temperatures to form their nitrides:

$$N_2 + 6Li \rightarrow 2Li_3N$$

$$N_2 + 3Ca \rightarrow Ca_3N_2$$

However, its reactions with heavy metals at elevated temperatures form hard refractory interstitial nitrides of nonstoichiometric compositions.

Nitrogen at low pressure under electric discharge conditions produces a greenish-yellow glow, which continues to glow after the discharge. The molecular nitrogen is converted into active nitrogen that is chemically reactive and probably consists of excited nitrogen atoms and molecules at high energy levels. Such active nitrogen readily reacts with many unreactive elements in cold, such as mercury and sulfur, forming their nitrides.

Analysis

Nitrogen is analyzed by GC using a thermal conductivity detector and a molecular sieve, 5Å or equivalent column, and helium as the carrier gas. Its presence may be confirmed by mass spectrometry. The characteristic mass ion for GC/MS identification of N_2 is 28.

NITROGEN DIOXIDE

[10102-44-0]
Formula: NO_2; MW 46.0055; dimerizes to dinitrogen tetroxide, N_2O_4
Synonym: nitrogen peroxide

Occurrence and Uses

Nitrogen dioxide is an intermediate in producing nitric acid. It also is used in the lead chamber process for making sulfuric acid. It is used as a nitrating and oxidizing agent, in rocket fuels, in the manufacture of hemostatic cotton and other oxidized cellulose compounds, and in bleaching flour. Nitrogen dioxide occurs in trace concentrations in the atmosphere due to oxidation of nitric oxide in air. It also is found in exhaust gases of internal combustion engines, in industrial waste gases from plants using nitric acid, and in cigarette smoke. Brown color of smog in many industrial urban areas is attributed to nitrogen dioxide.

Physical Properties

Reddish-brown gas; pungent irritating odor; liquefies to a yellow liquid at 21.2°C; liquefies under pressure to a brown fuming liquid, commercially known as nitrogen tetroxide which actually is an equilibrium mixture of nitrogen dioxide and dinitrogen tetroxide, N_2O_4; converts to a colorless crystalline solid at –11.2°C; refractive index 1.40 at 20°C; density of gas in air 1.58 (air=1); density of liquid 1.449 g/mL at 20°C; critical temperature 158.2°C; critical pressure 99.96 atm; decomposes in water forming nitric acid; reacts with alkalies; soluble in concentrated nitric and sulfuric acids; soluble in chloroform and carbon disulfide.

Thermochemical Properties

$\Delta H_f°$	7.93 kcal/mol
$\Delta G_f°$	12.26 kcal/mol
S°	57.35 cal/degree mol
C_ρ	8.89 cal/degree mol

Preparation

Nitrogen dioxide may be prepared by several methods. It is produced when an electric discharge is passed through air. It is made commercially from nitric oxide and air. Nitric oxide made by various processes (See Nitric Oxide) rapidly oxidizes to nitrogen dioxide. It is formed by decomposing nitric acid or by oxidizing ammonia with air:

$$HNO_3 \rightarrow NO_2 + H_2O$$

$$4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O$$

Also, nitrogen dioxide can be made by heating copper with nitric acid.

In the laboratory, nitrogen dioxide is formed by heating lead nitrate or nitrate of another heavy metal:

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

.

Gaseous mixture of nitrogen dioxide and oxygen is passed through a U-tube placed in a freezing mixture. Nitrogen dioxide condenses and is collected as liquid.

Reactions

The oxidation state of nitrogen in nitrogen dioxide is +4. The molecule has an unpaired electron. Both these factors contribute to its reactivity.

Nitrogen dioxide readily converts to other forms of nitrogen oxides. It coexists in equilibrium with its dimeric form, N_2O_4. The latter is more stable at ordinary temperatures.

When heated above 150°C, nitrogen dioxide dissociates to nitric oxide and oxygen:

$$2NO_2 \rightarrow 2NO + O_2$$

Nitrogen dioxide dissolves in cold water, forming a mixture of nitrous acid and nitric acid:

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

Nitrous acid readily decomposes to nitric acid and nitric oxide:

$$3HNO_2 \rightarrow HNO_3 + NO + H_2O$$

The overall reaction is as follows:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

When dissolved in warm water, no nitrous acid forms.

Nitrogen dioxide is a strong oxidizing agent. It oxidizes both nonmetals and metals, forming their oxides and itself reduced to nitrogen. Thus, sulfur, phosphorus and charcoal burn in nitrogen dioxide to yield oxides of these elements and nitrogen:

$$2NO_2 + 2S \rightarrow 2SO_2 + N_2$$

$$2NO_2 + 2C \rightarrow 2CO_2 + N_2$$

Copper, zinc, iron and many other metals are similarly converted to their oxides when heated with nitrogen dioxide:

$$2NO_2 + 2Cu \rightarrow 2CuO + N_2$$

$$2NO_2 + 4Zn \rightarrow 4ZnO + N_2$$

Nitrogen dioxide oxidizes an aqueous solution of iodide to iodine, hydrogen sulfide to sulfur, and carbon monoxide to carbon dioxide. In such reaction, it is reduced to nitric oxide, rather than nitrogen:

$$NO_2 + 2I^- + H_2O \rightarrow I_2 + NO + 2OH^-$$

$$NO_2 + H_2S \rightarrow NO + H_2O + S$$

$$NO_2 + CO \rightarrow NO + CO_2$$

With stronger oxidizing agents, nitrogen dioxide acts as a reducing agent. Thus, it reduces per manganate, MnO_4^-, to Mn^{2+} ion, decolorizing its solution. In this reaction, it is oxidized to nitrate ion:

$MnO_4^- + 5NO_2 + H_2O \rightarrow Mn^{2+} + 2H^+ + 5NO_3^-$

Reaction with fluorine forms nitryl fluoride, NO_2F:

$$2NO_2 + F_2 \rightarrow 2NO_2F$$

Nitrogen dioxide reacts with alkalies, giving a mixture of nitrite and nitrate:

$$2NO_2 + 2OH^- \rightarrow NO_2^- + NO_3^- + H_2O$$

Analysis

Nitrogen dioxide can be identified by color, odor, and physical properties. It is dissolved in warm water and converted to nitric acid. The latter may be measured by acid-base titration or from analysis of nitrate ion by nitrate ion-specific electrode or by ion chromatography. Alternatively, nitrogen dioxide may be passed over heated charcoal to produce nitrogen and carbon dioxide that may be analysed by GC-TCD or GC/MS (See Nitrogen, Analysis). The characteristic masses for N_2 and CO_2 formed for their identification are 28 and 44, respectively.

Hazard

Nitrogen dioxide is highly toxic. Exposure can cause strong irritation of the nose, throat, and respiratory tract. The toxic symptoms include cough, frothy sputum, chest pain, difficulty in breathing, and cyanosis with delayed effects—that may progress to hemorrhage, lung injury, and death (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons). Being a strong oxidant, its reactions with many oxidizable substances may proceed to explosive violence.

NITROGEN PENTOXIDE

[10102-03-1]
Formula: N_2O_5; MW 108.01
Synonyms: dinitrogen pentoxide; nitric anhydride; nitric acid anhydride.

Uses

Nitrogen pentoxide dissolved in chloroform is used as a nitrating agent in organic synthesis.

Physical Properties

Colorless hexagonal crystal; volatile solid; density 1.642 g/cm^3 at 18°C; melts at 30°C; decomposes at 47°C; soluble in water forming nitric acid; soluble in chloroform with some decomposition.

Thermochemical Properties

$\Delta H_f°$ (cry)	–10.31 kcal/mol
$\Delta H_f°$ (gas)	2.70 kcal/mol
$\Delta G_f°$ (cry)	27.2 kcal/mol
$\Delta G_f°$ (gas)	27.5 kcal/mol
S° (cry)	42.6 cal/degree mol
S° (gas)	85.0 cal/degree mol
C_ρ (cry)	34.2 cal/degree mol
C_ρ (gas)	20.2 cal/degree mol

Preparation

Nitrogen pentoxide is obtained by dehydration of pure nitric acid by phosphorus(V) oxide at low temperatures around –10°C:

$$2HNO_3 + P_2O_5 \rightarrow 2HPO_3 + N_2O_5$$

Reactions

Nitrogen pentoxide is an anhydride of nitric acid. It dissolves in water to form nitric acid:

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

Its reactions in aqueous medium are those of nitric acid.

Nitrogen pentoxide is an unstable compound. Its vapors decompose to nitrogen dioxide and oxygen when heated at 45°C:

$$2\ N_2O_5\ (g) \rightarrow\ 4NO_2\ (g) + O_2\ (g)$$

Analysis

Nitrogen pentoxide may be dissolved in water and the aqueous solution analyzed for nitric acid by acid-base titration or potentiometric titration. Alternatively, the oxide is dissolved in chloroform. diluted appropriately, and analyzed by GC/MS using a polar GC column.

Toxicity

Nitrogen pentoxide is toxic by ingestion and can produce mouth burn. Skin contact can cause irritation.

NITROGEN TETROXIDE

[10544-72-6]
Formula: N_2O_4; MW 92.011; a dimer of nitrogen dioxide, NO_2; exists in equilibrium with NO_2
Synonym: dinitrogen tetroxide

Uses

Nitrogen tetroxide is a solvent and a powerful and selective oxidizing agent. It's adducts with organic solvents are used to synthesize nitrates of noble metals.

Physical Properties

Colorless liquid or gas; exists in equilibrium with NO_2; density 1.45 g/mL at 20°C; boils at 21.25°C; freezes at –9.35°C to a colorless diamagnetic solid; critical temperature 157.85°C; critical pressure 99.64 atm; critical volume 167 cm^3/mol; reacts with water.

Thermochemical Properties

$\Delta H_f°$ (liq)	–4.66 kcal/mol
$\Delta H_f°$ (gas)	2.20 kcal/mol
$\Delta G_f°$ (liq)	23.30 kcal/mol
$\Delta G_f°$ (gas)	23.40 kcal/mol
S° (liq)	50.0 cal/degree mol
S° (gas)	72.73 cal/degree mol
C_ρ (liq)	34.11 cal/degree mol
C_ρ (gas)	18.48 cal/degree mol
ΔH_{vap}	9.11 kcal/mol
ΔH_{fus}	3.50 kcal/mol
ΔH_{diss} (gas)	13.6 kcal/mol

Preparation

Nitrogen tetroxide always is formed along with nitrogen dioxide during preparation of the dioxide (See Nitrogen Dioxide.) Mixed oxides are produced by oxidation of nitric oxide (NO) in air, heating metal nitrates, or by metals reacting with nitric acids or nitrates.

Reactions

The tetroxide occurs along with the dioxide, NO_2, in an equilibrium that is highly dependent on temperature.

$$N_2O_4 \leftrightarrow 2NO_2$$

While low temperature favors dimeric tetroxide, equilibrium shifts toward dioxide at higher temperatures. Thus, at 100°C the composition of the vapor is 90% NO_2 and 10% N_2O_4. At 140°C, the tetroxide completely dissociates into dioxide. At 150°C, thermal dissociation of dioxide begins, giving NO and O_2. Decomposition of NO_2 is complete at about 600°C. At 21.15°C, the boiling point of N_2O_4, the liquid composition is 99.9% N_2O_4 and 0.1% NO_2.

Reactions of N_2O_4 are the same as those involving NO_2 (See Nitrogen Dioxide, Reactions.) The tetroxide is a strong oxidizing agent in aqueous solution.

Nitrogen tetroxide readily forms adducts with many organic compounds including aromatics, and heterocyclic compounds of nitrogen and oxygen, such as pyridine (py) and tetrahydrofuran (THF), respectively. Examples are $N_2O_4 \cdot py$ and $N_2O_4 \cdot THF$.

Many metals, such as Cu, Zn, and Fe dissolve in a mixture of N_2O_4 and organic solvent forming their nitrate—N_2O_4 adducts. Nitrate adducts with N_2O_4 having compositions: $Cu(NO_3)_3 \cdot N_2O_4$, $Fe(NO_3)_2 \cdot 1.5N_2O_4$, and $Zn(NO)_3 \cdot 2N_2O_4$ are known. (Cotton, F. A., Wilkinson, G., Murillo, C.A. and M. Bochmann. 1999. *Advanced Inorganic Chemistry*, 6th ed. pp 329-30. New York: John Wiley & Sons.)

Nitrogen tetroxide dissociates completely in anhydrous nitric acid forming NO^+ and NO_3^- ions:

$$N_2O_4 \rightarrow NO^+ + NO_3^-$$

Nitrogen tetroxide reacts with concentrated sulfuric acid forming $NOHSO_4$ along with nitric acid and sulfur trioxide. A simplified balanced reaction may be written as follows:

$$N_2O_4 + 2H_2SO_4 \rightarrow NOHSO_4 + HNO_3 + SO_3 + H_2O$$

Analysis

Nitrogen tetroxide may be identified from physical and chemical properties and its ready conversion to NO_2 gas which may be identified by its brown red color, pungent odor, and chemical analysis (See Nitrogen Dioxide, Analysis.)

Hazard

See Nitrogen Dioxide, Hazard.

NITROGEN TRICHLORIDE

[10025-85-1]
Formula: NCl_3; MW 120.365
Synonyms: nitrogen chloride; chlorine nitride; trichlorine nitride

Uses

Nitrogen trichloride bleaches and sterilizes flour. It also preserves citrus fruits.

Nitrogen trichloride may be found in treated wastewater due to chlorine added as a bactericide reacting with dissolved ammonia. Such reactions may form monchloro- and dichloramine, and nitrogen trichloride:

$$3NHCl_2 + H^+ \rightarrow 2NCl_3 + NH_4^+$$

Physical Properties

Yellow, oily, heavy liquid; pungent odor; density 1.653 g/mL; freezes to rhombohedral crystalline solid below –40°C; evaporates in air rapidly; vapor pressure 150 torr at 20°C; explodes when heated at 93°C; highly unstable, decomposes explosively in light; insoluble in water, decomposes slowly in cold water after several hours; decomposes in hot water; soluble in benzene, chloroform, carbon tetrachloride, carbon disulfide and phosphorus trichloride.

Thermochemical Properties

$\Delta H_f°$ (liq)	54.97 kcal/mol

Preparation

Nitrogen trichloride is prepared by passing chlorine gas into slightly acid solution of ammonium chloride. The product is continuously extracted with carbon tetrachloride:

$$NH_4Cl + 3Cl_2 \rightarrow NCl_3 + 4HCl$$

Hypochlorous acid, HOCl, also may be used instead of chlorine in such preparation.

Nitrogen trichloride can be prepared by the action of anhydrous chlorine with anhydrous ammonia:

$$3Cl_2 + NH_3 \rightarrow NCl_3 + 3HCl$$

Nitrogen trichloride is made commercially by electrolyzing an acidified solution of ammonium chloride.

Hazard

Nitrogen trichloride is an explosive compound. It explodes when heated at 93°C or when exposed to sunlight. Also, explosive reactions occur with ozone and many organic substances.

NITROGEN TRIFLUORIDE

[7783-54-2]
Formula: NF_3; MW 71.002
Synonym: nitrogen fluoride

Physical Properties

Colorless gas; moldy odor; liquefies at –128.75°C; density of liquid 3.116 g/mL; vapor pressure at –158°C 96 torr; solidifies at –206.8°C; critical temperature –39.15°C; critical pressure 44.02 atm; critical volume 126 cm^3/mol; very slightly soluble in water.

Thermochemical Properties

$\Delta H_f°$	–31.57 kcal/mol
$\Delta G_f°$	–21.66 kcal/mol
S°	66.33 cal/degree mol

C_ρ	12.76 cal/degree mol
ΔH_{vap}	2.76 kcal/mol

Preparation

Nitrogen trifluoride is prepared by electrolysis of either molten ammonium fluoride, NH_4F, or melted ammonium acid fluoride, NH_4HF_2 (or ammonium fluoride in anhydrous HF). While the NH_4F method is preferred because it forms nitrogen trifluoride as the only product, electrolysis of ammonium acid fluoride yields a small amount of dinitrogen difluoride, N_2F_2, and NF_3.

Also, nitrogen trifluoride can be prepared by reaction of ammonia with fluorine diluted with nitrogen in a reactor packed with copper. Other nitrogen fluorides, such as N_2F_2, N_2F_4, and NHF_2 also are produced. The yield of major product depends on fluorine/ammonia ratio and other conditions.

Reactions

Nitrogen trifluoride is very stable at ambient temperatures. It is much less reactive than other nitrogen trihalides. The molecule has a very low dipole moment and the lone pair of electrons on the nitrogen atom does not usually form complexes.

Nitrogen trifluoride reacts with aluminum chloride at 70°C forming N_2, Cl_2 and AlF_3:

$$2NF_3 + 2AlCl_3 \rightarrow 2AlF_3 + 3Cl_2 + N_2$$

Nitrogen trifluoride also reacts with fluorine and strong Lewis acids, such as BF_3, AsF_5 and SbF_5 under pressure. Reactions occur at low temperatures and in the presence of UV radiation to form tetrafluoroamonium salts:

$$NF_3 + F_2 + BF_3 \xrightarrow{800\,^{\circ}C} NF_4BF_4$$

$$NF_3 + F_2 + SbF_3 \xrightarrow{\text{UV light}} NF_4SbF_4$$

Tetrafluoroammonium salts hydrolyze in water, regenerating NF_3.

Nitrogen trifluoride reacts with several metals at high temperatures. When heated with copper, it yields copper(II) fluoride and dinitrogen tetrafluoride:

$$2NF_3 + Cu \rightarrow CuF_2 + N_2F_4$$

Heating with powdered titanium, zirconium, tin, and other metals at 250°C produces fluorides.

Reactions with reducing agents such as H_2, H_2S, NH_3, CO, carbon, and diborane, especially under pressure and high temperatures, can be violent.

Toxicity

Nitrogen trifluoride is mildly toxic. Prolonged exposure can cause mottling of teeth and skeletal changes. LC_{50} inhalation (mouse): 2,000 ppm/4hr.

NITROSYL CHLORIDE

[2696-92-6]
Formula: ClNO; MW 65.459
Structure: Cl—N=O. bent molecule, N—O bond distance 1.139Å and N—Cl bond distance 1.975Å

Uses

Nitrosyl chloride is an important component of aqua regia. It is an oxidizing agent in organic synthesis. It also is used as a catalyst.

Physical Properties

Yellow gas; heavier than air, density 2.3 (air=1); gas density 2.872 g/L; liquefies at –5.55°C; liquid density 1.273 g/mL; freezes at –59.4°C; critical temperature 167°C; reacts with water; soluble in fuming sulfuric acid.

Thermochemical Properties

$\Delta H_f°$	12.37 kcal/mol
$\Delta G_f°$	15.81 kcal/mol
S°	62.55 cal/degree mol
C_ρ	10.68 cal/degree mol
ΔH_{vap}	6.16 kcal/mol

Preparation

Nitrosyl chloride can be prepared by the reaction of nitric oxide with chlorine:

$$2NO + Cl_2 \rightarrow 2ClNO$$

Also, nitrosyl chloride is produced by the action of chlorine on sodium nitrate; or by the reaction of nitrosyl sulfuric acid with hydrochloric acid:

$$NaNO_3 + Cl_2 \rightarrow ClNO + NaClO_2$$

$$ONHSO_4 + HCl \rightarrow ClNO + H_2\,SO_4$$

Nitrosyl chloride also is obtained as a byproduct in the manufacture of potassium nitrate from potassium chloride and nitric acid:

$$3KCl + 4HNO_3 \xrightarrow[\text{temperature}]{\text{elevated}} 3KNO_3 + Cl_2 + ClNO + 2H_2O$$

In the above preparative method, nitrosyl chloride must be separated from nitric acid; otherwise, in the presence of pure and excess nitric acid, it can decompose to nitrogen dioxide and chlorine:

$$2ClNO + HNO_3 \rightarrow 6NO_2 + Cl_2 + 2H_2O$$

Also, nitrosyl chloride can be synthesized from its elements by heating nitrogen, oxygen and chlorine gas at 400°C:

$$N_2 + O_2 + Cl_2 \rightarrow 2ClNO$$

Faraday obtained nitrosyl chloride by dissolving palladium in a mixture of hydrochloric and nitric acids (Faraday, M. *Trans. Roy. Soc.* (London), Vol. 136, pp. 48, 1846):

$$Pd + HNO_3 + 3HCl \rightarrow PdCl_2 + ClNO + 2H_2O$$

Reactions

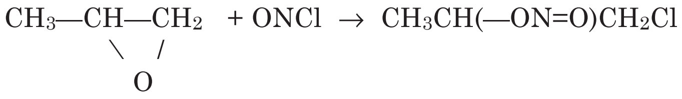
Nitrosyl chloride undergoes addition reactions with many unsaturated organic compounds. It adds to olefinic double bond as follows:

$$\text{—HC=CH— + Cl—N=O} \rightarrow \text{—ClCH—CHNO}$$

For example, it reacts with ketone to yield a nitroso derivative:

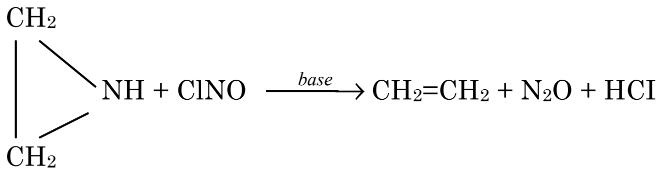
$$\underset{\text{(ketene)}}{CH_2=C=O} \xrightarrow{ClNO} \underset{\text{(nitroso derivative)}}{[ONCH_2CH_2COCl]}$$

Propylene oxide undergoes electrophilic addition, giving a nitroso derivative, $CH_3CH(\text{—}ON=O)CH_2Cl$:



$$CH_3\text{—}\underset{\diagdown\,O\,\diagup}{CH\text{—}CH_2} + ONCl \rightarrow CH_3CH(\text{—}ON=O)CH_2Cl$$

Reaction with a cyclic amine in the presence of a base and at ambient temperature forms alkene. Thus, nitrosyl chloride reacts with aziridine to form ethylene and nitrous oxide:



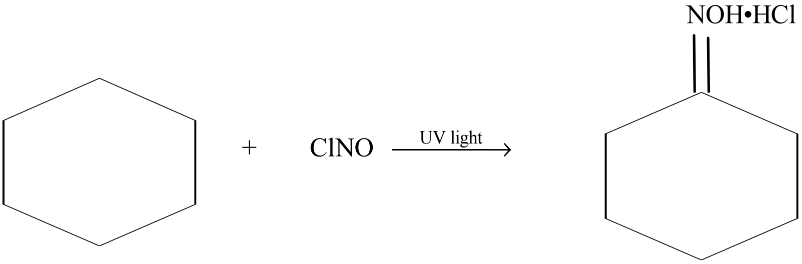
Nitrosyl chloride is oxidized by nitric acid to yield nitrogen dioxide, chlorine and water.

$$2ClNO + 4HNO_3 \rightarrow 6NO_2 + Cl_2 + 2H_2O$$

Reaction with sulfuric acid forms nitrosyl sulfuric acid:

$$H_2SO_4 + ClNO \rightarrow ONHSO_4 + HCl$$

Nitrosyl chloride reacts with cyclohexane in the presence of UV light to form cyclohexanone oxime hydrochloride:



Nitrosyl chloride in carbon tetrachloride reacts with silver thiocyanate to form silver chloride and nitrosyl thiocyanate:

$$ClNO + AgSCN \rightarrow AgCl + ONSCN$$

Analysis

Elemental composition: Cl 54.16%, N 21.40%, O 24.44%. The compound can be identified by its color and other physical properties. Analysis may be done by GC/MS using a diluent gas such as helium. Alternatively, it may be added to an olefinic double bond and the derivatives identified by physical properties, IR, and mass spectra. (See Reactions.)

Toxicity

Nitrosyl chloride is a toxic gas and a severe irritant to eyes, skin, and mucous membranes. Inhalation can result in pulmonary edema and hemorrhage.

NITROSYL FLUORIDE

[7789-25-5]
Formula: FNO; MW 49.00;
Structure: F—N=O
Synonym: nitrogen oxyfluoride

Uses

Nitrosyl fluoride is an oxidizer in rocket propellants. Other applications are in organic synthesis where it is a fluorinating agent. The compound also is a stabilizer for liquid sulfur trioxide.

Physical Properties

Colorless gas when pure; often appears bluish because of impurities; density 2.176 g/L; liquefies at –56°C; density of liquid 1.326g/mL at its boiling point; solidifies at –134°C; density of solid 1.719 g/cm^3; reacts with water.

Thermochemical Properties

$\Delta Hf°$	–15.9 kcal/mol
$\Delta Gf°$	–12.2 kcal/mol
S°	59.5 cal/degree mol
C_ρ	9.88 cal/degree mol

Preparation

Nitrosyl fluoride may be prepared by the reaction of fluorine with nitric oxide:

$$F_2 + 2NO \rightarrow 2FNO$$

Nitrosyl fluoride also can be obtained by heating nitrosyl fluborate, $NOBF_4$, and sodium fluoride:

$$NOBF_4 + NaF \rightarrow NaBF_4 + FNO$$

Nitrosyl fluoborate required for the above preparation may be obtained by dissolving boric acid in 40% HF, concentrating the solution till it fumes, and purifying the $NOBF_4$ formed by sublimation in a vacuum.

Nitrosyl fluoride also can be produced by the action of nitrosyl chloride with silver fluoride:

$$NOCl + AgF \rightarrow FNO + AgCl$$

All preparations must be done in complete absence of water.

Reactions

Nitrosyl fluoride decomposes in water forming nitrous acid, nitric acid, nitric oxide and HF:

$$FNO + H_2O \rightarrow HNO_2 + HF$$

$$2FNO + HNO_2 + H_2O \rightarrow HNO_3 + 2NO + 2HF$$

Reaction with iridium hexafluoride forms trifluoroamine oxide, NF_3O, and nitrosyl iridium hexafluoride, $NOIrF_6$:

$$3FNO + 2IrF_6 \rightarrow NF_3O + 2NOIrF_6$$

Nitrosyl fluoride reacts slowly with silica when heated at 150°C forming silicon tetrafluoride, SiF_4 and dinitrogen trioxide, N_2O_3:

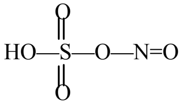
$$4FNO + SiO_2 \rightarrow SiF_4 + 2N_2O_3$$

Hazard

Nitrosyl fluoride is a dangerous irritant to the eyes, skin, and mucous membranes. Explosive reactions can occur with alkenes.

NITROSYLSULFURIC ACID

[7782-78-7]
Formula: HSO_4NO; MW 127.08
Structure:



$$HO\text{—}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{—}O\text{—}N{=}O$$

Synonyms: nitrosyl sulfate; chamber crystals; nitroxylsulfuric acid; nitrososulfuric acid; nitrosyl hydrogen sulfate

Uses

Nitrosylsulfuric acid is used in making caprolactam from benzoic acid and in preparing many disperse azo dyes. Other applications are bleaching, maturing, dough-conditioning cereal products, and in preparing crystalline diazonium sulfates.

Physical Properties

Colorless crystalline solid; rhombohedral structure; decomposes at 73.5°C; decomposes in water; soluble in sulfuric acid.

Preparation

Nitrosylsulfuric acid is produced as an intermediate in the manufacture of sulfuric acid using the lead chamber process by the reaction of sulfur dioxide, nitrogen dioxide, oxygen, and water.

Nitrosylsulfuric acid also is made from absorption of nitrogen oxides (NO_x) in oleum (fuming sulfuric acid):

$$N_2O_3 + 2H_2SO_4 \rightarrow 2ONSO_4H + H_2O$$

or by the reaction of nitrosyl chloride with concentrated sulfuric acid:

$$ClNO + H_2SO_4 \rightarrow ONSO_4H + HCl$$

Another method of preparation involves the reaction of nitrosyl bromide with silver bisulfate:

$$AgHSO_4 + BrNO \rightarrow ONHSO_4 + AgBr$$

In making disperse azo dyes, nitrosylsulfuric acid is produced by the addition of sodium nitrite, $NaNO_2$, to concentrated sulfuric acid (1g $NaNO_2$ per 13 g H_2SO_4)

Reactions

The compound decomposes in moist air forming nitric and sulfuric acids.

$$2ONHSO_4 + O_2 + 2H_2O \rightarrow 2HNO_3 + 2H_2SO_4$$

However, above 50°C decomposition in moist air forms nitric oxide, nitrogen dioxide, and sulfuric acid:

$$2ONHSO_4 + H_2O \rightarrow NO + NO_2 + 2H_2SO_4$$

Nitrosylsulfuric acid hydrolyzes in water forming sulfuric acid and oxides of nitrogen as shown above.

Nitrosylsulfuric acid reacts with cyclohexane carboxylic acid to form caprolactam. The starting material in such large-scale production of caprolactam is benzoic acid. The reactions are:

$$C_6H_5COOH \xrightarrow[Pd]{H_2} C_6H_{11}COOH \xrightarrow{ONHSO_4}$$

(benzoic acid) (cyclohexane carboxylic acid)

$$\text{cyclo—}(C_6H_{10}NH){=}O + CO_2 + H_2SO_4$$

(caprolactam)

Analysis

Elemental composition: S 25.23%, H 0.79%, N 11.02, O 62.95%. Nitrosylsulfuric acid may be analysed by IR, NMR and mass spectrometry, as well as by elemental microanalysis. Wet analysis involves hydrolyzing the compound in the presence of excess NaOH and measuring excess base by potentiometric titration.

NITROUS ACID

[7782-77-6]

Formula: HNO_2; MW 47.014; exists only in solution and has not been isolated.

Uses

Nitrous acid is a diazotizing agent. The acid diazotizes primary aromatic amines to diazo derivatives in manufacturing azo dyes.

Physical Properties

Pale blue solution; stable only in solution; weak acid, Ka 4.5×10^{-4}.

Thermochemical Properties

$\Delta H_f°$ (gas)	–19.00 kcal/mol
$\Delta G_f°$ (gas)	–10.99 kcal/mol
S° (gas)	60.73 cal/degree mol
C_ρ	10.90 cal/degree mol

Preparation

Nitrous acid may be obtained in solution by adding a strong acid to nitrite; e.g., adding hydrochloric acid to sodium nitrite solution:

$$H^+ + NO_2^- \rightarrow HNO_2$$

Reactions

Nitrous acid is unstable. It decomposes to form nitric acid and nitric oxide:

$$3HNO_2 \rightarrow NO_3^- + H_3O^+ + 2NO$$

Strong oxidizing agents, such as permanganate, readily oxidize nitrous acid to nitric acid.

Nitrous acid is an effective oxidizing agent. It oxidizes hydrogen sulfide to sulfur forming either nitric oxide or ammonia, depending on the acidity of the solution:

$$2HNO_2 + H_2S \rightarrow S + 2NO + 2H_2O$$

$$HNO_2 + 3H_2S \rightarrow 3S + NH_3 + 2H_2O$$

In acid medium it oxidizes iodide ion to iodine:

$$HNO_2 + I^- + 6H^+ \rightarrow 3I_2 + NH_3 + 2H_2O$$

Analysis

Nitrous acid in solution can be analysed by measuring the nitrite ion, NO_2^-, by ion chromatography, or a colorimetric method. The colorimetric test sees the reddish purple azo dye produced at pH 2.0 to 2.5 by coupling diazotized sulfanilamide with N-(1-naphthyl)ethylenediaminedihydrochloride (APHA, AWWA and WEF. 1998. *Standard methods for the Examination of Water and Wastewater*, 20th ed. Washington, DC: American Public Health Association). In addition to tests for nitrite ion, other tests should confirm that the NO_2^- is from nitrous acid and not any metal nitrite. This can be done by oxidizing iodide ion in acid medium and measuring the liberated iodide by titrating against a standard solution of sodium thiosulfate using starch indicator, and also by measuring ammonia liberated with an ammonium ion selective electrode. (See Reactions).

NITROUS OXIDE

[10024-97-2]
Formula: N_2O; MW 44.013; a diamagnetic molecule.
Synonyms: dinitrogen oxide; nitrogen monoxide; dinitrogen monoxide; hyponitrous acid anhydride; laughing gas.

History and Uses

Nitrous oxide was discovered by Priestley. It is found in the atmosphere in trace concentrations. The gas is used as an anesthetic, especially in dentistry and minor surgery. It produces mild hysteria and laughter preceding the anesthetic effect, for which reason it also is called “laughing gas.” It is used as an aerosol propellant, an aerating agent for whipped cream, and an oxidizing agent at high temperatures. Nitrous oxide also is used in the preparation of nitrites and as a flame gas in flame atomic absorption spectrometry of metals.

Physical Properties

Colorless gas with faint sweet odor and taste; heavier than air, density in air 1.53 (air=1); gas density 1.977 g/L at 0°C; noncombustible gas; supports combustion; liquefies to a colorless liquid at –88.5°C; liquid density 1.226 g/mL at –89°C; freezes to a cubic crystalline solid at –90.8°C; dipole moment 0.166 ; critical temperature 36.5°C; critical pressure 71.7 atm; solubility in water: 130 mL gas dissolves in 100mL water at 0°C and 56.7 mL in 100 mL water at 25°C; soluble in alcohol, ether and sulfuric acid.

Thermochemical Properties

$\Delta H_f°$	19.61 kcal/mol
$\Delta G_f°$	24.90 kcal/mol
S°	52.52 cal/degree mol
C_ρ	9.19 cal/degree mol

Preparation

Nitrous oxide may be prepared by heating molten ammonium nitrate carefully. Rapid and strong heating can cause explosion:

$$NH_4NO_3 \xrightarrow{250^\circ C} N_2O\uparrow + 2H_2O$$

Any nitric oxide produced in small amounts may be removed by passage through $FeSO_4$ solution.

Alternatively, the gas may be obtained by warming a solution of ammonium nitrate in nitric acid containing a small amount of hydrochloric acid.

Pure nitrous oxide may be prepared by treating a solution of sodium nitrite, $NaNO_2$ with that of hydroxyl amine hydrochloride, $NH_2OH \cdot HCl$:

$$NH_3OH^+ + NO_2^- \rightarrow N_2O\uparrow + 2H_2O$$

Reactions

Nitrous oxide at ambient temperature is chemically unreactive to most substances. It is not readily oxidized or reduced, unlike other oxides of nitrogen. When passed over heated metals such as iron, copper, and lead, nitrous oxide decomposes to nitrogen and oxygen, exothermically:

$$N_2O \rightarrow N_2 + \tfrac{1}{2}\ O_2$$

Because of its ability to release oxygen at high temperatures, nitrous oxide supports combustion only at high temperatures. Once the reaction initiates, the substances burn in oxygen liberated from nitrous oxide. Thus, nitrous oxide can oxidize many nonmetals, such as sulfur and phosphorus at high temperatures:

$$2N_2O + S \rightarrow SO_2 + 2N_2$$

$$5N_2O + 2P \rightarrow P_2O_5 + 5N_2$$

When passed over molten sodium amide, nitrous oxide yields sodium azide:

$$N_2O + 2NaNH_2 \rightarrow NaN_3 + NaOH + NH_3$$

Nitrous oxide reacts with dioxygen difluoride at ordinary temperatures forming various fluorinated products, such as FNO, FNO_2, and $FONO_2$:

$$N_2O + O_2F_2 \rightarrow FNO + FNO_2$$

$$FNO_2 + O_2F_2 \rightarrow FONO_2 + F_2$$

Analysis

Nitrous oxide can be analyzed by GC on a molecular sieve column using a thermal conductivity detector and helium as carrier gas. It may be identified by GC/MS from its mass spectra. The molecular ion is 44. Also, it can be oxidized to NO and identified by the brown-ring test, using $FeSO_4$ solution. (see Nitric Oxide.)

NITRYL CHLORIDE

[13444-90-1]
Formula: NO_2Cl; MW 81.47; planar structure;
Cl—N bond distance 1.84Å; N—O distance 1.202Å; O—N—O bond angle 130.6°

Uses

Nitryl chloride is used as a nitrating agent in organic synthesis. For example, benzene may be converted to nitrobenzene. The compound also is a chlorinating agent in many preparative reactions.

Physical Properties

Colorless gas; chlorine-like odor; gas density 2.81 g/L at 100°C; liquefies to a pale-yellow liquid at –14.3°C; density of the liquid 1.33 g/mL; solidifies at –145°C; decomposes above 120°C; reacts with water.

Preparation

Nitryl chloride is prepared most conveniently by reacting chlorosulfonic acid with anhydrous nitric acid at 0°C:

$$ClSO_3H + HNO_3 \xrightarrow{0^{\circ}C} NO_2Cl + H_2SO_4$$

An older preparation method involves passing dry chlorine gas slowly over dry silver nitrate heated to about 100°C. The gaseous reaction products are allowed to cool to low temperature. After several hours, nitryl chloride condenses to a pale yellowish-brown liquid. Chlorine is removed by purging with CO_2.

$$2AgNO_3 + 2Cl_2 \rightarrow 2NO_2Cl + 2AgCl + O_2$$

Reactions

Nitryl chloride hydrolyzes in water forming nitric acid and hydrochloric acid:

$$NO_2Cl + H_2O \rightarrow HNO_3 + HCl$$

The compound decomposes readily to nitrogen dioxide and chlorine on heating; slow decomposition can occur at ordinary temperatures:

$$2\ NO_2Cl \rightarrow 2NO_2 + Cl_2$$

Reaction with sodium hydroxide forms sodium nitrite and sodium hypochlorite:

$$2NaOH + NO_2Cl \rightarrow NaNO_2 + NaOCl + H_2O$$

Nitryl chloride is a strong oxidizing agent. It reacts explosively with reducing agents. It readily attacks many metals.

Nitryl chloride reacts with many organics forming their nitro derivatives. Such Friedel-Crafts nitration is catalyzed by a Lewis acid, such as $AlCl_3$. An example is nitration of benzene to nitrobenzene:

$$C_6H_6 + NO_2Cl \xrightarrow{AlCl_3} C_6H_5NO_2 + HCl$$

Nitration also may be achieved noncatalytically without using $AlCl_3$. For example, sodium tetrafluoroborate may be added to benzene to yield nitrobenzene:

$$C_6H_6 + NaBF_4 + NO_2Cl \rightarrow C_6C_5NO_2 + NaCl + HF + BF_3$$

Nitryl chloride reacts with acetic anhydride forming acetyl chloride and acetyl nitrate:

$$(CH_3CO)_2O + NO_2Cl \rightarrow CH_3COCl + CH_3\ CONO_3$$

Analysis

Nitryl chloride may be identified by its mass spectra. The characteristic mass ions are 81, 83, 46, 35, and 37. Alternatively, nitryl chloride may be identified from its physical and chemical properties (See Reactions). The wet analytical method involves treatment with an excess solution of NaOH and titrating the excess NaOH with a standard solution of H_2SO_4. Alternatively, nitryl chloride is decomposed in water, and the acids HNO_3 and HCl formed are measured by titration or the NO_3^- and Cl^- determined by ion specific electrodes or ion chromatography.

Hazard

Nitryl chloride is a strong oxidizing agent. Contact with strong reducing agents can cause explosion. The gas is highly corrosive and a strong irritant to eyes, nose and lungs. Exposure to high concentration can be fatal.

NITRYL FLUORIDE

[10022-50-1]
Formula: NO_2F; MW 65.00; planar structure; F—N distance 1.35Å; N—O distance 1.23Å; O—N—O angle 125°C (estimated).

Uses

Nitryl fluoride is an oxidizer in rocket propellants. It also is a fluorinating and nitrating agent in organic synthesis.

Physical Properties

Colorless gas; pungent odor; density 2.90 g/L; heavier than air, density in air 2.24 (air=1); liquefies to a colorless liquid at –63.5°C; solidifies at –139°C; decomposes in water; also decomposes in alcohol, ether and chloroform.

Preparation

Nitryl fluoride is obtained by reacting fluorine with nitrogen dioxide or nitric oxide:

$$N_2O_4 + F_2 \rightarrow 2NO_2F$$

$$4NO + F_2 \rightarrow 2NO_2F + N_2$$

Using nitrogen dioxide provides an easier preparation than nitric oxide.

A convenient method of preparing nitryl fluoride is to heat dinitrogen tetroxide with cobalt(III) fluoride at 300°C:

$$N_2O_4 + CoF_3 \xrightarrow{300^\circ C} 2NO_2F + 2CoF_2$$

Reactions

Nitryl fluoride is a strong oxidizing agent. Most reactions are similar to those of nitryl chloride, NO_2Cl (See Nitryl Chloride Reactions). Nitryl fluoride hydrolyzes rapidly in water forming nitric acid and hydrofluoric acid:

$$NO_2F + H_2O \rightarrow HNO_3 + HF$$

Reaction with ethanol produces ethyl nitrate:

$$NO_2F + C_2H_5OH \rightarrow C_2H_5NO_3 + HF$$

Reactions with reducing agents can be explosive. The compound attacks most metals almost as vigorously as fluorine. It spontaneously ignites boron, silicon, phosphorus, arsenic, antimony, and iodine at ordinary temperatures.

Nitryl fluoride can add a nitrate group to many organics forming their nitro derivatives:

$$C_6H_6 + NO_2F \rightarrow C_6H_5NO_2 + HF$$

Analysis

Nitryl fluoride may be identified from its physical and chemical properties. Its hydrolysis products, nitric and hydrofluoric acids, may be measured by selective ion electrodes or by ion chromatography. The gas, diluted in helium or hydrogen (in cold), may be identified by GC/MS.

NOBELIUM

[10028-14-5]

Symbol: No; atomic number 102; atomic weight 259; an actinide series, transuranium, synthetic radioactive element; electron configuration $[Rn]5f^{14}7s^2$; valence states +2, +3.

The element was discovered independently by several groups nearly simultaneously. In 1958, Ghiorso, Sikkeland, Walton, and Seaborg at Berkeley, California, synthesized an isotope of this new element by bombardment of a mixture of curium isotopes containing 95% Cm-244 and 4.5% Cm-246 with carbon-12 ions. This new element was named nobelium in honor of Alfred Nobel, discoverer of dynamite.

Prior to this, in 1957, two other groups also reported making isotopes of element 102. One team consisting of investigators from the USA, England, and Sweden irradiated Cm-244, –246, and –248 target with C-13 ions generated in the heavy ion cyclotron and produced an isotope of element 102 with mass 254. The other group, working at Dubna Institute in the USSR, bombarded plutonium-239 and –241 with oxygen-16 in the heavy ion cyclotron.

Nobelium may be synthesized by several methods involving irradiation of isotopes of curium, plutonium, and fermium in the form of thin targets with heavy ions of boron, carbon, and oxygen using double-recoil technique. The nuclear reaction in the synthesis of No-254 carried out by Ghiorso and his group is as follows:

$$^{246}_{96}Cm + ^{246}_{96}C \xrightarrow{8.5\ MeV} ^{227}_{88}No + 4\,^{4}_{2}n$$

Eleven isotopes of nobelium are known at present. Their masses range from 250 to 262. The longest-lived isotope is No-259 with a half life of 58 minutes.

OSMIUM

[7440-04-2]

Symbol: Os; atomic number 76; atomic weight 190.23; a Group VIII B (Group 8) transition metal element; a noble metal of platinum group; electron configuration [Xe]$4f^{14}5d^{6}6s^{2}$; valence states +1, +2, +3, +4, +5, +6, +7, +8; most common states +3, +4, +6; seven natural isotopes: Os-184 (0.02%), Os-186 (1.58%), Os-187 (1.61%), Os-188 (13.32%), Os-189 (16.13%), Os-190 (26.44%), Os-192 (41.03%); twenty-eight radioactive isotopes in the mass range 162–183, 185, 191 and 193-196; longest-lived radioisotope, Os-194 ($t_{1/2}$ 6.0 year).

History, Occurrence, and Uses

Osmium was discovered by English chemist Smithson Tennant in 1804. The element was named osmium after the Greek word, *osme*, which means a smell, because of the pungent and peculiar odor of its volatile oxide.

Osmium occurs in nature, always associated with other platinum group metals. It usually is found in lesser abundance than other noble metals. Its most important mineral is osmiridium (or iridosmine), a naturally occurring mineral alloyed with iridium.

The commercial applications of osmium are limited and considerably fewer than other platinum group metals. Its alloys are very hard and are used to make tips of fountain-pen nibs, phonograph needles, and pivots. The metal also exhibits effective catalytic properties in hydrogenation and other organic reactions. Such catalytic applications, however, are limited and osmium fails to replace other noble metals, particularly palladium and platinum, which are more effective as catalysts and cost less.

Physical Properties

Bluish-white lustrous metal; brittle and fairly hard; close-packed hexagonal crystal system; density 22.48 g/cm^3; Moh's hardness 7.0; melts at about 3,050°C; vaporizes above 5,300°C; electrical resistivity 8.12 microhms-cm at 0°C; Young's modulus 4.0×10^4 tons/in^2; magnetic susceptibility 0.052×10^{-6} cm^3/g; thermal neutron absorption coefficient 15 barns; insoluble in water; insoluble in HCl and H_2SO_4; slightly soluble in nitric acid and aqua regia; insoluble in ammonia; solubilized by fusion with caustic soda and sodium peroxide or caustic soda and potassium chlorate and the mass dissolved in water.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	189.0 kcal/mol
$\Delta G_f°$ (cry)	0.0
$\Delta G_f°$ (gas)	178.89 kcal/mol
S° (cry)	7.8 cal/degree mol
S° (gas)	46.00 cal/degree mol
C_ρ (cry)	5.90 cal/degree mol
C_ρ (gas)	4.97 cal/degree mol
Coefficient of linear expansion, at 20°C	6.1×10^{-6}/°C

Production

Osmium is recovered from platinum group minerals or certain ores of nickel and copper.

When recovered from the mineral osmiridium, the mineral is fused with zinc to convert it into a zinc alloy. The alloy is then treated with hydrochloric acid to dissolve the zinc away leaving a finely divided material. This finely divided solid then is fused with sodium peroxide and caustic soda to convert osmium and ruthenium into their water-soluble sodium salts, sodium osmate and sodium iridate, respectively. While osmium is fully converted to osmate salt, most ruthernium and a small part of iridium are converted to ruthenate and iridate, respectively. The fused mass is leached with water to separate metals from solid residues.

To separate osmium from ruthenium, the aqueous solution is acidified with nitric acid. While nitric acid oxidizes osmate ion to volatile osmium tetroxide, OsO_4, it converts ruthenium to a nitric oxide complex. Osmium tetroxide is removed from the solution by distillation in air and collected in an aqueous solution of caustic soda containing ethanol. Osmium tetroxide solution is heated with ammonium chloride, upon which osmium precipitates out as a complex chloride, $OsO_2(NH_3)_4Cl_2$. The precipitate is filtered, washed and decomposed by ignition with hydrogen to yield osmium metal.

The mineral osmiridium may alternatively be chlorinated at elevated temperatures on a bed of sodium chloride. Osmium is converted to water-soluble sodium chloroosmate. Iridium and ruthenium also are converted into water-soluble sodium chloroiridate and chlororuthenate. The insoluble residues are filtered out. Osmium is recovered from this solution in several steps as mentioned above.

Osmium and other precious metals also may be recovered from sludges generated at the anode from electrolytic refining of nickel and copper from certain nickel-copper ores. After removal of all nonplatinum group metals by a combination of various methods, the residual sludge is digested with aqua regia to solubilize osmium and other precious metals.

Reactions

Osmium in finely divided form reacts slowly with oxygen or air at ambient temperatures to form osmium tetroxide.

$$Os + 2O_2 \rightarrow OsO_4$$

The bulk metal is stable in oxygen at ordinary temperatures but reacts at 200°C, forming osmium tetroxide. When further heated to 800 to 1,500°C in air or oxygen, the tetroxide converts to volatile trioxide, OsO_3. When the metal is heated in a stream of OsO_4 vapor, osmium dioxide is produced:

$$Os + OsO_4 \rightarrow 2OsO_2$$

The metal converts to its fluoride, OsF_6 when heated with fluorine at 300°C. The reaction also yields the tetrafluoride, OsF_4, as a minor product. A similar reaction occurs with chlorine, but at much higher temperatures of 650 to 700°C, forming both the trichloride, $OsCl_3$, and the tetrachloride, $OsCl_4$. Formation of the tetrachloride is favored at higher temperatures.

Osmium is stable in mineral acids even under boiling conditions. The metal, however, is attacked by fused alkalies, such as caustic soda and caustic potash, particularly in the presence of an oxidizing agent such as sodium peroxide, sodium hypochlorite, or sodium nitrite, forming osmates.

Osmium is oxidized by nitric acid to form osmium tetroxide, OsO_4.

Analysis

Osmium in trace quantities can be determined by flame AA method using nitrous oxide-acetylane flame at wavelength 290.9 nm. The metal or its insoluble compounds can be solubilized by fusion with caustic soda and potassium perchlorate and dissolving the fused mass in water.

OSMIUM TETROXIDE

[20816-12-0]
Formula: OsO_4; MW 254.23
Synonym: osmium(VIII) oxide.

Uses

Osmium tetroxide is an intermediate in the separation of osmium from other platinum group metals. It is used as an oxidizing agent and also an oxidation catalyst in organic synthesis. It is used for hydroxylation of organic compounds at double bonds, such as conversions of olefins to glycols. The oxide also is used for fixing and staining biological materials for microscopic examination.

Physical Properties

Pale, yellow crystalline solid; chlorine-like acrid odor; monoclinic crystals having terahedral structure; density 5.1 g/cm^3; melts at 40.6°C; vaporizes at 129.7°C; sublimation begins below its boiling point; vapor pressure 11 torr at 27°C; critical temperature 405°C; critical pressure 170 atm; moderately soluble in water, 7.24 g/100mL at 25°C; soluble in most organic solvents.

Thermochemical Properties

$\Delta H_f°$ (cry)	–94.19 kcal/mol
$\Delta H_f°$ (gas)	–80.59 kcal/mol
$\Delta G_f°$ (cry)	–72.87 kcal/mol
$\Delta G_f°$ (gas)	–69.98 kcal/mol
S° (cry)	34.39 cal/degree mol
S° (gas)	70.22 cal/degree mol
C_ρ (gas)	17.71 cal/degree mol
ΔH_{fus}	2.34 kcal/mol

Preparation

Osmium tetroxide is obtained as an intermediate during recovery of osmium metal from osmiridium or other noble metal minerals (See Osmium). In general, oxidation of an aqueous solution of an osmium salt or complex, such as sodium osmate with nitric acid, yields the volatile tetroxide which may be distilled out from the solution. In the laboratory, the compound can be prepared by oxidation of the osmium tetrachloride, $OsCl_4$, or other halide solutions with sodium hypochlorite followed by distillation.

Osmium tetroxide may also be produced by heating finely divided osmium metal in a stream of oxygen or air at 300 to 400°C.

Reactions

Heating osmium tetroxide with osmium metal forms osmium dioxide:

$$OsO_4 + Os \rightarrow 2OsO_2$$

Reaction with sodium or potassium hydroxide forms *trans*-osmate ion, *trans*-$[OsO_4(OH)_2]^{2-}$, which is reduced by ethanol to form dark purple $[Os^{VI}(O)_2(OH)_4]^{2-}$. On the other hand, reaction of osmium tetroxide with rubidium or cesium hydroxide in stoichiometric ratios usually form the ions, $[OsO_4(OH)]^-$ and $[OsO(\mu\text{-}OH)OsO_4]$ in addition to *trans*-$[OsO_4(OH)_2]^{2-}$.

Reaction with fluoride ion forms the adduct oxofluoro ion, $[OsO_4F_2]^{2-}$. For example, osmium tetroxide reacts with sodium fluoride to form an oxofluoro salt of sodium:

$$OsO_4 + 2NaF \rightarrow Na_2[OsO_4F_2]$$

Osmium tetroxide forms various complexes with donor molecules under varying conditions. For example, with pyridine(*py*) it forms a bridged complex, $[(py)OsO_2(\mu\text{–}O)]_2$.

Reaction with ammonia in aqueous potassium hydroxide yields orange red crystalline "osmiamate", $K[N\equiv OsO_3]$.

Osmium tetroxide reacts with amines, undergoing partial substitution of NR^{2-} (where R=alkyl group) with O^{2-} to form compounds such as OsO_3 (NR) and $OsO(NR)_3$.

Osmium tetroxide reacts with phenyl Grignard reagent to produce a reactive intermediate, serving as a synthetic route to prepare polyphenyl osmium complexes. For example, reaction with *o*-tolyl magnesium bromide, *o*-tolMgBr, forms a purple, tetracoordinated osmium *ortho*-tolyl complex, Os(*o*-tol)$_4$, which reacts with trimethylphosphine or carbon monoxide to yield osmium π-aryl complexes.

Osmium tetroxide forms several thiolate complexes from interaction with thiols and triphenyl- or trialkylphosphines:

$$OSO_4 \xrightarrow[PPh_3]{CH_3SH} OS^{IV}(SCH_3)_4(PPh_3)_3$$

Osmium tetroxide forms halide complex ions, hexachloroosmates, such as $[OsCl_6]^-$, $[OsCl_6]^{2-}$, and $[OsCl_6]^{3-}$. The former ion $[OsCl_6]^-$ is obtained by reaction of the tetroxide with sulfur dichloride and chlorine at ambient temperature:

$$OsO_4 + SCl_2 + Cl_2 \rightarrow [SCl_3]^+ + [OsCl_6]^-$$

The ions, $[OsCl_6]^{2-}$ and $[OsCl_6]^{3-}$ are obtained by reducing OsO_4 in HCl with Fe^{2+}.

Analysis

Elemental composition: Os 74.82%, O 25.18%. The compound can be identified by its physical properties, such as, odor, color, density, melting-, and boiling points. Its acrid odor is perceptible at concentrations of 0.02 mg/liter in air. The oxide also produces an orange color when a small amount of the compound or its aqueous solution is mixed with an aqueous solution of ammonia in KOH (see Reactions). Aqueous solution of the tetroxide may be analyzed for osmium by AA or ICP spectrometry (see Osmium). Vapors of the tetroxide may be purged from an aqueous solution by helium, adsorbed over a trap, and desorbed thermally by helium onto a GC. Alternatively, a benzene or carbon tetrachloride solution may be injected onto the GC and the compound peak identified by mass spectrometry. The characteristic mass ions for its identification should be 190 and 254.

Toxicity

Osmium tetroxide is poisonous by all routes of exposure. The vapor is an eye irritant and can produce tears and damage. The vapor also can cause upper respiratory tract irritation.

LD_{50} oral (mouse): 162 mg/kg
LC_{LO} inhalation (mouse): 40 ppm (104 mg/m^3)/4 hr.

OXYGEN

[7782-44-7]
Symbol: O; atomic number 8; atomic weight 15.9994; a Group VI A (Group 16) nonmetallic element; electron configuration $[He]2s^22p^4$, ; valence states –2, –1; occurs as a diatomic molecule; bond length 1.48Å; electronegativity 3.5 (the second most electronegative element after fluorine); atomic radius 0.73Å; ionic radius 1.40Å (as O^{2-}). The element occurs in three stable isotopes; most stable isotope, O-16 [14797-70-7], natural abundance 99.76%; the other two isotopes are O-17 [13968-48-4] (0.038%) and O-18 [14797-71-8] (0.20%).

History, Occurrence, and Uses

The discovery of oxygen, its role in respiration and combustion processes, the synthesis and understanding of some of its most important compounds undoubtedly established the foundation of modern chemistry. Most of these pioneering works were done independently during the 1770's by Scheele, Priestley, Lavoisier, and Cavendish. While Scheele was first to prepare oxygen in 1772 by heating a mixture of silver carbonate and mercury carbonate, and later on heating oxides of different metals, his results were not published until 1777. Priestley, in 1774, prepared oxygen independently by heating mercuric oxide and is usually credited for discovering oxygen. Both Scheele and Priestley recognized that oxygen was a component of air that supported combustion and respiration. Priestley's discovery was tested and extended by Lavoisier who, in 1775, meticulously established a correct theory of combustion. Cavendish synthesized water by sparking a mixture of hydrogen and air or oxygen. He also made nitric oxide and nitrogen dioxide by sparking an air-oxygen mixture, and later produced sulfur dioxide from burning sulfur in oxygen.

Oxygen takes its name from the two words 'ox' meaning 'sharp (taste)' and 'gen', which means 'to form'. The element was named oxygen by Lavoisier, who mistakenly assumed that it was a component of all acids.

Oxygen is the most abundant and most widely distributed element on earth. More than 50% of the earth's mass constitutes oxygen. Oxygen is a component of the earth's crust, mantle, rocks, minerals, hydrosphere and the atmosphere. It occurs in all oxides and in a large number of minerals containing phosphates, sulfates, carbonates, nitrates and hydroxides. The oxygen content of the earth's oceans is about 88.7% by mass. Oxygen is a component of innumerable inorganic and organic compounds that include water, carbon dioxide, nitrogen oxides, sulfur oxides, oxo acids, most bases, alcohols, aldehydes, ketones, esters, carboxylic acids, lactones, sugars and carbohydrates. Oxygen is a major constituent of air, being the second most abundant gas of the earth's atmosphere constituting 20.8% of atmosphere. While the oxygen in the lower atmosphere essentially is diatomic O_2 molecule, at about 30 to 45 km height, a triatomic form of oxygen, ozone (O_3), coexists with O_2 at varying but significant concentrations. Atomic oxygen, O, is found with molecular oxygen in the upper atmosphere.

Elemental oxygen also is present in the sun in less than 1% mass composition, as a fusion product of carbon-12, and helium-4. No planet or its moon in the solar system, other than the earth is known to contain molecular oxygen in its atmosphere, although CO_2 is a major component of many planetary atmospheres.

Oxygen is present in all living organisms and is vital for sustenance of life in the animal kingdom. The animal respiration process provides energy for tissues, produced by oxidation of carbohydrates with oxygen. The process in all vertebrates and some invertebrates involves transport of oxygen through blood where oxygen binds to hemoglobin, forming oxyhemoglobin. Despite consumption of oxygen by animals, there is no depletion of its content in air, because carbon dioxide generated in such combustion is used by plants in photosynthesis, releasing oxygen.

Oxygen has numerous industrial applications. Most oxygen manufactured today is consumed in refining iron in the steel industry. Oxygen is used for removing carbon, silicon, sulfur, phosphorus, manganese, and other impurities from liquid iron in steel making. In nonferrous metallurgy, oxygen is used to enrich fuel-air flame in furnaces in producing copper and nickel from sulfide ores.

Oxygen also is a component of oxy-hydrogen flame and oxy-acetylene flame for welding and glass blowing.

Oxygen has major uses in the chemical industry too. It is used to oxidize methane, ethylene, and other hydrocarbons. Oxidation of methane produces synthesis gas. Ethylene oxidation yields products such as ethylene oxide, acetaldehyde, and acetic acid. Oxygen also is used in making many commercial inorganic compounds including various metal oxides, oxoacids, and oxosalts.

Oxygen is used in all breathing masks and life support devices; in space vehicles, high altitude flying, fire fighting, underground mining, submarines, and underwater operations. In medicine, oxygen is used in respirators, incubators, and life support devices. It is given to patients under hypoxia, respiratory distress, impaired respiratory function, and asthmatic attack. It also is administered to treat cyanosis and for poisoning by carbon monoxide and other toxicants that can bind to hemoglobin in the blood. Oxygen also is a component of most anesthetic mixtures.

Oxygen also is used in fermentation, bleaching wood chips, odor control, and as a flame-enhancing agent.

Physical Properties

Colorless, odorless, tasteless gas; gas density 1.429 g/L at 0°C and 1.309 g/L at 25°C; liquefies at –182.96°C; liquid density 1.149 g/mL at –183°C; solidifies at –218.4°C; density of the solid oxygen at –252.4°C 1.426 g/cm^3; critical temperature –118.56°C; critical pressure 49.77 atm; critical volume 73 cm^3/mol; viscosity of gas at 25°C and 1 atm 0.192 centipoise; diffusion coefficient into air at STP 0.178 cm^2/sec; velocity of sound in oxygen at 25°C and 1 atm 330m/sec; thermal neutron absorption cross section < 0.0002 barn; solubility in water, 0.0310 mL O_2 at STP per 1mL water at 20°C or 4.34 mg/100 g water at 20°C and 1 atm (760 torr = pressure of oxygen + water vapor pressure); solubility in water at 0°C 0.0489 mL O_2 measured at STP or 6.945 mg/100 g at 0°C and 1 atm (pressure of gas + water vapor).

Thermochemical Properties

$\Delta H_f°$	0.0
$\Delta G_f°$	0.0
S°	49.0 cal/degree mol
C_ρ	7.016 cal/degree mol
ΔH_{diss}	119.11 kcal/mol

Production

Most commercial oxygen at present is obtained from air by cryogenic separation processes. Although design of oxygen manufacturing plants and process conditions may vary depending on production capacity, purity desired, and cost, basic steps are similar.

Air first is filtered to remove dust particles. Water and carbon dioxide and most trace impurities are removed by silica gel (or other effective adsorbent) at a temperature slightly above 0°C. Acetylene and other hydrocarbons also can be removed by such adsorption processes. Alternatively, clean air is compressed and cooled to freeze out water and carbon dioxide, which can be trapped and removed in reversing exchangers. Compression and cooling of air is a critical step in its liquefaction. When cooled compressed air is allowed to expand it cools further (Joule-Thomson effect), converting the gaseous air to liquid air at about –196°C. Liquefied air is subjected to fractional distillation. More volatile argon and nitrogen distill out on warming, leaving behind oxygen with trace quantities of hydrogen, helium, and other inert gases.

Oxygen may be produced by electrolysis of water. In such electrolytic procedure, small amounts of H_2SO_4 or NaOH may be added to water. Electrolysis methods, however, are not used as much commercially as are air liquefaction processes which cost less. However, in making hydrogen from water by electrolysis, oxygen is obtained as a by-product.

In the laboratory oxygen may be prepared by several chemical methods that involve thermal decomposition of solid oxides or oxo salts. The most convenient method of preparing oxygen is to heat potassium chlorate in the presence of manganese dioxide catalyst:

$$2KClO_3 \xrightarrow[MnO_2]{heat} 2KCl + 3O_2$$

Early preparation of oxygen involved thermal dissociation of metal oxides, notably mercury(II) oxide, which was used independently by both Priestley and Scheele. Also, oxides of lead, silver, and barium or potassium nitrate and permanganate were used by these and later investigators to prepare oxygen. Some reactions that yield oxygen by thermal decomposition of metal oxides and metal oxo salts, are highlighted below:

$$2HgO\ (s) \rightarrow 2Hg\ (l) + O_2\ (g)$$

$$2BaO_2\ (s) \rightarrow 2BaO\ (s) + O_2\ (g)$$

$$2PbO_2\ (s) \rightarrow 2PbO\ (s) + O_2\ (g)$$

$$2KNO_3\ (s) \rightarrow 2KNO_2\ (s) + O_2\ (g)$$

$$2Ag_2O\ (s) \rightarrow 4Ag\ (s) + O_2\ (g)$$

$$2KMnO_4\ (s) \rightarrow K_2MnO_4\ (s) + MnO_2\ (s) + O_2\ (g)$$

$$2K_2S_2O_8\ (s) \rightarrow 2K_2SO_4\ (s) + 2SO_2\ (g) + O_2\ (g)$$

Barium peroxide was used in commercial production of oxygen in the past. Heating barium oxide in air at 500°C forms barium peroxide, which decomposes at 800°C to yield oxygen:

$$2BaO\ (s) + O_2\ (g) \xrightarrow{500^\circ C} 2BaO_2\ (s)$$

$$2BaO\ (s) \xrightarrow{800^\circ C} 2BaO_2\ (s) + O_2\ (g)$$

Oxygen can be prepared chemically at ordinary temperatures. Several reactions in solution are known that may produce small quantities of oxygen at room temperatures. One such convenient method of producing oxygen is to slowly add water to sodium peroxide. The reaction is exothermic; therefore, the addition of water must be done cautiously.

$$2Na_2O_2\ (s) + 2H_2O\ (l) \rightarrow 4NaOH\ (aq) + O_2\ (g)$$

Oxygen also is liberated when an acidified solution of potassium permangnate, acidified with sulfuric acid, is treated with a solution of hydrogen peroxide:

$$2MnO_4^-\ (aq) + 5H_2O_2\ (aq) + 6H^+\ (aq) \rightarrow 2Mn^{2+}\ (aq) + 8H_2O\ (l) + 5O_2\ \ (g)$$

Reactions

Oxygen reacts with practically all elements, a number of inorganic salts, and all organics under various conditions including elevated temperatures, pressures, and the presence of a catalyst. While certain reactive metals, such as sodium, potassium and calcium react vigorously at ordinary temperatures, most other metals react with oxygen at elevated temperatures. Among alkali metals, lithium, sodium, and potassium form the oxide, Li_2O; peroxide, Na_2O_2; the peroxide K_2O_2, and superoxide, KO_2, respectively. Alkaline earth metals form oxides, such as CaO and MgO. Transition metals combine with oxygen to form three oxides at different oxidation states, e.g., FeO, Fe_2O_3, Fe_3O_4. Rate of oxidation at ambient temperatures depends on the nature of the metal and its surface area. Most metals are pyrophoric in their finely divided state, but react very slowly in bulk form. Often metal surfaces are passivated by formation of a protective oxide film. Noble and coinage metals react extremely slowly with oxygen at ordinary temperatures.

All nonmetals except helium, neon, and argon react with oxygen. Nitrogen forms five oxides, N_2O, NO, NO_2 (N_2O_4), N_2O_3, and N_2O_5; sulfur yields SO_2 and SO_3; carbon forms CO and CO_2; phosphorus forms P_2O_3 and P_2O_5; hydrogen forms H_2O and H_2O_2; and halogens form various oxides, including OF_2, ClO, and ClO_2. Inert gases, krypton and xenon, are known to form oxides.

All organic compounds undergo combustion reactions when heated with oxygen. Hydrocarbons and compounds containing C, H, and O yield carbon dioxide and water as products, while nitrogen-containing organics also form NO_x. A few reactions are shown below:

$$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$$

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

$$4C_6H_5N + 33O_2 \rightarrow 24CO_2 + 10H_2O + 4NO_2$$

Many organics also undergo oxidation of a noncombustion nature to form various commercial products. Such reactions are mostly catalytic and include production of synthesis gas, a mixture of CO and H_2, conversion of ethylene to ethylene oxide, and cumene to phenol and acetone.

$$CH_4 + \tfrac{1}{2}\,O_2 \xrightarrow{\text{catalyst}} CO + 2H_2$$

$$C_2H_4 + \tfrac{1}{2}\,O_2 \xrightarrow{\text{catalyst}} C_2H_4O$$

(ethylene) (ethylene oxide)

$$C_6H_5\text{—}CH(CH_3)_2 + O_2 \xrightarrow{\text{UV light 350 nm}}$$

(cumene)

$$C_6H_5C(CH_3)_2COOH \longrightarrow C_6H_5OH + (CH_3)_2CO$$

(cumene hydroperoxide) (phenol) (acetone)

Certain classes of organic compounds containing oxygen atoms, such as aldehydes and ethers, may react with oxygen to form peroxy derivatives:

$CH_3CHO + O_2$	→	$CH_3C(=O)OOH$
(acetaldehyde)		(peracetic acid)

Analysis

Oxygen may be identified because it supports combustion. Thus, a glowing splinter will burst into flame when exposed to oxygen. Also, it combines readily with nitric oxide forming brown nitrogen dioxide. Oxygen may be identified by GC/MS using a suitable capillary GC column, preferably under cryogenic conditions. The characteristic mass for O_2 is 32.

OXYGEN DIFLUORIDE

[7783-41-7]
Formula OF_2 ; MW 54:00 ; a bent molecule with FOF angle 104° and O–F distance 0.14 nm.
Synonyms: fluorine monoxide; fluorine oxide.

Uses

Commercial applications of oxygen difluoride are limited. It is used in organic synthesis to prepare fluoropropylenes and acylfluorides. It is used as an oxidizing and fluorinating agent in many preparative reactions and as a monomer in diolefin copolymerization.

Physical Properties

Colorless gas with a characteristic odor; unstable in the presence of moisture, otherwise stable up to 250°C; gas density 2.21g/L at 25°C; liquefies to a yellowish-brown liquid at –144.8°C; density of the liquid 1.90g/ml at –223.8°C; solidifies at –223.8°C; slightly soluble in water, decomposing very slowly; solubility 68ml gas per liter of water at 0°C; slightly soluble in acids and alkali.

Thermochemical Properties

$\Delta H_f°$	7.60 kcal/mol
ΔH_{vap}	9.11 kcal/mol

Preparation

Oxygen difluoride may be prepared by passing fluorine gas slowly through a dilute solution of caustic soda. Usually a 2% solution of NaOH is suitable for the preparation:

$$2F_2 + 2\ NaOH \rightarrow 2NaF + OF_2 + H_2O$$

At a higher alkali concentration, oxygen is formed:

$$2F_2 + 4NaOH \rightarrow 4NaF + 2H_2O + O_2$$

Oxygen difluoride can be produced by electrolysis of an aqueous solution of HF or, alternatively, electroylzing molten potassium hydrogen difluoride, KHF_2, in the presence of water.

Reactions

Oxygen difluoride decomposes slowly in water forming oxygen and fluorine:

$$2OF_2 \xrightarrow{H_2O} O_2 + 2F_2$$

Such decomposition also occurs in dilute alkali solutions. The reaction, however, is slow:

$$OF_2 + 2OH^- \rightarrow O_2 + 2F^- + H_2O$$

Oxygen difluoride reacts with many common metals forming fluorides. The reaction stops when the metal surface is covered with a protective layer of fluoride:

$$2OF_2 + 2Zn \rightarrow 2ZnF_2 + O_2$$

Reactions with certain metals, especially metalloid type elements, yield metal fluorides and oxyfluorides. Such metals include B, Si, Ge, As, Sb, Se, and Te:

$$Sb + 2OF_2 \rightarrow SbF_3 + SbOF$$

Oxygen difluoride reacts with nonmetals, such as sulfur and phosphorus, forming fluorides and oxyfluorides:

$$6OF_2 + 4S \rightarrow SF_6 + 3SO_2F_2$$

Metal oxides react with oxygen difluoride forming fluorides:

$$CaO + OF_2 \rightarrow CaF_2 + O_2$$

$$As_2O_3 + 3OF_2 \rightarrow 2AsF_3 + 3O_2$$

Oxygen difluoride is a strong oxiding agent. When mixed with hydrogen, carbon monoxide, methane or carbon, and ignited with an electrical shock, the mixture explodes forming various products. It catches fire in contact with nitric oxide.

Oxygen difluoride oxidizes sulfur dioxide to sulfur trioxide:

$$OF_2 + SO_2 \rightarrow SO_3 + F_2$$

However, in the presence of UV radiation the products are sulfuryl fluoride, SO_2F_2, and pyrosulfuryl fluoride, $S_2O_5F_2$:

$$OF_2 + 2SO_2 \xrightarrow{\text{UV radiation}} S_2O_5F_2$$

Photochemical reaction with sulfur trioxide in the presence of UV light forms a peroxy compound, FSO_2OOF:

$$OF_2 + SO_3 \xrightarrow[\text{350 nm}]{\text{UV light}} FSO_2OOF$$

Oxygen difluoride oxidizes hydrochloric, hydrobromic, and hydriodic acids in aqueons solutions, liberating chlorine, bromine, and iodine, respectively:

$$OF_2 + 4HCl \rightarrow 2\ Cl_2 + 2HF + H_2O$$

$$OF_2 + 4HBr \rightarrow 2\ Br_2 + 2HF + H_2O$$

In aqueous solutions, halide salts (Cl^-, Br^- and I^-) are similarily oxidized to free halogens.

Oxygen difluoride reacts with carbonyl fluoride, COF_2, in the presence of a catalyst, cesium fluoride, to form bis(trifluorylmethyl)trioxide, CF_3OOOCF_3 (Solomon, Irvine J. 1980. *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., Vol. 3, pp 773-75. New York: John Wiley & Sons). The overall reaction is as follows:

$$OF_2 + 2COF_2 \xrightarrow{\text{CsF}} CF_3OOOCF_3$$

Oxygen difluoride oxidizes a number of organic compounds of the type, alcohols, aldehydes, amines and aromatics. Olefins yield fluorinated products. Reactions with ethylene under controlled conditions form fluoroethane, C_2H_5F, and 1, 2- difluoroethane, FCH_2CH_2F. Tetrafluoroethylene readily combines with oxygen difluoride, forming hexafluoroethane, C_2F_6 and carbonyl fluoride, COF_2. The overall reaction is:

$$3\ F_2C{=}CF_2 + 2OF_2 \rightarrow 2F_3CCF_3 + 2COF_2$$

Reaction with benzene produces quinone and hydroquinone.
Lower aliphatic alcohols are readily oxidized to carboxylic acids:

$$CH_3CH_2OH + 2OF_2 \rightarrow CH_3COOH + H_2O + 2F_2$$

Oxygen difluoride reacts with primany amines in fluorocarbon solvents under very cold conditions to form nitroso compounds:

$$CH^3CH_2NH_2 + OF_2 \xrightarrow[\textit{fluorocarbons}]{-42°\ C} CH_3CH_2N{=}O + 2HF$$

At ambient temperatures, these primary amines decompose.

Analysis

Oxygen difluoride may be analyzed by GC, GC/MS, IR, and NMR methods. The compound may be identified by GC/MS, the characteristic mass ions are 54, 38 and 35. The compound can be measured quantitatively by wet methods based on its strong oxidizing ability (see Reactions). It liberates I_2 from an acidified solution of potassium iodide and the liberated I_2 can be measured by iodometric titration using $Na_2S_2O_3$ titrant and starch indicator. Alternatively, the compound may be treated with a measured amount of excess NaOH and the unreacted excess NaOH measured by titrating against a standard solution of HCl. Also, the fluoride ion, F^-, may be measured by fluoride selective electrode.

Hazard

Oxygen difluoride is a highly toxic gas that attacks lungs, manifesting delayed symptoms. It causes irritation of eyes, lungs, and skin. Chronic exposure can lead to pulminary edema and congestion in lungs. Inhalation also can cause systemic toxic effects in humans. LC_{50} inhalation (rat): 136ppm/1 hr

The compound is a very powerful oxidizing agent. Contact with reducing agents can cause explosion.

OZONE

[10028-15-6]

Formula: O_3; MW 47.998; an allotrope of oxygen; O—O bond length 1.28Å; O—O—O bond angle 117°.

History, Occurrence, and Uses

Ozone was discovered in 1785 by the Dutch chemist Van Marum. He observed that when an electric spark passed through oxygen, a product was formed that had a peculiar, irritating odor and that tarnished mercury. Schonbein confirmed Van Marum's observation in 1840 and determined the oxidizing properties of this "irritating odor" gas. He named it ozone from the Greek word *ozo*, which means "smelling."

Ozone occurs in the stratosphere at an altitude of 20 to 40 km, known as ozonosphere, having maximum concentrations at about 25km. It is formed in the atmosphere by the decomposition of oxygen by short wavelength UV radiation (~185 nm or shorter). The stratospheric ozone layer is vital for sustenance of life on earth. It protects the earth by absorbing the harmful ultraviolet radiation from the sun of wavelengths 220 to 290 nm, which can cause skin cancer and cataracts. Certain substances, such as chloroflurocarbons used as refrigerants for air-conditioners, aerosol propellants and reagents for plastic foam, release reactive chlorine atoms that deplete ozone in the stratosphere. On a clear, sunny day, ozone also is found in the lower atmosphere (the troposphere, the air at ground level), at concentrations ranging between 0.02 to 0.05 ppm. The concentration may vary with location and may change at different times of day, being highest in summer mid-afternoons.

Ozone has many industrial applications. It is a sterilizing and deodorizing agent. It is used for disinfection of filtered drinking water and to purify wastewaters. It also is used in water treatment plants for removal of metal impurities by oxidizing them into insoluble compounds. This removes undesired taste, odor, and color from the water. Ozone also is used for odor control.

Ozone is used in the food industry to inhibit growth of bacterias and mold in fruits, vegetables, and meat products. In paper and textile industries, ozone is used as a bleaching agent on wet paper pulp and cloth.

Probably the biggest use of ozone is in chemical industries where it is a strong oxidizing agent. It is heavily used in organic synthesis (see Reactions). It readily attacks most kinds of double bonds.

Physical Properties

Pale blue gas (in undiluted form); irritating odor above a concentration of 0.15 ppm, but the odor may be pleasant and refreshing at about 0.05 ppm; density of gas 2.144g/L at 0ºC; liquefies at –111.9ºC to a dark blue liquid; density of liquid ozone 1.614 g/L at –195.4ºC; refractive index of liquid 1.2226; freezes at –192.7º C to a bluish-black solid; critical temperature –12.05°C; critical pressure 54.98 atm; critical volume 89cm^3/mol; slightly soluble in water.

Thermochemical Properties

$\Delta H_f°$	34.1 kcal/mol
$\Delta G_f°$	39.0 kcal/mol
S°	57.08 cal/degree mol
C_ρ	9.37 cal/degree mol

Production

Ozone is generated from oxygen by passing an electric spark or silent electrical discharge through dry, and pure oxygen. This electrical discharge may be applied between two glass surfaces between which oxygen is passed. Many types of ozonizers (ozone generating apparatus) are known and commercially available for small-scale production of this gas for various uses.

Ozone may be produced by electrolysis of chilled dilute sulfuric acid (e.g. 2.5N H_2SO_4) or perchloric acid at high current density (higher than that required to produce oxygen alone). A mixture of oxygen and ozone evolve at the anode.

Reactions

The most important reactions of ozone are in oxidation. It is a stronger oxidizing agent than oxygen and in acid solution it is a very powerful oxidizing agent. The standard electrode potential, Eº, for the half reaction $O_3(g) + 2H^+ (aq) + 2e^- \rightarrow O_2 (g) + H_2O (l)$ is + 2.07 V. At ordinary temperatures ozone oxidizes metals such as silver and mercury to form their oxides. It oxidizes halides to halogens, nitrogen oxides to higher oxides of nitrogen, sulfur dioxide to sulfur trioxide, ferrous to ferric salts, and sulfides to sulfates. Some typical reactions are illustrated below.

Oxidation of silver gives a black oxide, which probably is the AgO:

$$Ag + O_3 \rightarrow AgO + O_2$$

Mercury forms mercury(II) oxide:

$$Hg + O_3 \rightarrow HgO + O_2$$

The product mixture consists of mercury (II) oxide and mercury:

$$2Hg + O_3 \rightarrow (Hg + HgO) + O_2$$

Ozone oxidizes halides in acidified aqueous solutions, liberating halogens:

$$2Cl^- + 2H^+ + O_3 \rightarrow H_2O + Cl_2 + O_2$$

Iodine similarly is liberated from an acidified solution of potassium iodide. The reaction is used to measure ozone quantitatively:

$$2I^- + 2H^+ + O_3 \rightarrow H_2O + I_2 + O_2$$

Ozone converts black lead sulfide to white lead sulfate:

$$PbS + 4O_3 \rightarrow PbSO_4 + 4O_2$$

Ozone oxidizes ferrous to ferric ion in aqueous acidic solution:

$$2Fe^{2+} + 2H^+ + O_3 \rightarrow 2Fe^{3+} + H_2O + O_2$$

When an oxygen-ozone mixture containing 3.5% ozone is passed through a solution of cobalt sulfate, cobalt (III) hydroxide precipitates. This precipitation is quantitative within the pH range 1.8 to 2.5. The overall reaction is

$$2CoSO_4 + O_3 + 5H_2O \rightarrow 2Co(OH)_3 + 2H_2SO_4 + O_2$$

Ozone reacts with nitric oxide forming nitrogen dioxide:

$$NO + O_3 \rightarrow NO_2 + O_2$$

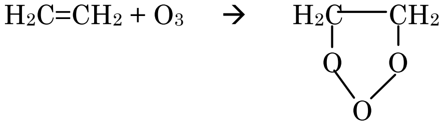
Smog formation in the atmosphere is caused by such reaction. Nitrogen dioxide is rapidly oxidized by ozone to form nitrogen pentoxide:

$$2NO_2 + O_3 \rightarrow N_2O_5 + O_2$$

Ozone decomposes readily to oxygen in the presence of a catalyst, such as manganese dioxide or other metal oxides. It also decomposes in the presence of chlorine or bromiae vapor. Such decomposition also occurs slowly noncatalytically at ordinary temperatures as well as in aqueous solution. Ozone can decompose explosively on heating.

Ozone forms red-brown potassium ozonide, KO_3, by reacting with dry potassium hydroxide. Ozonide is obtained by passing oxygen-ozone mixture containing 6 to 8% ozone over dry KOH at –10 to –15°C for several hours, followed by extraction with liquid ammonia at –60°C. Evaporation of the red solution forms red-brown needles of KO_3.

Ozone reacts with organics, attacking most kinds of double bonds. It reacts with ethylene forming ethylene ozonide, a cyclic compound containing three oxygen atoms:



Ozone attacks C=C in unsaturated compounds including olefins, cycloolefins, pinenes, aromatics, and polybutadienes (for example, causing rubber to crack).

Analysis

Many portable ozone detectors equipped with metal oxide semiconductor-type sensors are available commercially for detecting ozone, particularly for checking ozone leaks and monitoring ozone concentration in air. In the laboratory, ozone may be measured quantitatively by reaction with an aqueous solution of potassium iodide and measuring iodine liberated by titration with a standard solution of sodium thiosulfate or phenyl arsine oxide, using starch as colorimetric indicator. The reaction may be carried out in neutral solution because in acid solution other oxidizing agents can liberate iodine, too. Several other reactions may be applied to measure ozone (see Reactions). Alternatively, ozone may be separated from oxygen, nitrogen, argon, and other gases by passing the gaseous mixture over cooled silica gel, desorbing it thermally, and analyzing by GC using a TCD. It may be confirmed by mass spectrometry. The characteristic masses are 48(O_3), 32(O_2), and 16(O); 32 being the primary mass and the abundance of the mass 48 may range between 20 to 30% of mass 32 (depending on the MS conditions).

Ozone can be measured by UV and IR spectroscopy. It forms an intense band at 290nm.

Hazard

Ozone is a highly toxic gas. Inhalation can cause death in a short time. A 1-hour exposure to 100ppm can be lethal to humans. Chronic exposure can cause pulmonary disease.

LC_{50} inhalation (rat): 50ppm/4 hr. (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons)

A concentrated solution of ozone or the liquefied gas can explode on warming. Mixing liquid ozone with oxidizable organics can cause explosion. Low molecular weight ozonides formed with unsaturated organics are unstable and may cause explosive decomposition.

PALLADIUM

[7440-05-3]
Symbol: Pd; atomic number 46; atomic weight 106.42; a Group VIII (Group 10) platinum-group metal; electron configuration [Kr]$4d^{10}$; atomic radius 1.375Å; ionic radius, Pd^{2+} (coordination number 4, square planar) 0.64Å; valence states +2, +3, +4; most common valence state +2; six natural isotopes: Pd-102 (1.02%), Pd-104 (11.15%), Pd-105 (22.34%), Pd-106 (27.33%), Pd-108 (26.47%), Pd-110 (11.73%); twenty-one radioactive isotopes in the mass range 94–101, 103, 107, 109, 111–120; longest-lived radioisotope Pd-107, $t_{1/2}$ 6.5x0^6 year; shortest half-life Pd-120, $t_{1/2}$ 0.5 sec

History, Occurrence, and Uses

Palladium was discovered in 1803 by W.H. Wollaston during refining and purification of platinum metal. This new metal was found in the aqua regia extract of native platinum and was detected in solution after platinum was precipitated. It was removed as ammonium chloroplatinate. Treating this solution with mercurous cyanide precipitated a yellow palladium complex salt. The precipitate was washed and ignited to form palladium metal. Wollaston named the element palladium after the newly discovered asteroid *Pallas*.

Palladium in nature is always associated with other platinum group metals. Its abundance in earth's crust is estimated at 0.015 mg/kg, about three times more abundant than platinum. Palladium is used mostly in alloys and the majority of its alloys are used for electronics and telecommunications. They are contacts in electrical relays and automatic switching gear. Palladium-gold alloys are applied widely in dentistry and medicine. They are in devices for replacement of damaged bones and joints and as support in porcelain-overlay bridgework. Palladium alloys are used in decoration and jewelry as a substitute for gold. They are used in gems, watch cases and brooches.

One of the most important applications of palladium is to catalyze hydrogenation, dehydrogenation, and petroleum cracking. Such reactions are widely employed in organic syntheses and petroleum refining. Palladium and platinum are installed in catalytic converters in automobiles to cut down the emission of unsaturated hydrocarbon gasses.

Physical Properties

Silvery-white metal; face-centered cubic crystalline structure; density 12.02 g/cm^3; Vickers hardness, annealed 37-39; melts at 1,554°C; vaporizes at 2,970°C; electrical resistivity 9.93 microhm-cm at 0°C; Poisson's ratio 0.39; magnetic susceptibility 5.231x10^{-6} cm^3/g; thermal neutron cross section 8 barns; insoluble in water; dissolves in aqua regia, hot nitric acid and boiling sulfuric acid.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	90.2 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	81.2 kcal/mol
S° (cry)	8.98 cal/deg mol
S° (gas)	39.9 cal/deg mol
C_ρ (cry)	6.21 cal/deg mol
C_ρ (gas)	4.97 cal/deg mol
Thermal conductivity	75.3 W/(m.K)
Coefficient of thermal expansion, at 20°C	$11.1\text{x}10^{-6}/^\circ\text{C}$

Reactions

Among the platinum group metals, palladium is the least noble metal, exhibiting greater reactivity than other metals of the group. The metal forms mostly bivalent compounds, although a small number of tetravalent and a fewer trivalent compounds are known. Palladium exhibits a strong tendency to form complexes, most of which are four-coordinated square planar complexes of the metal in +2 oxidation state. When heated in air or oxygen above 350°C, palladium forms a black oxide, PdO coated over its surface. On further heating to over 790°C, the oxide decomposes back to the metal. Palladium dissolves more oxygen in molten state than in solid form.

Palladium reacts with fluorine and chlorine at 500°C forming its halides, the black PdF_3 and the red deliquescent solid $PdCl_2$.

Palladium is attacked by concentrated nitric acid, particularly in the presence of nitrogen oxides. The reaction is slow in dilute nitric acid. Finely divided palladium metal reacts with warm nitric acid forming palladium(II) nitrate, $Pd(NO_3)_2$. Hydrochloric acid has no affect on the metal. Reaction with boiling sulfuric acid yields palladium sulfate, $PdSO_4$, and sulfur dioxide.

Palladium readily dissolves in aqua regia forming chloropalladic acid, H_2PdCl_6. Evaporation of this solution yields palladium(II) chloride, $PdCl_2$.

Palladium absorbs hydrogen over 800 times its own volume over a range of temperature. By doing so, the metal swells, becoming brittle and cracked. Such absorption of hydrogen decreases the electrical conductivity of the metal. Also, such absorption activates molecular hydrogen, dissociating it to atomic hydrogen.

Production

The initial steps are similar to any other mineral extraction process. This involves crushing mineral, froth flotation, gravity concentration and other steps to obtain platinum metal concentrates that may contain about 30 to 40 wt% of platinum group metals. The concentrate is treated with aqua regia to separate soluble metals, gold, platinum, and palladium from other noble metals such as ruthenium, rhodium, iridium, osmium, and silver that remain in the insoluble residues. The solution is filtered and the filtrate consists of gold, platinum, and palladium as $HAuCl_4$, H_2PtCl_6 and H_2PdCl_4. Gold is removed by precipitation with dibutyl carbitol. Platinum is precipitated by treatment with ammonium chloride which forms an insoluble complex, ammonium chloroplatinate, $(NH_4)_2PtCl_6$. To the filtrate containing H_2PdCl_4, ammonia is added in excess, followed by hydrochloric acid. Palladium precipitates as palladium diamine dichloride, $Pd(NH_3)_2Cl_2$. The complex is purified by dissolving in excess ammonia and reprecipitating with HCl. The purified palladium complex is ignited to give a sponge of palladium metal at 99.99% purity. Alternatively, the palladium complex is heated with formic acid to obtain palladium black which on ignition yields palladium sponge.

Analysis

Palladium metal is digested in aqua regia, evaporated to near dryness. This is followed by addition of concentrated HCl and distilled water and the solution is warmed until dissolution is complete. The solution is aspirated directly into an air-acetylene flame. Palladium is detected by flame-AA spectrophotometry. Other instrumental techniques such as ICP/AES, x-ray fluorescence, and neutron activation analysis are used also.

PALLADIUM DICHLORIDE

[7647-10-1]
Formula $PdCl_2$; MW 177.33; forms a stable dihydrate, $PdCl_2 \cdot 2H_2O$.
Synonyms: palladium(II) chloride; palladous chloride.

Uses

Palladium dichloride is a starting material for preparing several palladium compounds. It also is used for detection of carbon monoxide. For such detection, a paper is soaked in very dilute solution of $PdCl_2$ which is decolorized by CO, methane and other reducing substances. It also is used in toning and electroplating solutions and in photography for porcelain pictures.

Physical Properties

Red rhombohedral crystal; hygroscopic; density 4.0g/cm^3; melts at 679°C; dissolves slowly in water; also soluble in ethanol and acetone; dissolves rapidly in hydrochloric acid.

Preparation

Palladium dichloride is prepared by dissolving palladium metal in aqua regia or hydrochloric acid in the presence of chlorine. Alternatively, it may be prepared by heating palladium sponge with chlorine gas at 500°C

Reactions

Palladium dichloride dissolves in HCl forming tetrachloropalladate ion, $[PdCl_4]^{2-}$:

$$PdCl_2+2Cl^- \rightarrow [PdCl_4]^{2-}$$

The complex ion catalyzes various types of organic reactions including oxidation of ethylene to acetaldehyde in aqueous solution (the Wacker Process):

$$PdCl_4^{2-} + C_2H_4 + H_2O \rightarrow CH_3CHO + Pd + 2HCl + 2Cl^-$$

Palladium dichloride forms polymeric carbonyl complexes when the dry chloride is heated in a stream of carbon monoxide charged with methane vapor. Such complexes include $[PdCl_2(CO)_n]$ and $[PdCl(CO)_2]_n$. The reaction also occurs in aqueous phase resulting in decolorization of the solution.

When H_2S is passed through palladium dichloride solution, it yields a brown-black precipitate of palladium monosulfide, PdS.

When heated with sulfur at 450 to 500°C, palladium dichloride forms palladium disulfide, PdS_2, a grey-black crystalline compound, insoluble in strong acids but soluble in aqua regia, and which converts to monosulfide, PdS, on heating at 600°C.

When ammonia gas is passed through an aqueous solution of $PdCl_2$, the product is tetrammine palladium(II) chloride, $Pd(NH_4)_2Cl_2$. The same product also is obtained in dry state by passing ammonia gas over anhydrous $PdCl_2$.

Analysis

Elemental composition: Pd 60.01%, Cl 39.99%. Palladium may be analyzed in aqueous solution by flame AA spectrophotometry. Its reddish solution is decolorized by reducing gases, such as, CO and CH_4. The compound also may be determined from its precipitation reactions (see Reactions).

PALLADIUM NITRATE

[10102-05-3]
Formula $Pd(NO_3)_2$; MW 230.43
Synonyms: palladium(II) nitrate; palladous nitrate.

Uses

Palladium nitrate is a catalyst in many organic synthesis.

Physical Properties

Brown crystalline solid; deliquesces; decomposes on heating; moderately soluble in water, forming a turbid solution; hydrolyzes in excess water forming a brown basic salt; soluble in dilute nitric acid.

Preparation

Palladirm nitrate may be prepared by dissolving palladium oxide hydrate in dilute nitric acid followed by crystallization. The nitrate crystallizes as yellow-brown deliquescent prisms. Alternatively, the compound may be obtained by reacting palladium metal with nitric acid.

Analysis

Elemental composition: Pd 46.18%, N 12.16%, O 41.66%. The compound may be characterized by x-ray diffraction. Its solution in dilute nitric acid may be analyzed for palladium by AA or ICP spectrophotometry.

PALLADIUM OXIDE

[1314-08-5]
Formula PdO; MW 122.42
Synonyms: palladium (II) oxide; palladium monoxide; palladous oxide

Uses

Palladium oxide is used to prepare palladium catalyst for hydrogenation. The oxide is readily reduced by hydrogen to metal.

Physcial Properties

Greenish black tetragonal crystals; density 8.3 g/cm^3; decomposes to Pd metal at 750°C; insoluble in water and acids; slightly soluble in aqua regia.

Thermochemical Properties

ΔH_f° (cry)	–20.4 cal/mol
ΔH_f° (gas)	83.4 kcal/mol
ΔG_f° (gas)	77.9 kcal/mol
S° (gas)	52.1 cal/deg mol
C_ρ (cry)	7.50 cal/deg mol

Preparation

Palladium oxide is prepared by heating palladium sponge in oxygen at 350°C. The oxide is obtained as a black powder. The oxide also may be prepared specially for catalytic use by heating a mixture of palladium chloride and potassium nitrate at 600°C and then leaching out water-soluble residue. A hydrated form of the oxide, which is acid soluble can be prepared by precipitation from solution, for example, by hydrolysis of palladium nitrate. The brown hydrated oxide converts to black anhydrous oxide on heating. Its solubility in acids decreases with lowering of water content.

Analysis

Elemental composition: Pd 86.93%. O 13.07%. The oxide may be identified by x-ray diffraction. The oxide readily can be reduced with hydrogen and the water formed can be measured by gravitmetry or other wet methods. Also, palladium metal obtained from reduction of the oxide may be digested in aqua regia, diluted, and analyzed by AA or ICP spectrometry.

PHOSGENE

[75-44-5]
Formula $COCl_2$; MW 98.92; planar molecule; Cl—C—Cl bond angle 117°; the C—Cl bond distance 1.68Å and C=O bond distance 1.28Å.
Synonyms: carbonyl chloride; carbon oxychloride; chloroformyl chloride; carbonic dichloride

History, Occurrence, and Uses

Phosgene was prepared first in 1812 by reacting carbon monoxide with chlorine. Phosgene was used historically as a military gas in warfare. At present, it is used extensively to make polyurethanes. These urethane polymers produce polycarbonates and chloroformates for making pesticides and pharmaceuticals.

Physical Properties

Colorless gas; density 4.34 g/L; heavier than air, density in air 3.41 (air=1); liquefies at 8.3°C; liquid density 1.432 g/mL; freezes at –118°C; slightly soluble in water with slow decomposition; also decomposed by alcohol and acids; soluble in benzene, toluene and acetic acid; critical temperature 182°C; critical pressure 56.04 atm; critical volume 190 cm^3/mol.

Thermochemical Properties

ΔH_f°	–52.3 kcal/mol
ΔG_f°	–48.9 kcal/mol
S°	67.74 cal/ deg mol
C_ρ	13.78 cal/deg mol
ΔH_{vap}	5.75 kcal/mol

Production

Phosgene is manufactured from carbon monoxide and chlorine:

$$CO + Cl_2 \rightarrow COCl_2$$

To obtain high-purity phosgene, starting materials must be pure and free from moisture. Equimolar amounts of chlorine and carbon monoxide are mixed in a reactor in the presence of a catalyst, activated charcoal. The reaction is exothermic. Heat exchangers are used to remove excess heat; otherwise the product may decompose back to carbon monoxide and chlorine. Product gases are passed into a condenser where phosgene is collected in liquid form. The gaseous mixture containing phosgene that is not condensed is passed through caustic soda solution to destroy any uncondensed phosgene. Phosgene also can be obtained by the reaction of nickel tetracarbonyl with chlorine gas:

$$Ni(CO)_4 + 4Cl_2 \rightarrow 4COCl_2 + NiCl_2$$

Phosgene is a highly toxic gas. All safety precautions must be followed during its preparation and handling. It is stored and shipped in leak-free steel cylinders in the complete absence of any water (or moisture).

Reactions

Phosgene decomposes on heating at 300°C forming chlorine and carbon monoxide:

$$COCl_2 \rightarrow Cl_2 + CO$$

Phosgene readily reacts with water at ordinary temperatures forming hydrogen chloride and carbon dioxide:

$$COCl_2 + H_2O \rightarrow 2HCl + CO_2$$

Metal oxides decompose phosgene at elevated temperatures, forming their chlorides and carbon dioxide

$$COCl_2 + CdO \rightarrow CdCl_2 + CO_2$$

$$COCl_2 + Fe_2O_3 \rightarrow 2FeCl_3 + 3CO_2$$

Similar decomposition occurs when phosgene is heated with metal sulfide; the products are usually the metal chloride and carbonyl sulfide:

$$COCl_2 + ZnS \rightarrow ZnCl_2 + COS$$

Analysis

The gas is adsorbed over activated characoal by sampling air. It is then desorbed out from charcoal with hexane or toluene and analyzed by GC-FID or GC/MS. Characteristic masses are 98, 100, 102, 63, 65.

Toxicity

Highly poisonous gas. It manifests delayed effects. Initial symptoms may be mild, but severe congestion of lungs occurs within 6 to 24 hours after exposure. Symptoms are dry burning of the throat, choking, chest pain, vomiting, labored breathing, and cyanosis.

PHOSPHINE

[7803-51-2]
Formula PH_3; MW 34.00; molecular geometry: trigonal pyramidal.
Synonyms: phosphorus trihydride; hydrogen phosphide

Occurrence and Uses

Phosphine is produced naturally in small amounts in marshy lands, especially in damp graveyards, resulting from bacterial decay of animal and vegetable matter containing phosphorus. The atmospheric oxidation of impure phosphine (containing trace amounts of diphosphine, P_2H_4) emits pale flickering lights, the so-called "Will o' the wisps" or "corpse candles" seen on dark nights.

The compound has very little commercial application. It is used to prepare phosphonium salts, which also can be made by other processes.

Physical Propertie

Colorless gas with an odor of decaying fish; flammable; burns with a luminous flame; density 1.492 g/L; liquefies at –87.7°C; solidifies at –133°C; critical temperature 51.35°C; critical pressure 64.55 atm; slightly soluble in water; the solution is weakly basic.

Preparation

Phosphine, unlike ammonia, is not made by direct union of elements. However, phosphine is prepared from other phosphorus compounds by several methods.

Phosphine can be prepared by alkaline hydrolysis of white phosphorus. Thus, a strong aqueous solution of caustic potash when boiled with white phosphorus yields hypophosphite with liberation of phosphine:

$$P_4 + 3KOH + 3H_2O \rightarrow 3KH_2PO_2 + PH_3\uparrow$$

Caustic soda or barium hydroxide can be used instead of caustic potash. The apparatus should be free from air. Either hydrogen or natural gas may be passed through the generator to purge out all residual oxygen out from the flask to prevent any explosion. A small amount of diphosphine, P_2H_4 also is produced in the reaction. The latter inflames spontaneously in air. Diphosphine, which is an unstable liquid at 20°C, may be removed by condensation in a tube immersed in a freezing mixture; or by passing through concentrated hydrochloric acid; or slowly by photochemical decomposition by exposing to light.

Phosphine also is prepared by reduction of a solution of phosphorus trichloride with lithium aluminum hydride in dry ether under warm conditions. The solution of the latter is added from a dropping funnel to phosphorus trichloride solution in dry ether placed in a water bath.

$$4\,PCl_3 + 3LiAlH_4 \rightarrow 3\,LiCl + 3AlCl_3 + 4PH_3\uparrow$$

The flask is connected to a reflux condenser to condense down solvent ether back into the flask. Phosphine is collected over water as a moist gas. Dry phosphine may alternatively be condensed in a U-tube placed in freezing mixture.

Phosphine may be produced by mixing a solution of phosphonium iodide with potassium hydroxide:

$$PH_4I + KOH \rightarrow KI + H_2O + PH_3\uparrow$$

Another preparation method involves treating metallic phosphide with dilute acids:

$$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3\uparrow$$

This method was applied earlier to produce floating signal flares at sea. Floating cans of calcium phosphide were punctuated to admit sea water to generate phosphine, which ignited spontaneously to emit flares. The flares could not be extinguished by wind or water.

Reactions

Phosphine is slightly soluble in water forming the phosphonium ion, PH_4^+ in very low yield:

$$PH_3 + H_2O \leftrightarrow PH_4^+ + OH^-$$

Phosphine ignites in air at 150°C. Impure phosphine containing diphosphine ignites at a lower temperature. Phosphoric acid is produced from oxidation of phosphine:

$$PH_3 + 2O_2 \rightarrow H_3PO_4$$

If phosphine is bubbled through water into air, the bubbles ignite at the surface of the water forming beautiful smoke rings.

Phosphine is a strong reducing agent. It inflames in chlorine at ordinary temperatures forming phosphorus trichloride and hydrogen chloride:

$$PH_3 + 3Cl_2 \rightarrow PCl_3 + 3HCl$$

When passed through a solution of gold chloride, phosphine reduces gold chloride, forming colloidal gold of very small particle size:

$$2AuCl_3 + PH_3 \rightarrow Au + PCl_3 + 3HCl$$

It reduces copper, silver and gold salts in solutions, precipitating metal phosphides or the metals themselves:

$$PH_3 + 3CuSO_4 + 3H_2O \rightarrow Cu_3P + H_3PO_3 + 3H_2SO_4$$

The phosphide produced above can decompose slowly on standing or rapidly on boiling to form the metal.

Phosphine combines with dry hydrogen iodide to yield crystalline phosphonium iodide, PH_4I:

$$PH_3 + HI \rightarrow PH_4I$$

The product cannot be made in aqueous solution as it readily hydrolyzes. The corresponding chloride salt, PH_4Cl, can be prepared from phosphine and anhydrous hydrogen chloride at –40°C or at room temperature under a pressure of 20 atm.

Phosphine forms complexes, such as, *cis*-$Cr(CO)_3(PH_3)_3$ with many transition metals.

Phosphine reacts with formaldehyde in hydrochloric acid solution to form a methanol derivative of phophonium chloride, $[P(CH_2OH)_4^+]Cl^-$:

$$PH_3 + 4CH_2O + HCl \rightarrow [P(CH_2OH)^+]Cl^-$$

Analysis

Phosphine can be analyzed by GC using a NPD detector in phosphorus mode or by GC/MS. The mass ion for its identification is 34. It can be identified also from its odor and formation of smoke ring and other chemical reactions (see Reactions).

Hazard

Phosphine is a highly toxic and flammable gas. Acute effects are irritation, tightness of chest, painful breathing, and lung damage. High concentration can be fatal. A fire hazard.

PHOSPHONIUM IODIDE

[12125-09-6]
Formula PH_4I; MW 161.91
Synonym: iodophosphonium

Uses

Phosphonium iodide is used to prepare phosphine

Physical Properties

Colorless tetragonal crystal; deliquesces; density 2.86 g/cm^3; sublimes at ordinary temperatures; vapor pressure 50 torr at 20°C, 760 torr at 61.8°C; melts at 18.5°C under its own vapor pressure; boils at 80°C; decomposes in water; soluble in acids and alkalies with decomposition; decomposes in ethanol.

Thermochemical Properties

ΔH_f°	–16.7 kcal/mol
S°	29.4 cal/deg mol
C_ρ	26.2 cal/deg mol
ΔH_{fus}	12.68 kcal/mol

Preparation

Phosphonium iodide may be prepared by the action of phosphine with dry hydrogen iodide:

$$PH_3 + HI \rightarrow PH_4I$$

Solid phosphonium iodide may be produced in the laboratory by slowly and very cautiously adding water to an intimate mixture of white phosphorus and iodine. Also, this phosphorus-iodine mixture may be obtained by mixing solutions in carbon disulfide and carefully evaporating the solvent in a stream of inert gas:

$$P_4 + I + H_2O \rightarrow PH_4I + H_3PO_4$$

$$2P + I_2 + 4H_2O \rightarrow PH_4I + H_3PO_4 + HI$$

Also, the compound can be prepared by hydrolysis of a mixture of diphosphorus tetraiodide and white phosphorus:

$$P_2I_4 + P + H_2O \rightarrow PH_4I + H_3PO_4$$

Reactions

Phosphonium iodide dissociates to phosphine and hydrogen iodide when heated at 60°C:

$$PH_4I \rightarrow PH_3 + HI$$

The compound decomposes in water evolving phosphine:

$$PH_4I + H_2O \rightarrow PH_3 + H_3O^+ + I^-$$

Reaction with alkali hydroxide in the cold liberates phosphine:

$$PH_4I + KOH \rightarrow PH_3 + KI + H_2O$$

Analysis

Elemental composition: P 19.13%, I 78.38%, H 2.49%. The compound may be decomposed cautiously in water and the iodide ion measured by ion chromatography or electrode method (see Iodine, Analysis). Liberated phosphine may be diluted with helium and analyzed by GC/MS (see Phosphine, Analysis).

PH_4I alternatively may be dissociated in the dry state by slow and cautious heating, and decomposition products may be analyzed as above.

Hazard

Phosphonium iodide detonates on rapid heating. It dissociates by water, alcohol or heat, evolving toxic phosphine gas.

PHOSPHORIC ACID, META

[37267-86-0]
Formula HPO_3; MW 79.98; the general formula $(HPO_3)_n$; in vapor phase it probably exists as monomeric HPO_3
Synonyms: metaphosphoric acid; glacial phosphoric acid. Long chain linear or cyclic metaphosphoric acids of formula $(HPO_3)_n$ are also called polymetaphosporic acids.

Uses

Metaphosphoric acid is used in making oxyphosphate dental cement. It also is used as an analytical reagent.

Physical Properties

Glass-like colorless solid; soft and transparent; deliquesces; density 2.2 to 2.5 g/cm^3; sublimes at red heat; dissolves slowly in cold water, decomposing to phosphoric acid; soluble in alcohol.

Thermochemical Properties

ΔH_f°	–226.7 kcal/mol

Preparation

Metaphosphoric acid is obtained as a polymeric glassy solid by prolonged heating of phosphoric acid. Either phosphoric acid, H_3PO_4, or pyrophosphoric acid, $H_4P_2O_7$, when heated above 300°C, on cooling yields the transparent glassy mass of composition $(HPO_3)_n$.

Metaphosphoric acid also is obtained from partial hydration of phosphorus pentoxide by dissolving it in cold water.

Analysis

Elemental composition: P 38.73%, H 1.26%, O 60.01%. The compound may be identified by physical properties alone. It may be distinguished from ortho and pyrophosphates by its reaction with a neutral silver nitrate solution. Metaphosphate forms a white crystalline precipitate with $AgNO_3$, while PO_4^{3-} produces a yellow precipitate and $P_2O_7^{3-}$ yields a white gelatinous precipitate. Alternatively, metaphosphate solution acidified with acetic acid forms a white precipitate when treated with a solution of albumen. The other two phosphate ions do not respond to this test. A cold dilute aqueous solution may be analyzed for HPO_3^- by ion chromatography using a styrene divinylbenzene-based low-capacity anion-exchange resin.

PHOSPHORIC ACID, ORTHO

[7664-38-2]
Formula H_3PO_4; MW 97.995; also forms a hemihydrate $H_3PO_4 \cdot 1/2\ H_2O$ [16271-20-8], known as diphosphoric acid; crystals of anhydrous acid or hemi-

hydrate consist of tetrahedral PO_4 units linked by hydrogen bonding.
Structure $(OH)_3P=O$.
Synonyms: phosphoric acid; trihydrogen phosphate.

History and Uses

Phosphoric acid was prepared first by Robert Boyle in 1694 by dissolving phosphorus pentoxide in water. Phosphoric acid is probably the most important compound of phosphorus. It is the second largest inorganic chemical by volume, after sulfuric acid, marketed in the United States. The single most important application of this acid is manufacturing phosphate salts for fertilizers. Such fertilizer phosphates include sodium, calcium, ammonium, and potassium phosphates. Other applications are in metal pickling and surface treatment for removal of metal oxides from metal surfaces; electropolishing of aluminum; as a bonding agent in various refractory products such as alumina and magnesia; as a catalyst in making nylon and gasoline; as a dehydrating agent; in fireproofing wood and fabrics; in lithographic engraving; in textile dyeing; in dental cement; in coagulating rubber latex; in purifying hydrogen peroxide; and as a laboratory reagent. Dilute solutions of phosphoric acid are used as additives to carbonated beverages for a pleasing sour taste. Also, dilute acid is used in refining sugar; as a nutrient; and as a buffering agent in preparing jam, jelly, and antibiotics. The commercial phosphoric acid is 85% (w/w) in strength.

Physical Properties

White orthorhombic crystals in pure and anhydrous state or a clear, syrupy liquid; melts at 42.35°C; hygroscopic; can be supercooled into a glass-like solid; crystallizes to hemihydrate, $H_3PO_4 \cdot 1/2H_2O$ on prolonged cooling of 88% solution; hemihydrate melts at 29.32°C and loses water at 150°C; density 1.834 g/cm^3 at 18°C; density of commercial H_3PO_4 (85%) 1.685 g/mL at 25°C; pH of 0.1N aqueous solution 1.5; extremely soluble in water, 548 g/100mL at room temperature; soluble in alcohol.

Thermochemical Properties

ΔH_f°	–305.7 kcal/mol
ΔG_f°	–243.5 kcal/mol
S°	26.41 cal/deg mol
C_ρ	25.35 cal/ degree mol
ΔH_{soln}	2.79 kcal/mol

Production

Low-purity technical grade phosphoric acid for use in fertilizers is produced from phosphate rocks by digestion with concentrated sulfuric acid. The apatite types, primarily consisting of calcium phosphate phosphate rocks, are used:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4 \cdot 2H_2O)$$

The insoluble calcium sulfate slurry is filtered out. Acid from this wet process is impure but can be purified by various methods. Purification steps involve precipitation, solvent extraction, crystallization, and ion exchange techniques.

Phosphoric acid also can be made by many different methods. Dissolution of phosphorus pentoxide in water and boiling yields phosphoric acid. Pure phosphoric acid can be obtained by burning phosphorus in a mixture of air and steam:

$$P_4\ (l) + 5O_2\ (g) \rightarrow P_4O_{10}\ (s)$$

$$P_4O_{10}\ (s) + H_2O\ (g) \rightarrow 4H_3PO_4\ (l)$$

The acid also may be prepared by heating violet phosphorus with 33% nitric acid:

$$4P + 10HNO_3 + H_2O \rightarrow 4H_3PO_4 + 5NO\uparrow + 5NO_2\uparrow$$

or by heating red phosphorus with nitric acid (1:1). The overall equation is:

$$P + 3HNO_3 \rightarrow H_3PO_4 + NO + 2NO_2$$

Reactions

Phosphoric acid is a tribasic acid. It is not an oxidizing acid. In aqueous solution phosphoric acid dissociates to $H_2PO_4^-$, HPO_4^{2-} and PO_3^{3-} ions. The dissociation constants are as follows:

$$H_3PO_4 + H_2O \leftrightarrow H_3O^+ + H_2PO_4^- \qquad K_{a1} = 7.1\times10^{-3}$$

$$H_2PO_4^- + H_2O \leftrightarrow H_3O^+ + HPO_4^{2-} \qquad K_{a2} = 8.0\times10^{-8}$$

$$HPO_4^{2-} + H_2O \leftrightarrow H_3O^+ + PO_4^{3-} \qquad K_{a3}\ \ 4.8\times10^{-13}$$

Thus, out of the three ionizable hydrogens in phosphoric acid, the first H^+ is removed more easily than the second, and the second H^+ dissociates more easily than the third. When phosphoric acid is titrated with sodium hydroxide,it forms both acidic and basic salts:

$$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$$
(moderately acidic)

$$H_3PO_4 + 2NaOH \rightarrow Na_2HPO_4 + 2H_2O$$
(very weakly basic)

$$H_3PO_4 + 3NaOH \rightarrow Na_3PO_4 + 3H_2O$$
(weakly basic)

At first, the pH of the solution suddenly changes to 4.5 upon completing formation of NaH_2PO_4, and there is a second change of pH to around 9.0 after Na_2HPO_4 is formed completely. The titration curve for H_3PO_4=NaOH shows two pH inflection points. Mixtures of Na_2HPO_4 and NaH_2PO_4, therefore, exhibit buffer properties at pH 6 to 8. Because of a big difference in the first two ionization constants, phosphoric acid can be titrated as a monobasic or a dibasic acid. Aqueous solution of trisodium phosphate, Na_3PO_4 is basic.

Heating phosphoric acid converts it to metaphosphoric acid, HPO_3, and pyrophosphoric acid, $H_4P_2O_7$. If anhydrous phosphoric acid is melted and allowed to stand for several weeks, it partially converts to pyrophosphoric acid, $H_4P_2O_7$. The equilibrium occurs in liquid phase:

$$2H_3PO_4 \leftrightarrow H_4P_2O_7 + H_2O$$

However, when heated at 215°C, it is fully converted to pyrophosphoric acid.

When heated at 300°, phosphoric acid converts to metaphosphoric acid, HPO_3:

$$H_3PO_4 \rightarrow HPO_3 + H_2O$$

Phosphoric acid reacts with most metals and their oxides at temperatures above 400°C forming metal phosphates. Reactive metals, such as magnesium, react with phosphoric acid solutions forming magnesium phosphate and evolving hydrogen:

$$2H_3PO_4 + 3Mg \rightarrow Mg_3(PO_4)_2 + 3H_2$$

When ammonia gas is bubbled through phosphoric acid solution, diammonium hydrogen phosphate is produced:

$$H_3PO_4\,(aq) + 2NH_3\,(g) \rightarrow (NH_4)_2HPO_4\,(s)$$

Reaction with calcium triphosphate fluoride yields calcium dihydrogen phosphate, a component of superphosphate fertilizer:

$$7H_3PO_4 + Ca(PO_4)_3F + 5H_2O \rightarrow 5\,Ca(H_2PO_4)HPO_4 + HF$$

When heated with solid sodium bromide, phosphoric acid yields sodium dihydrogen phosphate, liberating hydrogen bromide:

$$H_3PO_4\,(l) + NaBr\,(s) \rightarrow NaH_2PO_4\,(s) + HBr\,(g)$$

Analysis

The orthophosphate anion, PO_4^{3-} can be analyzed readily in aqueous solution by either ion chromatography or colorimetry. The aqueous solution must be diluted for such analyses. In colorimetric measurement, the solution is treated with a reagent mixture containing ammonium molybdate and ammonium metavanadate under acid conditions to form the yellow color of vanadomolybdophosphoric acid. The yellow absorbance or transmittance may be measured at λ 470nm. Alternatively, the solution after treatment with ammonium molybdate may be reduced by stannous chloride to produce an intense blue color of molybdenum blue which may be measured at λ 650 nm. The concentration of PO_4^{3-} may be calculated from a standard calibration curve. The normality of phosphoric acid can be measured by titration with a standard solution of NaOH using a suitable color indicators or a pH meter.

PHOSPHORIC ACID, PYRO

[2466-09-3]
Formula: $H_4P_2O_7$; MW 177.98
Structure: $(HO)_2P(=O)—O—P(=O)(OH)_2$
Synonym: disphosphoric acid

Uses

No commercial application of this acid is known. The pyrophosphate salts usually are not made from the acid.

Physical Properties

Colorless needles or liquid; hygroscopic. Crystallizes in two anhydrous forms: a metastable form melting at 54.3°C and a second and more stable form melting at 71.5°C; extremely soluble in cold water, reacting very slowly to form phosphoric acid; decomposing much faster in hot water; very soluble in alcohol and ether.

Preparation

Pyrophosphoric acid may be prepared by heating orthophosphoric acid at 215°C:

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$

The acid solution in pure form can be obtained by ion exchange, passing an aqueous solution of sodium pyrophosphate, $Na_4P_2O_7$, through a suitable cation exchange column.

Reactions

The acid has four replacable H^+ ions. Its dissociation constants indicate that two H^+ ions are strongly acidic while the other two protons are weakly acidic. The first dissociation constant especially is very large:

$$H_4P_2O_7 + H_2O \leftrightarrow H_3O^+ + H_3P_2O_7^- \qquad K_{a1} \sim 10^{-1}$$

$$H_3P_2O_7^- + H_2O \leftrightarrow H_3O^+ + H_2P_2O_7^{2-} \qquad K_{a2} \sim 1.5x10^{-2}$$

$$H_2P_2O_7^{2-} + H_2O \leftrightarrow H_3O^+ + HP_2O_7^{3-} \qquad K_{a3} \sim 2.7\text{x}10^{-7}$$

$$HP_2O_7^{3-} + H_2O \leftrightarrow H_3O^+ + P_2O_7^{4-} \qquad K_{a4} \sim 2.4\text{x}10^{-10}$$

Pyrophosphoric acid forms acid salts, such as $NaH_3P_2O_7$ and $Na_2H_2P_2O_7$.

Analysis

Pyrophsophoric acid may be converted into its acid salts which may be characterized individually by physical and x-ray properties and elemental compositions.

PHOSPHORUS

[7723-14-0]
Symbol P; atomic number 15; atomic weight 30.974; a Group VA (Group 15) nonmetallic element of nitrogen group; electron configuration $[Ne]3s^23\rho^3$; valence states $^-3$, +3, +5; most stable valence state +3; atomic radius 1.10Å; one natural isotope P-31 (100%); nine radioactive isotopes in the mass range 26, 28–30, 32–36; the longest-lived radioisotopes P-33, $t_{1/2}$ 25.3 day

History, Occurrence, and Uses

Elemental phosphorus was discovered in 1669 by Hennig Brand. About two hundred years later James Readman developed a process for phosphorus recovery from phosphatic rocks using an electric furnace.

Phosphorus is one of the most widely distributed elements on earth. It is found as phosphate salts in nearly all igneous rocks and in sedimentary deposits and sea beds. Phosphorus occurs in more than three hundred minerals, usually associated with Ca, Mg, Fe, Sr, Al, Na, and several other metals, and with anions such as silicates, sulfates, oxides, hydroxides, and halides.

Phosphorus is an essential element present in all living matter and is vital in biological and ecological processes. It occurs in DNA and other nucleic acids, and in bones.

Phosphorus is used in pyrotechnics, smoke bombs, incendiary shells, and safety matches. It also is used in organic syntheses, manufacture of phosphoric acid, phosphorus trichloride, phosphine, and other compounds.

Physical Properties

Elemental phosphorus in solid phase exists in three major allotropic forms: (1)white or yellow phosphorus that may occur in alpha or beta modification, (2) red phosphorus, and (3) black phosphorus.

White phosphorus is a white, soft, wax-like transparent mass which often acquires a yellow appearance due to impurities, especially traces of red phosphorus. It has a garlic-like odor. It is made up of cubic crystals, has a density 1.82 g/cm^3, and melts at 44.1°C to a colorless or yellowish liquid. X-ray diffraction studies and ^{31}P-NMR analysis indicate tetrahedral P_4 molecules with an interatomic distance of 2.21Å , and the molecules are able to rotate freely in the crystals. When cooled below –76.9°C, the cubic alpha form converts to a hexagonal beta modification with a density 1.88 g/cm^3. The beta form, unlike the alpha form, does not rotate freely in the crystal but has a fixed orientation of P_4 molecules in the lattice.

Red phosphorus is obtained from white phosphorus by heating at 230 to 240°C, allowing complete conversion to occur in about 48 hours. Conversion is catalyzed by sulfur, iodine, and selenium. The red allotrope also slowly deposits from liquid phosphorus or from a solution of white phosphorus, the rate and yield depending on catalysts, temperature, light, and other factors. Red phosphorus exhibits various modifications. Three important ones are an amorphous form at ordinary temperatures and two crystalline modifications which include a triclinic form and a hexagonal or a tetragonal form that may prevail at higher temperatures. There also are a few more modifications, all of which may coexist, accounting for variability in physical properties of red phosphorus. The triclinic variety of red phosphorus is the most stable of all allotropes of phosphorus at ordinary temperatures. Red phosphorus possesses a density of 2.0 to 2.31 g/cm^3 and melts at 590°C.

Black phosphorus is the third major allotropic form of phosphorus. It occurs in two forms, one is an amorphous modification having a laminar structure similar to graphite and the other is an orthorhombic crystalline form. The density of black phosphorus may vary between 2.20 to 2.69 g/cm^3. Black phosphorus is obtained from white phosphorus by heating the latter at 220°C under an extremely high pressure of about 10,000 atm.

When solid phosphorus of any form—white, red, or black—is melted, it forms the same liquid phosphorus. This liquid has a density of 1.74 g/cm^3 and viscosity 1.69 centipoise at 50°C. Liquid phosphorus boils at 280.5°C. Upon cooling, liquid phosphorus solidifies to only white phosphorus. Liquid phosphorus and its vapors consist of tetrahedral P_4 molecules. The vapors, on rapid condensation, convert to white phosphorus.

While white and red phosphorus have high electrical resistivity, the black variety has a low resistivity of 0.71 ohm-cm at 0°C. Solubility also varies widely. White phosphorus is soluble in a number of organic solvents. It is very highly soluble in carbon disulfide, about 400 g/100 g solvent at 0°C and moderately soluble in benzene (~3.59 g/100g at 25°C) and exhibits lower solubility in ether (~1.5g/100g at 25°C). Red and black phosphorus are insoluble in organic solvents. White phosphorus is a flammable solid, igniting spontaneously in air at 35°C. Red and black phosphorus are nonflammable. The latter is difficult to ignite.

Production

White phosphorus usually is obtained by heating some form of calcium phosphate with quartz and coke, usually in an electric furnace. The reactions may be written in two steps as follows:

$$Ca_3(PO_4)_2 + 3SiO_2 \rightarrow 3CaSiO_3 + P_2O_5$$

$$P_2O_5 + 5C \rightarrow 2P + 5\ CO$$

In commercial scale, white phosphorus is manufactured mostly from the mineral fluorapatite by heating with silica and coke in an electric-arc or blast furnace at a temperature of 1,200 to 1,500°C. An overall reaction may be represented in the following equation.

$$4Ca_5F(PO_4)_3 + 18SiO_2 + 30C \rightarrow \underset{\text{(slag)}}{18CaO \cdot SiO_2 \cdot 2CaF_2} + 30CO\uparrow + 3P_4\uparrow$$

White phosphorus also can be produced by a wet process using phosphoric acid, a process that was practiced historically in commercial production. In this method the starting material, phosphoric acid, usually is prepared in large vats by reacting phosphate rock with sulfuric acid:

$$Ca_5F(PO_4)_3 + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5CaSO_4 \cdot 10H_2O + HF$$

Phosphoric acid is filtered out of the mixture. It is then mixed with coke, charcoal or sawdust; dried; charred; and finally heated to white heat in a fireclay retort:

$$H_3PO_4 + 16C \rightarrow P_4 + 6H_2 + 16CO$$

The vapor is condensed to obtain white phosphorus.

As stated earlier, all other forms of phosphorus can be made from white phosphorus. Thus, heating white phosphorus first at 260°C for a few hours and then at 350°C gives red phosphorus. The conversion is exothermic and can become explosive in the presence of iodine as a catalyst. When a solution of white phosphorus in carbon disulfide or phosphorus tribromide is irradiated the scarlet red variety is obtained.

Black phosphorus allotrope is produced by heating white phosphorus at 220°C under 12,000 atm pressure. The conversion is initially slow, but can became fast and explosive after an induction period.

White phosphorus is stored under water as it ignites in air. It may be cut into appropriate sizes only under water.

Reactions

Reactivity of white phosphorus is much greater than red or black phosphorus. Black phosphorus is the least reactive of all phosphorus allotropes.

White phosphorus ignites in air spontaneously. When placed on a paper, the paper catches fire after a short delay. It catches fire at about 35°C. At room temperature white phosphorus glows in the dark on exposure to air emitting faint green light. Such chemiluminescence is attributed to the oxidation of P_4 molecules in the vapor phase in contact with the surface of solid phosphorus:

$$P_4(g) + 5O_2(g) \rightarrow P_4O_{10}(s) + \text{light}$$

The mechanism involves a complicated oxidative process that occurs only at certain partial pressures of oxygen and not in pure oxygen at atmospheric pressure, nor in vacuum.

Red phosphorus ignites when struck with a hammer blow or when heated at 260°C. Black phosphorus ignites in contact with flame.

White phosphorus reacts spontaneously with halogens at ordinary temperatures forming phosphorus trihalides. However, in excess halogen the product is phosphorus pentahalide:

$$P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3\,(l)$$

$$P_4\,(s) + 10Cl_2\,(g) \rightarrow 4PCl_5\,(s)$$

White phosphorus reacts with sulfur on warming forming phosphorus trisulfide:

$$P_4(s) + 6S(s) \rightarrow 2P_2S_3\,(s)$$

White phosphorus reacts with strong aqueous alkali solution forming hypophosphite with evolution of phosphine, PH_3:

$$P_4 + 3KOH + 3H_2O \rightarrow 3KH_2PO_2 + PH_3\uparrow$$

Strong oxidzing agents, such as nitric acid (cold and concentrated), oxidize phosphorus to phosphoric acid.

Reaction with copper sulfate solution forms a mixture of metallic copper and copper(I) phosphide. The two reactions may be written separately as follows:

$$P_4 + 10CuSO_4 + 16H_2O \rightarrow 10Cu + 4H_3PO_4 + 10H_2SO_4$$

$$3P_4 + 12CuSO_4 + 24H_2O \rightarrow 4Cu_3P + 8H_3PO_3 + 12H_2SO_4$$

Similar reactions occur with the salts of other easily reducible metals, such as silver and gold, in aqueous salt solutions.

Phosphorus combines with several metals on heating, forming their phosphides.

$$P_4 + 6Ca \rightarrow 2Ca_3P_2$$

Reactions with alkali metals occur under warm conditions producing the corresponding metal phosphides:

$$P_4 + 12Na \rightarrow 4Na_3P$$

Analysis

The allotropes of phosphorus may be identified from their physical properties. White phosphorus can be identified from its chemiluminescence (a pale green glow) at a specific range of oxygen partial pressure at room temperature. Furthermore, it spontaneously ignites in air at 35°C. It also imparts chemiluminescence to water when boiled. Elemental phosphorus can be analyzed by GC/MS. Its solution in a suitable organic solvent, such as benzene may be injected, onto the GC and identified from the mass spectra. In solution it exists as P_4 molecule, thus the characteristic molecular ion should have the mass 124. Red phosphorus can be converted into its white allotrope by heating in the absence of air to above 260°C and condensing the vapors and trapping in an organic solvent for analysis by GC/MS.

Hazards

White phosphorus is a highly toxic substance, both an acute and chronic toxicant. Chronic exposure to it's vapors can cause "phossy jaw;" necrosis of the jaw. Other symptoms are bronchopneumonia, bone changes, anemia and weight loss, Ingestion can cause nausea, vomiting, abdominal pain, diarrhea and coma. Skin contact can cause severe burns. In the eye it damages vision. Red phosphorus is much less toxic than its white allotrope. Its fumes, when burned, are highly irritating. White phosphorus is a flammable solid, igniting spontaneously when exposed to air.

PHOSPHORUS ACID

[13598-36-2]
Formula: H_3PO_3; MW 82.00; a dibasic acid
Structure: $HP(=O)(OH)_2$
Synonym: orthophosphorus acid

Uses

Phosphorus acid is used to prepare phosphite salts. It is usually sold as a 20% aqueous solution.

Physical Properties

White crystalline mass; deliquescent; garlic-like odor; density 1.651 g/cm^3 at 21°C; melts at 73.6°C; decomposes at 200°C to phosphine and phosphoric acid; soluble in water, about 310 g/100mL; K_1 5.1×10^{-2} and K_2 1.8×10^{-7}; soluble in alcohol.

Thermochemical Properties

$\Delta H_f°$ –230.5 kcal/mol

Preparation

Phosphorus acid can be prepared by the reaction of phosphorus trichloride with water:

$$PCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

The reaction is violent. Addition of PCl_3 should be extremely cautious and slow. The addition can be carried out safely in the presence of concentrated HCl. Alternatively, a stream of air containing PCl_3 vapor is passed into ice-cold water and solid crystals of H_3PO_4 form.

Alternatively, phosphorus acid can be prepared by adding phosphorus trichloride to anhydrous oxalic acid:

$$PCl_3 + 3(COOH)_2 \rightarrow H_3PO_3 + 3CO + 3CO_2 + 3HCl$$

In this reaction, all products except H_3PO_3 escape as gases leaving the liquid acid.

Dissolution of phosphorus sesquioxide in water also forms phosphorus acid. When shaken with ice water, phosphorus acid is the only product .

$$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$$

However, in hot water part of the phosphorus acid disproportionates to phosphoric acid and phosphorus or phosphine.

Reactions

Phosphorus acid on heating at 200°C converts to phosphoric acid and phosphine:

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$

Phosphorus acid is a moderately strong dibasic acid. It reacts with alkalies forming acid phosphites and normal phosphites. Thus, reaction with sodium hydroxide gives sodium dihydrogen phosphite and disodium hydrogen phosphite, but not sodium phosphate, Na_3PO_4.

$$H_3PO_3 + NaOH \rightarrow NaH_2PO_3 + H_2O$$

$$H_3PO_3 + 2NaOH \rightarrow Na_2HPO_3 + 2H_2O$$

Phosphorus acid is a powerful reducing agent. When treated with a cold solution of mercuric chloride, a white precipitate of mercurous chloride forms:

$$H_3PO_3 + 2HgCl_2 + H_2O \rightarrow Hg_2Cl_2 + H_3PO_4 + 2HCl$$

Mercurous chloride is reduced further by phosphorus acid to mercury on heating or on standing:

$$H_3PO_3 + Hg_2Cl_2 + H_2O \rightarrow 2Hg + H_3PO_4 + 2HCl$$

Phosphorus acid reacts with silver nitrate in dilute solution yielding a white precipitate of silver phosphite, Ag_3PO_3 , which reduces to metallic silver.

$$H_3PO_3 + 2Ag_3PO_3 + H_2O \rightarrow 6Ag + H_3PO_4 + 2HPO_3$$

Analysis

Elemental composition: P 37.78%, H 3.69%, O 58.54%. The acid in solid form may be identified by its physical properties. Aqueous solution may be heated and phosphorus acid is converted to phosphoric acid which is measured for orthophosphate ion by ion chromatography or colorimetry (see Phosphoric Acid). A cold aqueous solution may be analyzed for phosphite ion by ion chromatography, following appropriate dilution. Strength of the acid in an aqueous solution may be measured by acid-base titration using a standard solution of alkali. Also, titration against a standard solution of silver nitrate using potassium chromate as indicator may serve as an additional confirmatory test.

PHOSPHORUS OXYCHLORIDE

[100025-87-3]
Formula: $POCl_3$; MW 153.33
Synonym: phosphoryl chloride

Uses

Phosphorus oxychloride is a chlorinating agent in many organic preparative reactions. It also is a solvent in cryoscopy.

Physical Properties

Colorless fuming liquid with a pungent odor; density 1.645 g/mL; freezes at 1°C; boils at 105.5°C; reacts with water and ethanol.

Thermochemical Properties

$\Delta H_f°$ (liq)	–142.7 kcal/mol
$\Delta H_f°$ (gas)	–133.5 kcal/mol
$\Delta G_f°$ (liq)	124.5 kcal/mol
$\Delta G_f°$ (gas)	–122.6 kcal/mol
S° (liq)	53.2 cal/deg mol
S° (gas)	77.8 cal/deg mol
C_ρ (liq)	33.2 cal/deg mol
C_ρ (gas)	20.3 cal/deg mol
ΔH_{fus}	3.13 kcal/mol
ΔH_{vap}	8.21 kcal/mol

Preparation

Phosphorus oxychloride can be prepared from phosphorus trichloride or phosphorus pentachloride. It can be obtained from phosphorus trichloride by cautious addition of potassium chlorate:

$$3PCl_3 + KClO_3 \rightarrow 3POCl_3 + KCl$$

The oxychloride also is obtained by the action of boric acid or oxalic acid with phosphorus pentachloride:

$$3PCl_5 + 2B(OH)_3 \rightarrow 3POCl_3 + B_2O_3 + 6HCl$$

$$PCl_5 + (COOH)_2 \rightarrow POCl_3 + CO + CO_2 + 2HCl$$

Phosphorus oxychloride also is made by heating calcium phosphate in a current of chlorine and carbon monoxide at 350°C:

$$2Ca_3(PO_4)_2 + 9Cl_2 + 6CO \rightarrow 4POCl_3 + 6CaCO_3$$

Alternatively, heating a mixture of calcium phosphate and carbon in a current of chlorine at 750°C yields the oxychloride.

Reactions

Phosphorus oxychloride hydrolyzes in water forming phosphoric acid:

$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 6HCl$$

When the vapors of phosphorus oxychloride are passed over carbon at red heat, phosphorus trichloride is produced:

$$POCl_3 + C \rightarrow PCl_3 + CO$$

The oxychloride also is reduced by hydrogen, carbon monoxide and other reducing agents.

Analysis

Elemental composition: P 20.20%, O 10.43%, Cl 69.36%. The compound is hydrolyzed in water and the products phosphoric and hydrochloric acids are measured by a colorimetric method for orthophosphate ion (see Phosphoric Acid, Analysis), and titration with silver nitrate for the chloride ion. Also, phosphate and chloride ions can be measured by ion chromatography.

Toxicity

The compound is highly irritating to skin, eyes and mucous membranes. Inhaling its vapors can cause pulmonary edema.

PHOSPHORUS PENTACHLORIDE

[10026-13-8]
Formula: PCl_5; MW 208.24

Uses

Phosphorus pentachloride is used as a chlorinating agent in many organic syntheses, such as production of alkyl and acid chlorides. It also is a catalyst in manufacturing acetylcellulose.

Physical Properties

Yellowish-white tetragonal crystals; pungent odor; fumes in air; deliquescent; density 2.1 g/cm^3; decomposes on heating; melts at 166.8°C under the pressure of its own vapor(triple point); sublimes at 160°C; critical temperature 373°C; hydrolyzes in water; soluble in carbon disulfide and carbon tetrachloride.

Thermochemical Properties

ΔH_f°	–106 kcal/mol

Preparation

Phosphorus pentachloride is prepared by reacting white phosphorus with excess dry chlorine. The white phosphorus is placed over sand in a retort from which air and moisture have been purged. The reaction is indicated by inflaming phosphorus:

$$P_4 + 10Cl_2 \rightarrow 4PCl_5$$

Also, the compound is obtained by reaction of dry chlorine with phosphorus trichloride:

$$PCl_3 + Cl_2 \rightarrow PCl_5$$

Reactions

Phosphorus pentachloride absorbs moisture from air forming phosphoryl chloride:

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$

The above reaction is difficult to control and progresses to complete hydrolysis. Thus, in the presence of excess water or when treated with water, the pentachloride is hydrolyzed to phosphoric acid:

$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$$

Reaction with sulfur dioxide yields thionyl chloride and phosphoryl chloride:

$$PCl_5 + SO_2 \rightarrow SOCl_2 + POCl_3$$

Reaction with liquid hydrogen sulfide forms thiophosphoryl chloride, $PSCl_3$:

$$PCl_5 + H_2S \rightarrow PSCl_3 + 2HCl$$

Phosphorus pentachoride converts arsenic to arsenic trichloride:

$$3PCl_5 + 2As \rightarrow 3AsCl_3 + 3PCl_3$$

Reaction with oxalic acid or boric acid yields phosphoryl chloride:

$$PCl_5 + (COOH)_2 \rightarrow POCl_3 + CO + CO_2 + 2HCl$$

$$3PCl_5 + 2B(OH)_3 \rightarrow 3POCl_3 + B_2O_3 + 6HCl$$

Reaction with phosphorus pentoxide produces phosphoryl chloride:

$$3PCl_5 + P_2O_5 \rightarrow 5POCl_3$$

Analysis

Elemental composition: P 14.88%, Cl 85.12%. The compound may be hydrolyzed with water and the products phosphoric and hydrochloric acids are measured for phosphate and chloride ions by ion chromatography and colorimetric methods (see Phosphoric Acid, Hydrochloric Acid).

Toxicity

The compound is strongly irritating to skin, eyes and mucous membranes.

PHOSPHORUS PENTAFLUORIDE

[7647-19-0]
Formula: PF_5; MW 125.97
Synonym: phosphorus(V)fluoride

Uses

Phosphorus pentafluoride is a catalyst in ionic polymerization reactions.

Physical Properties

Colorless gas; fumes in air; density 5.527g/L; heavier than air, density in air 4.35 (air=1); liquefies at –84.6°C; freezes at –93.8°C; reacts with water.

Thermochemical Properties

$\Delta H_f°$	–381.1 kcal/mol
$\Delta G_f°$	–363.5 kcal/
S°	1.9 cal/deg mol
C_ρ	20.3 cal/ deg mol
ΔH_{ap}	4.11 kcal/mol

Preparation

Phosphorus pentafluoride may be prepared by several methods, among which are:

1. Treating phosphorus trifluoride with bromine and then heating the product phosphorus trifluoride dibromide, PF_3Br_2:

$$PF_3 + Br_2 \rightarrow PF_3Br_2$$

$$5PF_3Br_2 \rightarrow 3PF_5 + 2PBr_5$$

2. Heating phosphorus pentachloride with arsenic trifluoride:

$$PCl_5 + 5AsF_3 \rightarrow 3PF_5 + 5AsCl_3$$

3. Subjecting phosphorus trifluoride to an electric spark in the absence of air (a disproportion reaction occurs):

$5PF_3 \rightarrow 3PF_5 + 2P$ (in the presence of air, the product is phosphorus oxyfluoride, POF_3)

4. Heating a mixture of phosphorus pentoxide and calcium fluoride:

$$P_2O_5 + 5CaF_2 \rightarrow 2PF_5 + 5CaO$$

5. Heating a mixture of phosphorus oxyfluoride, hydrogen fluoride and sulfur trioxide:

$$POF_3 + 2HF + SO_3 \rightarrow PF_5 + H_2SO_4$$

The gas should be stored in steel cylinders in the absence of moisture.

Reactions

Phosphorus pentafluoride hydrolyzes in water, the products formed depend on the reaction conditions. When exposed to moisture it forms phosphorus oxyfluoride:

$$PF_5 + H_2O \rightarrow POF_3 + 2HF$$

Hydrolysis with water proceeds through formation of intermediates, oxyfluophosphates and ultimately gives phosphoric acids. The overall reaction may be written as follows:

$$PF_5 + 4H_2O \rightarrow H_3PO_4 + 5HF$$

The pentafluoride also is known to form adducts. With nitrogen dioxide it forms an adduct, $PF_5 \cdot NO_2$, at –10°C which decomposes on warming.

Many complexes also are known, particularly with amines, pyridine, sulfoxides, and ethers.

Analysis

Elemental composition: P 24.59%, F 75.41%. The compound may be completely hydrolyzed in water and the ultimate hydrolysis products, phosphoric acid and HF, may be determined for PO_4^{3-} and F^- by ion chromatography. The compound may be confirmed by GC/MS. Its diluent mixture in helium or other inert gas may be introduced onto the GC column and PF_5 may be identified from its mass spectra. The characteristic mass ions are 126, 31, 107.

Toxicity

Phosphorus pentafluoride is a highly toxic gas. Inhalation can cause severe irritation of mucous membrane and pulmonary edema. It is corrosive to skin and can damage eyes.

PHOSPHORUS PENTOXIDE

[1314-56-3]
Formula: P_2O_5; MW 141.95; exists as P_4O_{10} units as molecular entities
Synonyms: phosphorus pentaoxide; phosphorus(V) oxide; phosphoric anhydride

Uses

Phosphorus pentoxide is a very effective drying and dehydrating agent. It also converts acids to their anhydrides.

Physical Properties

White, deliquescent, powdery solid; exhibits polymorphism; converts to several different crystalline forms on heating; the commercial material consists of hexagonal crystals; the hexagonal crystals on very rapid heating first melt at 420°C and then resolidify immediately to glassy orthorhombic crystals; slow heating of hexagonal crystals causes melting at 340°C which, on solidification, gives the same metastable orthorhombic form; the glassy material melts at about 580°C to a colorless and heavily viscous liquid; sublimes at 360°C; density of the commercial product 2.39g/cm^3; reacts with water.

Thermochemical Properties

ΔH_f° (hexagonal)	–713.2 kcal/mol
ΔH_f° (amorphous)	–727.0 kcal/mol
ΔG_f° (hexagonal)	–644.8 kcal/mol
S° (hexagonal)	54.7 cal/deg mol
C_ρ (hexagonal)	50.6 cal/ deg mol

Preparation

Phosphorus pentoxide is prepared by burning phosphorus in a plentiful supply of dry air or oxygen:

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

The crude product may contain a small amount of sesquioxide, P_2O_3, which may be removed by sublimation in ozonized oxygen.

Reactions

The most important reaction of phosphorus pentoxide is its hydrolysis. The hexagonal form reacts with water vigorously to form metaphosphoric acid $(HPO_3)_n$ which hydrolyzes further to yield phosphoric acid, H_3PO_4:

$$P_4O_{10} + 2H_2O \rightarrow 4HPO_3$$

$$HPO_3 + H_2O \rightarrow H_3PO_4$$

In finely divided hexagonal form, the compound reacts violently with water. The orthorhombic allotrope reacts much less vigorously than the hexagonal form.

Phosphorus pentoxide dehydrates nitric acid at low temperatures (about –10°C) forming metaphosphoric acid and nitrogen pentoxide:

$$P_4O_{10}\,(s) + 4HNO_3\,(l) \rightarrow 4HPO_3(\,s) + 2N_2O_5\,(s)$$

Reaction with phosphorus pentabromide yields phosphorus oxybromide:

$$P_2O_5 + 3PBr_5 \rightarrow 5POBr_3$$

Analysis

Elemental composition: P 43.64%, O 56.36%. The pentoxide is dissolved in water and the ultimate hydrolysis product, H_3PO_4, is analyzed for PO_4^{3-} by ion chromatography. Alternatively, the solution is treated with ammonium molybdate—ammonium vanadate reagent to produce a yellow colored vanadomolybdophosphoric acid. Absorbance or transmittance of the solution may be measured at a wavelength between 400 to 490 nm, depending on. concentration of PO_4^{3-}. The solution must be diluted for analysis. The solution may further be reduced with stannous chloride to form an intensely colored molybdenum blue for measuring absorbance or transmittance at 690nm.

Toxicity

Phosphorus pentoxide is a strong irritant. It is corrosive to skin and contact with eyes can be injurious.

PHOSPHORUS TRICHLORIDE

[7719-12-2]
Formula: PCl_3; MW 137.33

Uses

Phosphorus trichloride is used to prepare phosphine and other phosphorus compounds.

Physical Properties

Colorless fuming liquid; pungent odor; refractive index 1.516 at 14°C; density 1.574g/mL at 21°C; boils at 76°C; freezes at –112°C; decomposes in water; soluble in benzene, carbon disulfide, ether and chloroform and other halogenated organic solvents.

Thermochemical Properties

ΔH_f° (liq)	–76.4 kcal/mol
ΔH_f° (gas)	–68.6 kcal/mol
ΔG_f° (liq)	–65.1 kcal/mol
ΔG_f° (gas)	–64.0 kcal/mol
S° (liq)	74.5 cal/deg mol
C_ρ (liq)	17.17 cal/deg mol

Preparation

Phosphorus trichloride is prepared by reacting white phosphorus with dry chlorine present in limited quantity. Excess chlorine will yield phosphorus pentachloride, PCl_5.

$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$

$$P_4 + 10Cl_2 \rightarrow 4PCl_5$$

The compound is prepared in a retort attached to inlet tubes for dry chlorine and dry carbon dioxide and a distillation flask. White phosphorus is placed on sand in the retort. All air, moisture, and any phosphorus oxide vapors present in the apparatus are expelled by passing dry carbon dioxide. Dry chlorine is then introduced into the apparatus. If a flame appears on phosphorus it indicates presence of excess chlorine. In that event, the rate of chlorine introduction should be decreased. For obtaining phosphorus trichloride, flame should appear at the end of the chlorine-entry tube. The trichloride formed is collected by condensation in the distillation flask. A soda lime tube is attached to the apparatus to prevent moisture entering the flask.

Phosphorus trichloride also can be prepared by reducing phosphorus oxychloride vapors with carbon at red heat:

$$POCl_3 + C \rightarrow PCl_3 + CO$$

Reactions

Phosphorus trichloride reacts violently with water forming phosphorus acid:

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

When dry chlorine gas is passed into the liquid trichloride under cooling, phosphorus pentachloride is obtained:

$$PCl_3 + Cl_2 \rightarrow PCl_5$$

Phosphorus trichloride reacts with concentrated sulfuric acid forming chlorosulfuric acid and metaphosphoric acid:

$$PCl_3 + 2H_2SO_4 \rightarrow HSO_3Cl + HPO_3 + SO_2 + 2HCl$$

Reaction with sulfur trioxide produces phosphoryl chloride:

$$PCl_3 + SO_3 \rightarrow POCl_3 + SO_2$$

Oxidation of trichloride produces phosphorus trichloride oxide which may be used as the starting material to prepare alkyl-and alkoxyphosphine oxides:

$$PCl_3 + O_2 \rightarrow O{=}PCl_3$$

$$O{=}PCl_3 + 3CH_3OH \rightarrow (CH_3O)_3P{=}O + 3HCl$$

$$O{=}PCl_3 \xrightarrow{RMgX} R_3P{=}O$$

Phosphorus trichloride reacts with thionyl chloride to form phosphoryl chloride, thiophosphoryl chloride and phosphorus pentachloride:

$$3PCl_3 + SOCl_2 \rightarrow POCl_3 + PSCl_3 + PCl_5$$

It reacts violently with potassium chlorate forming phosphoryl chloride:

$$3PCl_3 + KClO_3 \rightarrow 3POCl_3 + KCl$$

Phosphorus trichloride reacts with iodine in warm glacial acetic acid solution, which on cooling yields orange crystals of phosphorus diiodide:

$$2PCl_3 + 5I_2 \rightarrow P_2I_4 + 6ICl$$

Reaction with potassium iodide yields phosphorus triiodide:

$$PCl_3 + 3KI \rightarrow PI_3 + 3KCl$$

Phosphorus trichloride reacts with organics that contain hydroxyl groups.

However, with ethanol two competing reactions occur:

$$PCl_3 + 3C_2H_5OH \rightarrow H_3PO_3 + 3C_2H_5Cl$$

$$PCl_3 + 3C_2H_5OH \rightarrow P(OC_2H_5)_3 + 3HCl$$

With acetic acid the products are acetyl choride and phosphorus acid:

$$PCl_3 + 3CH_3COOH \rightarrow 3CH_3COCl + H_3PO_3$$

Similar reactions occur with other carboxylic acids.

Reactions with ammonia under controlled conditions produce phosphorus triamine:

$$PCl_3 + 3NH_3 \rightarrow P(NH_2)_3 + 3HCl + PCl_3$$

Reaction with sulfur forms phosphorus trichloride sulfide:

$$PCl_3 + S \rightarrow S = PCl_3$$

Phosphorus trichloride is converted to phosphorus trifluoride by heating with flouride of arsenic, anitmony or zinc:

$$2PCl_3 + 3ZnF_2 \rightarrow 2PF_3 + 3ZnCl_2$$

Reaction with silver isocyanate or silver thiocyanate yields phosphorus triisocyanate or phosphorus trithiocyanate:

$$PCl_3 + 3AgNCO \rightarrow P(NCO)_3 + 3AgCl$$

$$PCl_3 + 3AgSCN \rightarrow P(SCN)_3 + 3AgCl$$

Reaction with lower alcohols in the presence of a base yields the corresponding trialkoxyphosphine:

$$PCl_3 + 3C_2H_5OH \rightarrow P(OC_2H_5)_3 + 3HCl$$

However, in the absence of a base the product is dialkoxyphosphine oxide, $(C_2H_5O)_2PH(=O)$.

Phosphorus trichloride forms a tetracoordinated nickel complex by action with nickel tetracarbonyl:

$$4PCl_3 + Ni(CO)_4 \rightarrow P[Ni(PCl_3)]_4 + 4CO$$

Analysis

Phosphorus trichloride may be dissolved in a suitable organic solvent such as benzene or chloroform and analyzed by GC-NPD in phosphorus mode. Its solution in CS_2 may be analyzed by GC—FID. The most definitive test is by mass spectrometry.

Hazard

Phosphorus trichloride is highly corrosive. Its vapors are an irritant to mucous membranes. Chronic exposure to its vapors can cause bronchitis. It reacts violently with water and explodes in contact with acetic and nitric acids, and several other substances (Patnaik. P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd. Ed. New York: John Wiley & Sons).

PLATINIC ACID, HEXACHLORO

[16941-12-1]
Formula: H_2PtCl_6; MW 409.81; crystallized as a hexahydrate, $H_2PtCl_6 \cdot 6H_2O$
Synonyms: chloroplatinic acid; hexachloroplatinic acid; hexachloro platinic-(IV) acid

Uses

Chloroplatinic acid is used in preparing most platinum salts and complexes. It also is used as an electroplating bath for plating and coating of platinum. Other applications are in catalysis.

Physical Properties

The hexahydrate consists of red to brownish-red cubic crystals; deliquesces; density 2.431g/cm^3; melts at 60°C; very soluble in water and alcohol; soluble in ether.

Preparation

Hexachloroplatinic acid is obtained in an intermediate step during extraction of platinum from minerals. The compound is formed when platinum is dissolved in aqua regia containing a higher proportion of HCl and subsequently is evaporated repeatedly with hydrochloric acid, preferably in a chlorine atmosphere. Alternatively, hexachloroplatinic acid may be obtained by dissolving platinum tetrachloride, $PtCl_4$, in water.

Pure hexachloroplatinic acid may be prepared by dissolving platinum sponge in hydrochloric acid under chlorine.

Reactions

Hexachloroplatinic acid decomposes completely when ignited, leaving a residue of spongy platinum. Hexachloroplatinic acid on heating at 300°C in chlorine forms platinum tetrachloride:

$$H_2PtCl_6 \rightarrow PtCl_4 + 2HCl$$

Reactions with ammonium chloride or other ammonium salts form a lemon yellow precipitate of ammonium hexachloroplatinate, $(NH_4)_2PtCl_6$:

$$H_2PtCl_6 + 2NH_4Cl \rightarrow (NH_4)_2PtCl_6 + 2HCl$$

Treatment with caustic alkali yields a white precipitate of hexahydroxoplatinic acid, $H_2Pt(OH)_6$:

$$H_2PtCl_6 + 6OH^{-} \rightarrow H_2Pt(OH)_6 + 6Cl^{-}$$

When hydrogen sulfide is bubbled into a boiling solution of hexachloroplatinic acid, a black precipatate of platinum disulfide, PtS_2 (soluble in aqua regia) is obtained:

$$H_2PtCl_6 + 2H_2S \rightarrow PtS_2 + 6HCl$$

The above reaction is accompanied simultaneously with reduction of $[PtCl_6]^{2—}$ into platinum in metallic state. Metalic platinum, however, is a minor product.

Addition of silver nitrate produces a yellow precipitate of silver hexachloroplatinate, Ag_2PtCl_6:

$$H_2PtCl_6 + 2AgNO_3 \rightarrow Ag_2PtCl_6 + 2HNO_3$$

Hexachloroplatinic acid may be reduced to tetrachloroplatinic(II) acid, H_2PtCl_4, by sulfur dioxide and other reducing agents.

Analysis

Elemental composition (anhydrous salt): Pt 47.60%, H 0.49%, Cl 51.90%. The compound may be identified by its physical and chemical properties. Platinum in an aqueous solution of the compound can be analyzed by flame AA or ICP spectroscopy. Also, the compound can be measured by gravimetry following precipitation with ammonium chloride, hydrogen sulfide, or silver nitrate (see Reactions above).

PLATINUM

[7440-06-4]

Symbol Pt; atomic number 78; atomic weight 195.08; a Group VIII (Group 10) noble metal; atomic radius 1.39Å; ionic radius of Pt^{2+} and Pt^{4+} in crystals having coordination numbers 4 and 6 are 0.60 Å and 0.63Å respectively; electron configuration $[Xe]4f^{14}5d^{9}6s^{1}$; valence states +2, +3, +4, most common valence +4; six stable isotopes: Pt-190 (0.011%), Pt-192 (0.80%), Pt-194 (32.96%), Pt-195 (33.86%), Pt-196 (25.36%), Pt-198 (7.22%); twenty-nine radioactive isotopes in the mass range 168–190, 193, 197, 199–202; the longest lived radioactive isotope is naturally occurring Pt-190, $t_{1/2}$ 6.5×10^{11} years.

History, Occurrence, and Uses

Platinum was discovered in Colombia, South America by Ulloa in 1735 and six years later in 1741 by Wood. The metal was isolated from native platinum by de l'Isle in 1775 and produced in malleable form by Chabaneau in 1786. Wollaston in 1803 developed a method of obtaining pure malleable platinum from crude platinum by extraction with aqua regia. The process led to the discovery of two other platinum group metals, palladium and rhodium, that were found in the aqua regia extract after platinum precipitated. Platinum derived its name from *platina* originating from the Spanish word *plata* for silver, because it was thought to be a trivial unwanted material associated with gold in gold mines of Central America.

Platinum occurs in nature as a bright-white cubic crystalline solid with metallic luster associated with other noble metals of its group. Platinum also occurs as the mineral sperrylite, $PtAs_2$, found as tin-white brittle cubic crystals containing 52–57% platinum in certain nickel-bearing deposits. Some other minerals of platinum are cooperite PtS (Pt 80-86%); and braggite(Pt, Pd, Ni)S (Pt 58-60%). The abundance of platinum in the earth's crust is estimated to be 0.005 mg/kg.

Platinum metal and its alloys have numerous applications. As a precious metal it is used extensively in jewelry. Other important applications include construction of laboratory crucibles and high temperature electric furnaces; in instruments as thermocouple elements; as wire; for electrical contacts; as electrodes; in dentistry; in cigarette lighters; and for coating missile and jet engine parts.

Platinum also is used extensively as a catalyst in hydrogenation, dehydrogenation, oxidation, isomerization, carbonylation, and hydrocracking. Also, it is used in organic synthesis and petroleum refining. Like palladium, platinum also exhibits remarkable ability to absorb hydrogen. An important application of platinum is in the catalytic oxidation of ammonia in Ostwald's process in the manufacture of nitric acid. Platinum is installed in the catalytic converters in automobile engines for pollution control.

Physical Properties

Silvery-white lustrous metal; remains bright at all temperatures; face-centered cubic crystal; density 21.5g/cm^3; Vickers hardness, annealed 38-40; melts at 1,768.4°C; vaporizes at 3,825°C; vapor pressure at melting point 0.00014 torr; electrical resistivity 9.85 microhm-cm at 0°C; magnetic susceptibility 9.0×10^{-6} cm^3/g; Poisson's ratio 0.39; thermal neutron cross section 8 barns; insoluble in water and acids; soluble in aqua regia

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	135.1 kcal/mol
$\Delta G_f°$ (cry)	0.0
$\Delta G_f°$ (gas)	124.4 kcal/mol
S° (cry)	9.94 cal/deg mol
S° (gas)	46.0 cal/deg mol

C_ρ (cry)	6.19 cal/deg mol
C_ρ (gas)	6.09 cal/deg mol
ΔH_{fus}	5.30 kcal/mol
Thermal conductivity	71.1 W/(m.K)
Coefficient of linear expansion, at 20°C	$9.1x10^{-6}$/°C

Reactions

At ordinary temperatures platinum is inert to practically all substances except aqua regia and, to a small extent, chlorine water. The metal is not attacked by strong acids except aqua regia. It dissolves in aqua regia forming chloroplatinic acid, H_2PtCl_6.

Platinum reacts with oxygen only at elevated temperatures. Finely divided metal forms platinum oxide, PtO, at about 500°C. When heated at 1,000°C in air or oxygen, platinum loses weight probably due to the evaporation of the thin layer of PtO_2 from its surface.

Fused alkalies, particularly potassium and barium hydroxides, are corrosive to platinum. In the presence of oxygen or oxidizing agents this corrosive action of fused alkalies increases. Also, cyanide and nitrates of alkali metals in fused state are corrosive to platinum.

Platinum combines with dry chlorine above 250°C forming platinum dichloride, $PtCl_2$. Reaction with fluorine occurs at dull red heat forming platinum tetrafluoride, PtF_4, as the major product, with small amounts of difluoride, PtF_2.

Platinum can be alloyed with many elements at elevated temperatures. Such elements include other noble metals, as well as, cobalt, selenium, silicon, and arsenic and nonmetals like carbon, phosphorus, and sulfur.

Platinum, like palladium, absorbs a large volume of hydrogen, particularly when heated. Hydrogen also diffuses through hot platinum sheet.

Platinum retains hydrogen at ordinary temperature and gives off the gas when heated in vacuum.

Production

Platinum metal concentrate obtained after the mineral is subjected to various mechanical processes including froth flotation and gravity separation is treated with aqua regia. Gold, platinum and palladium dissolve in aqua regia leaving behind other noble metals and silver in the insoluble residues. Gold is precipitated from the aqua regia extract by treating the solution with dibutyl carbitol. Alternatively, gold may be removed from the chloride solution by reduction with sulfur dioxide or ferrous salt to yield metallic gold. The filtrate solution contains platinum and palladium in the form of chloroplatinic and chloropalladic acids, H_2PtCl_6 and H_2PdCl_4, respectively. Ammonium chloride is added to this solution to precipitate ammonium chloroplatinate $(NH_4)_2PtCl_6$ leaving palladium in solution. The precipitate obtained at this stage contains trace impurities. Crude complex is refined in a series of steps to obtain purified metal. Such refining steps may include igniting the complex; dissolving the impure platinum sponge in aqua regia; treatment with sodium chloride to precipitate sodium platinum chloride, Na_2PtCl_6, and converting pure

Na_2PtCl_6 to ammonium platinum chloride $(NH_4)_2PtCl_6$. The purified ammonium complex is then ignited to form platinum sponge.

Analysis

Platinum in metallic form is brought into aqueous phase by boiling with aqua regia and evaporating almost to dryness. This is followed by adding concentrated HCl and a small amount of NaCl and again evaporating to dryness. Finally, the residue is dissolved in dilute HCl and diluted further for analysis. The aqueous solution is analyzed by flame-atomic absorption spectrophotometry using an air-acetylene flame. Measurement may be carried out at the wavelength 265.9 nm. Platinum may be measured by other instrumental techniques such as X-ray fluorescence and neutron activation analysis.

PLATINUM DICHLORIDE

[10025-65-7]
Formula: $PtCl_2$; MW 265.99
Synonyms: platinum(II) chloride; platinous chloride

Uses

The compound does not have any notable commercial applications. It is used to prepare tetrachloroplatinic(II) acid (choroplatinous acid) and tetrachloroplatinate salts.

Physical Properties

Olive green hexagonal crystals; density 6.05 g/cm^3; decomposes to platinum metal and chlorine on heating at 581°C; insoluble in water and alcohol; soluble in hydrochloric acid and ammonia solution.

Thermochemical Properties

ΔH_f°	–29.5 kcal/mol

Preparation

Platinum dichloride is prepared by heating platinum sponge in chlorine at about 500°C:

$$Pt + Cl_2 \rightarrow PtCl_2$$

It also may be obtained by thermal decomposition of platinum tetrachloride, $PtCl_4$, or hexachloroplatinic acid:

$$PtCl_4 \rightarrow PtCl_2 + Cl_2$$

$$H_2PtCl_6 \rightarrow PtCl_2 + 2HCl + Cl_2$$

Reactions

Platinum dichloride dissolves in hydrochloric acid to form a dark brown complex acid, tetrachloroplatinic(II) acid, H_2PtCl_4 in the solution:

$$PtCl_2 + 2HCl \rightarrow H_2PtCl_4$$

Tetrachloroplatinic(II) acid formed above may decompose to a small extent forming metallic platinum and hexachloroplatinic(II) acid.

Reactions with carbon monoxide at moderate temperatures yield complexes $[PtCl_2(CO)]_2$, $[PtCl_2(CO)_2]$, and $[(PtCl_2)_2(CO)_2]$, having melting points 194°, 142°, and 130°C, respectively.

Platinum dichloride forms complexes with ammonia, $[Pt(NH_3)_4]Cl_2$, which on heating yields $[PtCl_2(NH_3)_2]$.

Analysis

Elemental composition: Pt 73.36%, Cl 26.64%. The compound is dissolved in concentrated HCl, diluted, and analyzed for platinum by flame-AA spectrophotometry (see Platinum). The salt may be identified by its olive green color and other physical and x–ray properties. It forms a dark brown color in HCl.

PLATINUM DIOXIDE

[1314-15-4]
Formula: PtO_2; MW 227.08; forms mono-, di-, and tetrahydrates
Synonyms: platinum(IV) oxide; platinic oxide; Adams' catalyst

Uses

Platinum dioxide, also known as Adams' catalyst, is used commercially in many hydrogenation reactions at ordinary temperatures, such as reduction of olefinic and acetylenic unsaturation, aromatics, nitro, and carbonyl groups.

Physical Properties

Black solid; density 10.2 g/cm^3; melts at 450°C; thermally decomposes; insoluble in water, alcohol, acids and aqua regia; soluble in caustic potash solution.

Thermochemical Properties

ΔH_f° (g)	41.0 kcal/mol
ΔG_f° (g)	40.1 kcal/mol

Preparation

Platinum dioxide is obtained as its monohydrate, $PtO_2 \cdot H_2O$, a brown-red precipitate, upon boiling a solution of platinum tetrachloride, $PtCl_4$, with sodium carbonate.

The anhydrous black dioxide, PtO_2, may be prepared by treating a solution of hexachloroplatinic acid, H_2PtCl_6, with sodium carbonate. The yellow hexahydroxoplatinic acid, $H_2Pt(OH)_6$, is carefully heated below 100°C to yield the black PtO_2. Strong heating may decompose the dioxide to platinum metal.

Analysis

Elemental composition: Pt 85.91%, O 14.09%. The oxide may be characterized by its physical properties and by x-ray diffraction. The compound may be thermally decomposed at elevated temperatures or reduced by hydrogen to form platinum metal which may be digested with aqua regia and HCl, diluted, and analyzed by flame AA, ICP/AES or ICP/MS.

PLATINUM HEXAFLUORIDE

[13693-05-5]
Formula PtF_6; MW 309.07; monomeric in vapor phase; Pt–F bond length is about 1.82Å

Uses

Platinum hexafluoride does not have many commercial applications. It is used as a strong oxidizing agent and can oxidize oxygen from the air. It is used in research. Platinum hexafluoride forms compounds with molecular oxygen and xenon, $[O_2^+][PtF_6^-]$ and $XePtF_6$, respectively.

Physical Properties

Dark-red octahedral crystals; volatile and unstable; density 3.83g/cm^3; melts at 61.3°C; vaporizes at 69.14°C; reacts violently with water.

Preparation

Platinum hexafluoride may be prepared by heating platinum with fluorine under pressure. The preparation should be in nickel or Monel apparatus as the compound reacts with glass.

Reaction

The hexafluoride is a very powerful oxidizing agent reacting violently with most oxidizable substances. Reaction with liquid water is violent forming HF, oxygen, lower fluorides of platinum, and other products. In vapor phase hydrolysis occurs more smoothly.

The hexafluoride decomposes on heating; also decomposed by UV radiation to lower fluorides; and reacts with the inert gas xenon, forming a solid product, $Xe(PtF_6)$. It reacts with molecular oxygen to produce $O_2^+PtF_6^-$ The compound attacks glass at ordinary temperatures.

Hazard

Platinum hexafluoride is dangerously corrosive. Inhalation of its vapors or skin contact causes serious injury. Also, it can react explosively with a number of substances.

PLATINUM MONOXIDE

[12035-82-4]
Formula PtO; MW 211.08
Synonyms: platinum oxide; platinum(II) oxide

Uses

Platinum monoxide is used to prepare platinum-based catalysts.

Physical Properties

Violet-black solid; density 14.9g/cm^3; decomposes on heating at 550°C; insoluble in water and alcohol; soluble in aqua regia.

Preparation

Platinum monoxide is prepared by thermal decomposition of platinum(II) hydroxide, $Pt(OH)_2$, under careful heating.

$$Pt(OH)_2 \rightarrow PtO + H_2O$$

If the hydroxide is heated too strongly and rapidly it disproportionates forming platinum metal and platinum dioxide:

$$2Pt(OH)_2 \rightarrow PtO_2 + Pt + 2H_2O$$

Platinum monoxide may be obtained as a black precipitate when an alkali hydroxide is added to an aqueous solution of potassium tetrachloroplatinate(II) (potassium chloroplatinate), K_2PtCl_4.

Analysis

Elemental composition: Pt 92.41%, O 7.59%. The oxide can be identified by its physical and x-ray properties. Additionally, platinum may be measured by flame-AA following digestion of the solid with aqua regia and HCl (see Platinum).

PLATINUM TETRACHLORIDE

[37773-49-2]
Formula: $PtCl_4$; MW 336.89; also forms a pentahydrate, $PtCl_4 \cdot 5H_2O$
Synonyms: platinum(IV) chloride; platinic chloride

Uses

Platinum tetrachloride is used to prepare chloroplatinic acid and many platinum complexes, particularly with ammonia. Such complexes were prepared and studied by Alfred Werner to support his theory on coordination compounds.

Physical Properties

Brown-red crystalline solid; density 4.303g/cm^3; decomposes at 370°C; readily dissolves in water; dissolves in hydrochloric acid forming chloroplatinic acid, H_2PtCl_6; soluble in acetone; slightly soluble in ethanol; insoluble in ether.

The pentahydrate $PtCl_4 \cdot 5H_2O$ constitutes red monoclinic crystals; density 2.43g/cm^3; loses water on heating; very soluble in water; soluble in alcohol and ether.

Thermochemical Properties

$\Delta H_{f°}$ (g)	–55.4 kcal/mol

Preparation

Platinum tetrachloride is prepared by decomposition of hexachloroplatinic(IV) acid, H_2PtCl_6, in a stream of chlorine gas at 300°C.

Analysis

Elemental composition: Pt 52.56%, Cl 47.44%. Platinum tetrachloride may be dissolved in water and analyzed for platinum (see Platinum). Also, it may be identified by its physical properties and certain precipitation reactions after dissolving in HCl (see Platinic Acid, Hexachloro).

PLUTONIUM

[7440-07-5]

Symbol Pu; atomic number 94; atomic weight 244; an actinide series transuranium element; a man-made radioactive element; electron configuration [Rn]$5f^67s^2$; partially filled *f* subshell; valence states +3, +4, +5, +6; eighteen isotopes in the mass range 228-230, 232-246; all isotopes radioactive; the longest lived isotope Pu-244, $t_{1/2}$ 8.2×10^7 year; the shortest lived isotope Pu-233, $t_{1/2}$ 20.9 minute.

History, Occurrence, and Uses

Plutonium was discovered by Wahl, Seaborg, and Kennedy in 1941 at Berkeley, California when they separated and identified its isotope of mass 238 produced from bombarding uranium isotopes with neutrons in a cyclotron. In the same year the isotope Pu-239 was found to be fissionable. However, only microgram quantities of Pu-239 were generated by cyclotron bombardment. In 1943 Enrico Fermi and his group developed a process for successful generation of much larger quantities of plutonium for nuclear weapons. They achieved a self-sustaining nuclear chain reaction in a reactor using uranium and graphite. This work eventually led to the first successful testing of an atom bomb in the desert of New Mexico in July 1945.

Plutonium is the second transuranium element after neptunium. The element was named after the planet Pluto.

Plutonium is the most important transuranium element. Its two isotopes Pu-238 and Pu-239 have the widest applications among all plutonium isotopes. Plutonium-239 is the fuel for nuclear weapons. The detonation power of 1 kg of plutonium-239 is about 20,000 tons of chemical explosive. The critical mass for its fission is only a few pounds for a solid block depending on the shape of the mass and its proximity to neutron absorbing or reflecting substances. This critical mass is much lower for plutonium in aqueous solution. Also, it is used in nuclear power reactors to generate electricity. The energy output of 1 kg of plutonium is about 22 million kilowatt hours. Plutonium-238 has been used to generate power to run seismic and other lunar surface equipment. It also is used in radionuclide batteries for pacemakers and in various thermoelectric devices.

Physical Properties

Silvery-white metal; warm to touch because of its ionizing radiation; when in appreciable amounts the metal can generate enough heat to boil water; attains yellowish appearance when slightly oxidized. Six allotropic modifications are known: (1) alpha monoclinic form with sixteen atoms per unit cell; stable at ordinary temperatures; density 19.86g/cm^3; converts to beta form at 115°C. (2) beta form; body-centered monoclinic crystal structure; thirty-four atoms per unit cell; density 17.70 g/cm^3; stable between 115 to 200°C; converts to gamma form at about 200°C. (3) gamma modification; face-centered orthorhombic structure; eight atoms in unit cell; density 17.14g/cm^3; exists between 200 to 310°C; converts to delta form at 310°C. (4) delta allotrope; face-centered cubic structure; four atoms per unit cell; density 15.92g/cm^3; stable in the temperature range 310 to 452°C; converts to a delta-prime form at 452°C. (5) delta-prime form; body-centered tetragonal crystals; two atoms per unit cell; density 16.00g/cm^3; stable between 452 to 480°; converts to another allotropic form, known as epsilon at 480°C. (6) epsilon form; body-centered cubic structure; two atoms per unit cell; density 16.51g/cm^3; stable at temperatures between 480 to 640°C.

Plutonium melts at 640°C; vaporizes at 3,228°C; electrical resistivity 146.4 microhm-cm at 0°C; Young's modulus 14x10^6 psi; Poisson's ratio 0.17; dissolves in concentrated hydrochloric, hydriodic, and perchloric acids (with reaction).

Thermochemical Properties

$\Delta H_f°$	0.0
Thermal conductivity	0.0674 W/cmK
Coefficient of linear expansion	46.7 x 10^{-6}/°C
C_ρ	8.84 cal/g-atom
C_ρ (liquid at 675°C)	10.0 cal/g-atom
$\Delta H\alpha \rightarrow \beta$	900 ± 20 cal/g-atom

ΔHβ→γ	160 ± 10 cal/g-atom
ΔHγ→δ	148 ± 15 cal/g-atom
ΔHδ→δ‘	10 ± 10 cal/g-atom
ΔHδ’→ε	444 ± 10 cal/g-atom
ΔHε→liquid	676 ± 10 cal/g-atom

Production

Plutonium is produced from natural uranium which is a mixture of nonfissionable uranium-238 (99.3%) and fissionable uranium-235(0.7%). The first synthesis of this element was in a cyclotron generating plutonium in microgram quantities. The isotope Pu-239 can be produced in much larger quantities in a nuclear reactor, either a conventional thermal reactor or a breeder type reactor by neutron bombardment of uranium- 238. The nuclear reactions are shown below.

$$^{238}_{92}U+^{1}_{0}n\rightarrow^{239}_{92}U+\gamma$$

$$^{238}_{92}U+^{1}_{0}n\rightarrow^{239}_{92}U+\gamma$$

$$^{239}_{92}U\xrightarrow{\beta^-}{}^{239}_{93}Np$$

$$^{239}_{93}Np\xrightarrow{\beta^-}{}^{239}_{94}Pu$$

Higher isotopes such as Pu-240, -241, -242, etc. can be obtained from Pu-239 by continued neutron bombardment.

Plutonium-239 also is produced from natural uranium by the so-called “pile reactions” in which irradiation of uranium-235 isotope with neutrons produces fission, generating more neutrons and high energy (~200 MeV). These neutrons are captured by the uranium-238 to yield plutonium-239.

Synthesis of plutonium in significant quantities requires a sufficiently long reactor fuel irradiation period. Uranium, plutonium, and the fission products obtained after neutron irradiation are removed from the reactor and stored under water for several weeks. During such cooling periods most neptunium-239 initially formed from uranium and present in the mixture transforms to plutonium-239. Also, the highly radioactive fission products, such as xenon-133 and iodine-131 continue to decay during this period.

Plutonium is recovered from uranium and fission products by solvent extraction, precipitation, and other chemical methods. In most chemical processes, plutonium first is converted to one of its salts, usually plutonium fluoride, before it is recovered in purified metallic form. The fluoride is reduced with calcium metal to yield plutonium. Electrorefining may produce material of higher purity.

Plutonium is cast into small ingots by arc melting. All melting operations must be carried out in vacuum or in an inert atmosphere to prevent any air oxidation at high temperatures. Also, being a reactive metal, its recovery and purification should be done in crucibles made of highly refractory and stable materials.

Reactions

Plutonium is a reactive metal forming mostly tri-, tetra-, and hexavalent compounds. The solutions of Pu^{3+} are blue. The trivalent Pu^{3+} is stable in solution in the absence of air. In the presence of air or oxygen, Pu^{3+} slowly oxidizes to Pu^{4+}. In cold acid medium, permanganate ion oxidizes Pu^{3+} to Pu^{4+}. In aqueous solutions Pu^{4+} salts impart pink or greenish color to the solutions. Tetravalent Pu^{4+} converts to hexavalent plutonium, Pu^{6+} by the action of strong oxidizing agents, such as dichromate, $Cr_2O_7^{2-}$, permanganate, MnO_4^- or Ce^{4+} salts.

The metal ion in higher oxidation states can be reduced by most common reducing agents, such as, sulfur dioxide, carbon monoxide, ferrocyanide ion, hydrazine hydrochloride, and hydroxylamine hydrochloride to form Pu^{3+} (or Pu^{4+}) ions in solution.

Plutonium combines with oxygen at high temperatures to form plutonium dioxide, PuO_2 , and other oxides. The dioxide also is formed in the presence of water vapor. Ignition of the metal in air at 1,000°C yields PuO_2.

Plutonium reacts with hydrogen at high temperatures forming hydrides. With nitrogen, it forms nitrides, and with halogens, various plutonium halides form. Halide products also are obtained with halogen acids. Reactions with carbon monoxide yields plutonium carbides, while with carbon dioxide, the products are both carbides and oxides. Such reactions occur only at high temperatures.

Plutonium forms several complexes in oxidation states +3, +4, and +6.

Hazard

Plutonium is one of the most dangerous substances known. The metal and it's salts are all highly toxic. Its ionizing radiation can cause cancer. The metal can incorporate with bone marrow forming insoluble plutonium (IV) phosphate. The metal only leaves the body very slowly. All operations must be carried out by remote control devices with proper shields. In production, processing, handling, and storage of large quantities of plutonium or its compounds one must bear in mind its critical mass, which can vary with the shape and the specific solid form or the quantities of plutonium contained in solutions.

POLONIUM

[7440-08-6]
Symbol Po; atomic number 84; atomic weight 209; a Group VIA (Group 16) radioactive element; electron configuration $[Xe]4f^{14}5d^{10}6s^26p^4$; valence states –2, 0, +2, +4, +6; atomic radius 1.64Å; atomic volume 23.53cc/g-atom; the last radioactive member of radium series; twentyfive isotopes; all radioactive; the longest lived isotope is the alpha emitter Po–209, $t_{1/2}$ 105 ± 5 year.

History, Occurrence, and Uses

Polonium was discovered by Marie Curie in 1898 while investigating the radioactivity of pitchblende. Mme. Curie named this new element after her native country Poland. Polonium is a very rare element, found in exceedingly small quantities in uranium ores. Its abundance in uranium ore is about 100mg/ton. Its applications are only a few. Polonium is used on brushes to remove dusts from photographic film. It also is used in instruments to eliminate static charges. Polonium is used as a small source to generate alpha particles and neutrons; as a power source in devices where its radioactive decay energy is converted into electrical energy. For this application the metal is combined with lighter elements.

Physical Properties

Two crystalline forms exist; (1) alpha allotrope; a simple cubic low temperature form; density 9.196 g/cm^3, and (2) beta modification: a rhombohedral high temperature form; density 9.398 g/cm^3

Both allotropic forms coexist between 18 to 54°C; melt at 254°C; vaporize at 962°C; electrical resistivity 42 and 44 microhm-cm at 0°C for alpha- and beta- forms, respectively; practically insoluble in water; soluble in dilute mineral acids.

Thermochemical Properties

ΔH_f°	0.0
ΔG_f°	0.0
ΔH_{vap}	24.6 kcal/mol
ΔH_{sub}	34.5 kcal/g-atom
Coeff. linear expansion	$(23.0\pm1.5)\times10^{-6}$/°C

Production

Polonium can be recovered from natural pitchblende. The yield, however, is exceedingly small as 1 g of polonium is contained in about 25,000 tons of pitchblende. The element may be isolated from the pitchblende extract by deposition on a bismuth plate immersed in chloride solution.

Polonium can be produced from other sources, too, that offer much higher yield than pitchblende. Two such processes are as follows:

(1) The element may be obtained from radioactive lead-210 (also, known as RaD, the lead fraction in the extraction of radium from uranium ore) by successive beta decay:

$$\underset{\text{(RaD)}}{{}^{210}_{82}Pb} \xrightarrow[t_{11/2}\ 22\ \text{yr}]{\beta-} \underset{\text{(RaE)}}{{}^{210}_{83}Bi} \xrightarrow[t_{11/2}\ 22\ \text{yr}]{\beta-} \underset{\text{(RaF)}}{{}^{210}_{84}Po}$$

The alpha emitter radioactive Po-210 that has a half-life of 138 days transforms to nonradioactive lead-206, the stable end product:

$$\underset{(\mathrm{RaF})}{{}^{210}_{84}\mathrm{Po}} \xrightarrow[t_{1/2}\ 138\ \text{days}]{\alpha\text{–emission}} \underset{(\mathrm{RaG})}{{}^{206}_{82}\mathrm{Pb}(\text{stable})}$$

(2) Polonium also can be synthesized by neutron irradiation of natural bismuth in a reactor:

$${}^{209}_{83}\mathrm{Bi} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{210}_{83}\mathrm{Bi} \xrightarrow{\beta-} {}^{210}_{83}\mathrm{Po}$$

After neutron irradiation bismuth (canned in aluminum jackets) is dissolved in a mixture of hydrochloric and nitric acids and excess NO_3^- is removed by adding a reducing agent, such as, urea or formic acid. If bismuth is used as an anode, the reducing agent is dissolved in HCl. Various methods are applied for concentration of polonium in the acid mixture and its subsequent separation from bismuth. Such processes include spontaneous deposition of polonium over a less electropositive metal and coprecipitation with tellurium. In the latter method, a Te^{4+} or Te^{6+} salt is added to the extract, followed by addition of stannous chloride, which reduces both the tellurium and polonium to their metallic state, coprecipitating them from bismuth in the extract mixture.

Another method to separate polonium from bismuth involves heating at 650°C to convert the metals into their oxides. This is followed by further heating to about 800°C at reduced pressure in which polonium metal is removed by volatilization.

Polonium may be purified by various processes. Such purification methods include precipitation of polonium as sulfide and then decomposing the sulfide at elevated temperatures; spontaneous decomposition of polonium onto a nickel or copper surface; and electrolysis of nitric acid solutions of polonium-bismuth mixture. In electrolytic purification polonium is electrodeposited onto a platinum, gold, nickel, or carbon electrode.

Reactions

Polonium resembles tellurium, the element above it in the same Group, in chemical behavior.

At ordinary temperatures polonium oxidizes slowly in air forming the basic oxide, PoO_2:

$$Po + O_2 \rightarrow PoO_2$$

The metal dissolves in dilute hydrochloric acid forming pink-red polonium dichloride:

$$Po + 2HCl \rightarrow PoCl_2 + H_2$$

The unstable dichloride converts to yellow tetrachloride, $PoCl_4$.

Polonium dissolves in concentrated nitric acid and aqua regia, oxidizing to Po^{4+} state. Reaction with nitric acid forms adducts that probably have the compositions $4PoO_2 \cdot N_2O_5$; $4PoO_2 \cdot 3N_2O_5$ and $Po(NO_3)_4 \cdot N_2O_4$. The metal also dissolves in concentrated sulfuric and selenic acids forming polonium sulfate, $Po(SO_4)_2$ and $Po(SeO_4)_2$, respectively. Another product, $2PoO_2 \cdot SO_3$, also has been identified.

Because of its radioactivity and alpha emission, polonium forms many types of radiolytic oxidation-reduction products.

Analysis

At trace levels, polonium can be separated effectively by solvent extraction, ion exchange, paper chromatography, and other techniques. Diisopropyl ketone, di-n-octylamine, and tri-n-butylphosphate are suitable solvents for extraction. Trace amounts of polonium in solutions or solid mixtures containing no other emitters can be determined by measuring its alpha activity.

Hazard

As with other radioactive substances, exposure to its ionizing radiation can cause cancer. When ingested it tends to accumulate in the liver, kidney, and spleen causing radiation damage from the alpha particles. All operations and handling must be carried out in leak-proof boxes by mechanical means behind thick neutron shields.

POTASSIUM

[7440-09-7]

Symbol K; atomic number 19; atomic weight 39.098; a Group 1A (Group1) alkali metal element; atomic radius 2.35Å; ionic radius, K^+ 1.33Å; electron configuration $[Ar]4s^1$; valence state +1; ionization potential 4.341eV; standard redox potential, E^o $K^+ + e^- \leftrightarrow K(s)$ –2.925V; three natural isotopes: K-39(93.258%), K-40 (0.0117%) and K-41 (6.730%); naturally occurring K-40 is radioactive, $t_{1/2}$ $1.25x10^9$ year, beta emitter; fourteen synthetic radioisotopes in the mass range 35–38 and 42–51.

History, Occurrence, and Uses

Potassium was first isolated as a free metal in 1807 by Sir Humphry Davy. It was the first alkali metal to be discovered, produced by electrolysis of potassium carbonate (potash). The element was earlier called Kalium, derived from the Arabic word *qili*, meaning grass wort, the ash of which was a source of potash. The element derived its symbol K from Kalium. The English name potassium came from potash (pot ash), the carbonate salt of the metal.

Potassium is distributed widely in nature. The metal is too reactive to occur in native elemental form. It is the seventh most abundant element on earth, constituting 2.40% by weight of the earth's crust. It is abundantly present in sea water. Oceans contain 0.07% (wt to volume) potassium chloride.

Potassium occurs in many igneous rocks, such as, feldspar (potassium aluminum silicate), $KAlSi_3O_8$ (leucite) and mica, $KH_2Al_3(SiO_4)_3$. Disintegration of these rocks adds potassium to soil and water. Deposits of potassium chloride are found in practically all salt beds, associated with sodium chloride. Some important potassium minerals are leucite, $KAlSi_2O_6$; glauconite (a complex silicoaluminate structure of varying compositions); sylvite, KCl; carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$; langbeinite, $K_2SO_4 \cdot 2MgSO_4$; and polyhalite, $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$.

Potassium, along with nitrogen and phosphorus, is an essential element needed for plant growth. In plants, it occurs mostly as K^+ ion in cell juice. It is found in fruit or seed. Deficiency can cause curling leaves, yellow or brown coloration of leaves, weak stalk and diminished root growth. Potassium deficiency has been associated with several common animal ailments. Potassium is in extracellular fluid in animals at lower concentrations than sodium.

Physical Properties

Silvery metal; body-centered cubic structure; imparts crimson-red color to flame; density 0.862g/cm³ at 20ºC; melts at 63.25ºC; density of liquid potassium at 100ºC is 0.819 g/cm³ and 0.771g/cm³ at 300ºC; vaporizes at 760ºC; vapor pressure 123 torr at 587ºC; electrical resistivity 6.1 microhm-cm at 0ºC and 15.31 microhm-cm at 100ºC; viscosity 0.25 centipoise at 250ºC; surface tension 86 dynes/cm at 100ºC; thermal neutron absorption cross section 2.07 barns; reacts violently with water and acids; reacts with alcohol; dissolves in liquid ammonia and mercury

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	21.33 kcal/mol
ΔG_f° (cry)	0.0
ΔG_f° (gas)	14.49 kcal/mol
S°(cry)	15.34 cal/deg mol
S°(gas)	38.29 cal/deg mol
C_ρ (cry)	7.07 cal/deg mol
C_ρ (gas)	4.97 cal/deg mol
ΔH_{fus}	0.555 kcal/mol
ΔH_{vap}	0.496 kcal/mol
Thermal conductivity at 200ºC	44.77 W/m.K

Production

Potassium can be produced by several methods that may be classified under three distinct types: (1) electrolysis, (2) chemical reduction, and (3) thermal decomposition.

Electrolysis processes have been known since Davy first isolated the metal in 1807. Electrolysis, however, suffers from certain disadvantages. A major problem involves miscibility of the metal with its fused salts. Because of this molten potassium chloride, unlike sodium chloride, cannot be used to produce the metal. Fused mixtures of potassium hydroxide and potassium carbonate or chloride have been used as electrolytes with limited success.

Chemical reduction processes are employed nowadays in commercial, as well as, laboratory preparation of potassium. In one such process, molten potassium chloride is reduced with sodium at 760 to 880ºC and the free metal is separated by fractionation:

$$KCl + Na \rightarrow K + NaCl$$

Potassium is obtained at over 99.5% purity. The metal, alternatively, may be alloyed with sodium for further applications.

Reduction of potassium fluoride with calcium carbide at 1,000 to 1,100ºC (Greisheim process) is an effective production method (Greer, J.S., Madaus, J.H and J.W. Mausteller. 1982. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed. p. 914, New York: Wiley Interscience):

$$2KF + CaC_2 \rightarrow CaF_2 + 2C + 2K$$

Some other chemical reduction methods that may be applied for laboratory generation of small quantities of potassium from its salts at high temperatures require a suitable reducing agent such as carbon, calcium, or calcium carbide:

$$K_2CO_3 + 2C \rightarrow 3CO + 2K$$

$$2KCl + Ca \rightarrow CaCl_2 + 2K$$

$$2KCl + CaC_2 \rightarrow CaCl_2 + 2C + 2K$$

$$2K_2CO_3 + \ +3Si + 3CaO \rightarrow 4K + 2C + 3CaSiO_3$$

$$2K_2SiO_3 + Si + 3\ CaO \rightarrow 4K + 3CaSiO_3$$

Potassium can be produced by thermal decomposition of potassium azide:

$$2KN_3 \rightarrow 2K + 3N_2$$

High purity metal may be produced by distillation of technical grade metal. Potassium (technical grade) may be packed under nitrogen. Argon should be used for packing high purity metal. Metal is shipped in stainless steel or carbon containers. In small quantities potassium is transported in glass or metal ampules.

Reactions

Potassium reacts with oxygen or air forming three oxides: potassium monoxide, K_2O; potassium peroxide, K_2O_2; and potassium superoxide, KO_2. The nature of the product depends on oxygen supply. In limited supply of oxygen potassium monoxide is formed, while in excess oxygen, superoxide is obtained:

$$4K + O_2 \rightarrow 2K_2O$$

$$2K + O_2 \rightarrow K_2O_2$$

$$K + O_2 \rightarrow KO_2$$

Potassium reacts violently with water, forming potassium hydroxide:

$$2K + 2H_2O \rightarrow 2KOH + H_2$$

Potassium reacts with hydrogen at about 350ºC to form potassium hydride:

$$2K + H_2 \rightarrow 2KH$$

Reactions with halogens, fluorine, chlorine and bromine occur with explosive violence. Thus, in contact with liquid bromine it explodes forming potassium bromide:

$$2K + Br_2 \rightarrow 2KBr$$

Potassium ignites in iodine vapor forming potassium iodide.

Violent reactions can occur with many metal halides. For example, with zinc halides or iron halides, single replacement reactions take place. Such potassium-metal halide mixtures can react violently when subjected to mechanical shock.

At ordinary temperatures, potassium does not combine with nitrogen but with an electric charge, potassium azide is formed.

Reaction with carbon (graphite) at above 400ºC produces a series of carbides, such as KC_4, KC_8, and $KC_{24.}$ With carbon monoxide, an unstable explosive carbonyl forms:

$$K + CO \rightarrow KCO$$

Potassium reduces carbon dioxide to carbon, carbon monoxide and potassium carbonate:

$$6K + 5CO_2 \rightarrow CO + C + 3K_2CO_3$$

Potassium reacts with ammonia gas to form potassium amide with liberation of hydrogen:

$$2K + 2NH_3 \rightarrow 2KNH_2 + H_2$$

Reactions with phosphorus, arsenic and antimony form phosphide, arsenide, and antimonide of potassium, respectively:

$$K + As \rightarrow K_3As$$

Reaction with sulfur forms three sulfides. When reactants are in molten state, the product is K_2S, but in liquid ammonia K_2S_2 and KS_2 are the main products.

Potassium reacts explosively with sulfuric acid, forming potassium sulfate with evolution of hydrogen:

$$K + H_2SO_4 \rightarrow K_2SO_4 + H_2$$

Potassium liberates hydrogen from ethanol forming potassium ethoxide:

$$2K + 2C_2H_5OH \rightarrow 2C_2H_5OK + H_2$$

Reaction with potassium nitrate yields potassium monoxide and nitrogen:

$$10K + 2KNO_3 \rightarrow 6K_2O + N_2$$

Analysis

Potassium and its salts can be identified by flame test. It imparts lilac color to the flame. Potassium ion in aqueous solution can be identified by reaction with sodium tetraphenylborate, $NaB(C_6H_5)_4$. In weakly acid solution, a white precipitate of the potassium salt $KB(C_6H_5)_4$ is obtained. The precipitate is filtered, dried, and weighed to measure potassium. The test is quantitative.

Potassium at trace concentrations in aqueous samples can be measured by a flame photometer at a wavelength of 766.5 nm. Either a flame photometer or an atomic absorption spectrometer operating in flame emission mode can be used for such analysis.

Potassium also can be measured by ICP/AES. The wavelengths at which it can be analyzed without interference from other metals are 766.49 and 769.90 nm. Other wavelengths may be used. Potassium ion in aqueous solution can be identified quantitatively by using a potassium ion-selective electrode attached to a pH meter having an expanded millivolt scale or to a specific ion meter having a direct readout concentration scale for potassium.

Hazard

Potassium metal can be dangerous to handle if proper precautions are not taken. Many of its reactions at ordinary temperatures can proceed to explosive violence (see Reactions). Also, it liberates flammable hydrogen gas when combined with water, acids, and alcohols.

POTASSIUM ACETATE

[127-08-2]
Formula: $KC_2H_3O_2$ or CH_3COOK; MW 98.14

Uses

Potassium acetate is used in the manufacture of glass; as a softening agent for papers and textiles; as a dehydrating agent; and as a buffer. In medicine it is used as an expectorant and diuretic.

Physical Properties

White lustrous powder or colorless deliquescent crystals; density 1.57 g/cm³; melts at 292ºC; highly soluble in water, 253g/100mL at 20ºC, more soluble in hot water, 492g/100mL at 62ºC; aqueous solution alkaline, pH of 0.1M solution 9.7; soluble in methanol, ethanol and liquid ammonia; insoluble in ether and acetone.

Thermochemical Properties

ΔH_f° (cry)	–172.8 kcal/mol
ΔH_f° (amp)	–176.5 kcal/mol
ΔG_f° (amp)	–156.0 kcal/mol
S° (amp)	45.2 cal/deg mol
C_ρ (amp)	3.7 cal/deg mol

Preparation

Potassium acetate is prepared by addition of potassium carbonate in a small volume of water to acetic acid solution, followed by evaporation and crystallization:

$$K_2CO_3 + 2CH_3COOH \rightarrow 2CH_3COOK + H_2O$$

Analysis

Elemental composition: K 39.85%, C 24.48%, H 3.08%, O 32.60%. Potassium may be identified by flame testing. An aqueous solution can be analyzed for potassium by flame photometry, ICP/AES, or ion selective electrode (see Potassium). Acetate anion may be measured in aqueous solution by ion chromatography under appropriate conditions.

POTASSIUM BICARBONATE

[298–14–6]
Formula $KHCO_3$; MW 100.12
Synonyms: potassium hydrogen carbonate; potassium acid carbonate

Uses

Potassium bicarbonate is used in baking powder and effervescent salts. In medicine, the salt is a gastric antacid and an electrolyte replenisher. It also is dry powder in fire extinguishers.

Physical Properties

Colorless transparent crystal or white powder; monoclinic structure; density 2.17 g/cm^3; decomposes above 100°C; soluble in water, 22.49 g/100ml at 20°C, 60 g/100ml at 60°C pH of 0.1M aqueous solution 8.2; practically insoluble in alcohol.

Preparation

Potassium bicarbonate is obtained by passing carbon dioxide through a cold, concentrated solution of potassium carbonate:

$$K_2CO_3 + CO_2 + H_2O \rightarrow 2\ KHCO_3$$

Alternatively, $KHCO_3$ is produced by passing excess carbon dioxide through aqueous potassium hydroxide. At first, potassium carbonate is formed which then converts to the bicarbonate as shown in the above reaction.

Potassium bicarbonate cannot be made by Solvay process because of its high solubility in water.

Reactions

Heating the bicarbonate yields normal carbonate, liberating carbon dioxide and water:

$$2KHCO_3 \rightarrow K_2CO_3 + CO_2 \uparrow + H_2O\uparrow$$

When the salt is added to dilute acids, carbon dioxide is liberated:

$$KHCO_3 + HCl \rightarrow K^+ + Cl^- + CO_2\uparrow + H_2O$$

Reaction with caustic potash in solution forms potassium carbonate:

$$KHCO_3 + KOH \rightarrow K_2CO_3 + CO_2 + H_2O$$

Analysis

Elemental composition: K 39.05%, C 11.99%, H 1.01%, O 47.94%. Potassium may be analyzed by AA spectroscopy in emission mode or by flame photometry (see Potassium). The aqueous solution may be treated with HCl and the CO_2 evolved may be noted from effervescence and tested by GC-TCD or by GC/MS. The characteristic mass ion for CO_2 is 44. Alternatively, the HCO_3^- anion or the CO_3^{2-} anion (converted by heating the bicarbonate) may be identified by ion chromatography.

POTASSIUM BISULFIDE

[1310–61–8]
Formula KHS; MW 72.17; usually exists as a hemihydrate
Synonyms: potassium hydrosulfide; potassium hydrogen sulfide; potassium

sulfhydrate

Preparation

Potassium bisulfide is made by reacting calcium hydrogen sulfide with potassium sulfate:

$$Ca(HS)_2 + K_2SO_4 \rightarrow 2KHS + CaSO_4$$

The compound can be made by reacting hydrogen sulfide with potassium sulfide:

$$H_2S + K_2S \rightarrow 2KHS$$

Purer compound may be produced by passing dry hydrogen sulfide through a solution of potassium metal dissolved in absolute ethanol:

$$2H_2S + 2K \rightarrow 2KHS + H_2$$

Physical Properties

Colorless crystals or white crystalline mass; rapidly deliquesces; converts to a yellow rhombohedral crystalline mass upon exposure to air, forming polysulfides and H_2S; density 1.68g/cm^3; the hemihydrate loses water at about 175°C; melts at 455°C to a dark red liquid; decomposes in water; soluble in alcohol.

Thermochemical Properties

$\Delta H_f°$	62.5 kcal/mol
ΔH_{soln} (at 17°C)	0.77 kcal/mol
ΔH_{soln} (hemihyadrate at 16°C)	0.62 kcal/mol

Analysis

Elemental composition: K 54.18%, S 44.42%, H 1.40%. An aqueous solution may be analyzed for potassium by various methods (see Potassium). The compound on exposure to air evolves H_2S which can be detected from its odor, as well as by various tests (see Hydrogen Sulfide).

POTASSIUM BOROHYDRIDE

[13762–51–1]
Formula KBH_4; MW 53.95
Synonym: potassium tetrahydroborate

Uses

Potassium borohydride, unlike sodium borohydride, has very limited applications. The compound is a reducing agent.

Physical Properties

White crystalline solid; stable in air; nonhygroscopic; density 1.11g/cm^3; decomposes at about 500°C without melting; soluble in water, 19g/100ml at 25°C; stable in alkaline solution; soluble in liquid ammonia and dimethyl formamide; slightly soluble in methanol, 0.7 g/100ml at 20°C.

Preparation

Potassium borohydride may be prepared by reacting potassium hydroxide with sodium borohydride. The salt precipitates from an aqueous solution of sodium borohydride with addition of potassium hydroxide:

$$NaBH_4 + KOH \rightarrow KBH_4 + Na^+ + OH^-$$

Also, potassium borohydride can be made by reacting potassium hydride with methyl borate at high temperature:

$$4\ KH + B(OCH_3)_3 \rightarrow KBH_4 + 3KOCH_3$$

Potassium borohydride also may be prepared by reacting potassium tetramethoxyborohydride with diborane at low temperatures; or by passing diborane through a solution of potassium methylate in methanol.

Analysis

Elemental composition: K 72.47%, B 20.06%, H 7.47%. The salt is dissolved in water and the solution analyzed for potassium and boron (see Potassium and Boron).

POTASSIUM BROMATE

[7758–01–2]
Formula: $KBrO_3$; MW 167.00

Uses

Potassium bromate is an oxidizing reagent in bromate-bromide mixture for titrimetric analysis. It also is a bread- and flour-improving agent.

Physical Properties

Colorless trigonal crystals or fine white crystals or granules; density 3.27 g/cm^3 at 18°C; melts at 350°C; decomposes at about 370°C evolving oxygen; moderately soluble in water, 13.3 g/100mL at 40°C; slightly soluble in alcohol; insoluble in acetone.

Thermochemical Properties

$\Delta H_f°$	–86.10 kcal/mol
$\Delta G_f°$	–64.82 kcal/mol

S°	35.65 cal/deg mol
C_ρ	28.72 cal/deg mol

Preparation

Potassium bromate can be produced by electrolysis of potassium bromide solution. Alternatively, the compound is obtained by adding potassium bromide to a saturated solution of sodium bromate or calcium bromate. The salt is recovered from solution by crystallization.

Analysis

Elemental composition: K 23.41%, Br 47.85%, O 28.74%. Aqueous solution of the salt after sufficient dilution may be analyzed for its potassium content by AA, ICP, or flame photometry (see Potassium) and for bromate anion by ion chromatography. Also, bromate content can be measured by iodometric titration using a standard solution of sodium thiosulfate and starch as indicator. The redox reactions are as follows:

$$BrO_3^- + 5\ Br^- \text{ (excess)} + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

Liberated iodine is titrated against a standard solution of thiosulfate until the starch solution's blue decolorizes.

Toxicity

Ingestion of the salt or its solution can cause nausea, vomiting, diarrhea, and renal injury. Also, it can induce methemoglobinemia.

POTASSIUM BROMIDE

[7758–02–3]
Formula: KBr; MW 119.00

Uses

Potassium bromide is used to make photographic plates and papers and in engraving. Other uses are as a brominating agent in organic synthesis and in the bromate-bromide mixture in titrimetric analysis. In medicine potassium bromide is a sedative and anticonvulsant.

Physical Properties

Colorless cubic crystals or white granules or powder; density 2.75 g/cm^3 at 25°C; melts at 734°C; vaporizes at 1,435°C; readily dissolves in water, solubility at 0°C 53.5 g/100mL and at 100°C 102 g/100mL; aqueous solution neutral; soluble in glycerol, 21.7 g/100mL; sparingly soluble in boiling ethanol 4.76 g/100mL.

Thermochemical Properties

$\Delta H_f°$ (cry)	–94.12 kcal/mol
$\Delta H_f°$ (gas)	–43.04 kcal/mol
$\Delta G_f°$ (cry)	–90.98 kcal/mol
$\Delta G_f°$ (gas)	–50.89 kcal/mol
S° (cry)	22.92 cal/deg mol
S° (gas)	59.95 cal/deg mol
C_ρ(cry)	12.50 cal/deg mol
C_ρ(gas)	8.52 cal/deg mol

Preparation

Potassium bromide is prepared by reacting bromine with potassium carbonate:

$$3K_2CO_3 + 3Br_2 \rightarrow KBrO_3 + 5KBr + 3CO_2$$

Potassium bromate, $KBrO_3$, is less soluble than the bromide. Thus, most potassium bromate may be removed by filtration. Remaining bromate can be converted to bromide by reduction with iron. After filtering iron from the solution, potassium bromide is obtained by evaporation and crystallizaton.

Another method of preparation involves treating bromine with warm concentrated aqueous solution of potassium hydroxide:

$$3Br_2 + 6KOH \rightarrow 5KBr + KBrO_3 + 3H_2O$$

Bromide-bromate solution is evaporated to dryness. The residue is heated with charcoal:

$$2KBrO_3 + 3C \rightarrow 2KBr + 3CO_2$$

Potassium bromide also can be prepared by treating iron turnings with a 35 wt% aqueous solution of bromine. The product ferrosoferric bromide is boiled in potassium carbonate solution containing a slight excess of 15% potassium carbonate (Dancy, W.B. 1980. Potassium Compounds. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed. p. 963. New York: Wiley Interscience). The method does not involve bromate formation. The second step of the process may be represented in the following reaction:

$$Fe_3Br_8 \cdot 16H_2O + 4K_2CO_3 \rightarrow 8KBr + 4CO_2 + Fe_3O_4 + 16H_2O$$

Potassium bromide also can be produced by electrolytic process.

Analysis

Elemental composition: K 32.85%, Br 67.15%. Potassium can be determined in solid form by flame testing. In aqueous solution, potassium can be measured by flame photometry, ICP/AES or electrode methods. Bromide ion can be analyzed in aqueous solution by ion chromatography.

Toxicity

Potassium bromide ingested in large doses can cause CNS depression. Other symptoms of chronic intake are mental deterioration and an acne-type skin eruption.

POTASSIUM CARBONATE

[584–08–7]
Formula: K_2CO_3; MW 138.21
Synonyms: potash; pearl ash; salt of tartar

Occurrence and Uses

Potassium carbonate occurs in wood ashes. It is one of the first known salts of potassium and was used historically in recovering metalic potassium. The compound has numerous potential applicatons. However, in most cases the cheaper and equivalent sodium carbonate is used. An important application of potassium carbonate involves making specialty television glass. Other applicatons are in pottery; soaps and liquid shampoos; process engraving and lithography; to depress the freezing point of water in fire extinguishers for unheated warehouses; and in tanning and leather work. An important use of this compound is preparing several other potassium salts.

Physical Properties

Colorless monoclinic crystals or granular powder; hygroscopic; density 2.428 g/cm^3 at 20°C; melts at 891°C; decompses on further heating; very soluble in water 112 g/100mL at 20°C and more soluble in boiling water, 156 g/100mL at 100°C; aqueous solution strongly alkaline; insoluble in alcohol and acetone.

Thermochemical Properties

$\Delta H_f°$	–275.1 kcal/mol
$\Delta G_f°$	–254.2 kcal/mol
S°	37.17 cal/deg mol
C_ρ	27.35 cal/deg mol

Preparation

Potassium carbonate is produced most conveniently by passing carbon dioxide into an aqueous solution of caustic potash, evaporating the solution to obtain the bicarbonate, and heating the bicarbonate:

$$KOH + CO_2 \rightarrow KHCO_3$$

$$2KHCO_3 \rightarrow K_2CO_3 + CO_2\uparrow + H_2O\uparrow$$

The carbonate salt also can be prepared by heating potassium formate in air or oxygen:

$$2HCOOK + O_2 \rightarrow K_2CO_3 + CO_2\uparrow + H_2O\uparrow$$

Potassium formate obtained from purified producer gas (see Potassium Formate) is heated in a rotary furnace having free access to air.

At ordinary temperatures, the carbonate salt crystallized from water is obtained as a dihydrate, $K_2CO_3 \cdot 2H_2O$

The carbonate also can be made from potassium chloride, magnesium carbonate trihydrate and carbon dioxide under 30 atm at ordinary temperatures by Engel-Precht process:

$$2KCl + 3\ MgCO_3 \cdot 3H_2O + CO_2 \rightarrow 2KHCO_3 \cdot MgCO_3 \cdot 4H_2O + MgCl_2$$

The hydrated double salt on ignition decomposes giving potassium carbonate that may be extracted with water:

$$2KHCO_3 \cdot MgCO_3 \cdot 4H_2O \rightarrow K_2CO_3 + 2MgCO_3 + 9H_2O + CO_2$$

Small amounts of potassium carbonate were derived historically from leaching wood ash. The process is now obsolete.

Reactions

When carbon dioxide is passed into an aqueous solution of potassium carbonate, potassium bicarbonate is produced:

$$K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_3$$

Reactions with dilute acids evolve carbon dioxide:

$$K_2CO_3 + H_2SO_4 \rightarrow 2K^+ + SO_4^{2-} + CO_2\uparrow + H_2O$$

Potassium carbonate-carbon mixture reacts with ammonia at high temperatures to form potassium cyanide:

$$K_2CO_3 + 4C + 2NH_3 \rightarrow 2KCN + 3CO\uparrow + 3H_2\uparrow$$

Analysis

Elemental composition: K 56.58%, C 8.69%, O 34.73%. The salt can be identified from its physical and chemical properties. Its aqueous solution is highly alkaline. Reaction with dilute acids evolves CO_2 with effervescence. The latter can be identified by GC–TCD or GC/MS. The primary characteristic mass ion for CO_2 is 44. Also, CO_3^{2-} anion can be measured by ion chromatography. Potassium can be analyzed by various instrumental and wet methods (see Potassium).

POTASSIUM CHLORATE

[3811–04–9]
Formula: $KClO_3$; MW 122.50

Uses

Potassium chlorate is an oxidizing agent in matches, fireworks and explosives. The head of safety matches is coated with potassium chlorate which is struck on a surface consisting of red phosphorus, antimony(III) sulfide and an adhesive to light the fire. It also is used in laboratory preparation of oxygen. Its dilute aqueous solution is an antiseptic.

Physical Properties

Colorless crystals or white granular powder; monoclinic structure; density 2.32 g/cm^3; melts at 356°C; decomposes at 400°C; moderately soluble in cold water, 7.19 g/100mL at 20°C, solubility increasing with temperature, 57 g/100mL at 100°C; insoluble in acetone and liquid ammonia.

Thermochemical Properties

$\Delta H_f°$	–95.06 kcal/mol
$\Delta G_f°$	–70.82 kcal/mol
S°	34.2 cal/deg mol
C_ρ	24.0 cal/deg mol

Preparation

Potassium chlorate may be prepared by mixing concentrated solutions of sodium chlorate and potassium chloride. Potassium chlorate crystallizes when the solubility product $[K^+]\ [ClO_3^{2-}]$ is exceeded.

Potassium chlorate also can be prepared by passing chlorine gas into a hot solution of caustic potash:

$$3Cl_2(g) + 6KOH\ (aq) \rightarrow KClO_3\ (aq) + 5KCl\ (aq) + 3H_2O(l)$$

Reactions

Potassium chlorate decomposes on heating below its melting point and in the presence of a catalyst, forming potassium chloride and oxygen. The reaction is catalyzed by manganese dioxide and is used in laboratory preparation of oxygen:

$$2KClO_3 \xrightarrow{\text{heat + MnO}_2} 2KCl + 3O_2\uparrow$$

On heating (in the absence of a catalyst) potassium chlorate converts to potassium perchlorate:

$$4KClO_3 \rightarrow 3KClO_4 + KCl$$

Potassium chlorate is a strong oxidizing agent. In aqueous solution, it exhibits redox reactions of ionic ClO_3^-. Many are similar to potassium permanganate (see Potassium Permanganate).

Analysis

Elemental composition: K 31.91%, Cl 28.93%, O 39.17%. The salt is dissolved in water and the solution analyzed for potassium by AA, ICP, or other techniques. The ClO_3^- ion in solution may be identified by ion chromatography.

Toxicity

The salt is moderately toxic by ingestion and other routes causing irritation of the GI tract and kidney. Also, it can cause breakdown of red blood cells, producing methemoglobinemia.

POTASSIUM CHLORIDE

[7447–40–7]
Formula: KCl; MW 74.55

Occurrence and Uses

Several ores containing potassium chloride are found commonly in nature. The principle ores are sylvite, KCl; carnallite, $KCl{\cdot}MgCl_2{\cdot}6H_2O$; kainite, $KCl{\cdot}MgSO_4{\cdot}3H_2O$ and sylvinite, a naturally occuring mixture of sylvite and halite (common salt). Potassium chloride also is found in sea water at an average concentration of 0.076% (w/v).

Potassium chloride is the most important salt of potassium from the perspective of its abundant occurrence and applications. This salt, along with potassium sulfate, is used heavily in fertilizers as the primary source of potassium, an essential element for crops. Over 90% salt manufactured is consumed as fertilizer. Also, potassium chloride is a raw material for producing potassium metal and several important potassium salts including potassium nitrate, potassium hydroxide, and potassium sulfate. Other applications are in electrode cells; photography; buffer solutions and measurement of salinity in water.

Physical Properties

Colorless crystals or white crystalline solid; cubic structure; salty taste; density 1.984 g/cm^3; melts at 770°C; sublimes at 1,500°C; soluble in water 34.4 g/100mL at 20°C, 56.7 g/100mL at 100°C; soluble in ether, glycerol and alkalies; slightly soluble in alcohol.

Thermochemical Properties

$\Delta H_f°$	–104.4 kcal/mol
$\Delta G_f°$	–97.8 kcal/mol
S°	19.7 cal/deg mol
C_ρ	12.3 cal/deg mol

Production

Potassium chloride is produced by several processes. The salt is recovered from natural brine by solar evaporation in shallow ponds. Various methods are employed in mining ores from their natural deposits. Usually it is recovered from sylvinite or a naturally occuring complex mixture of langbeinite and kainite.

Refining potassium chloride is mostly by crystallization and froth flotation processes. Crystallization refining is based on great difference in solubility of potassium, sodium and magnesium chlorides. While potassium chloride at the boiling point of water is much more soluble than at ordinary temperatures, magnesium chloride, on the other hand, is highly soluble even at ordinary temperatures. In contrast, the solubility of sodium chloride varies slightly with temperature.

Fractional crystallization is carried out at temperatures from 30 to 100°C under various modifications of the solution at different stages.

Refining by flotation is more common, accounting for about 80% of potassium chloride produced in the USA. The process involves several steps: (1) ore crushing (2) removal of water-insoluble clays by scrubbing the ore with brine saturated with NaCl–KCl in agitated tanks, (3) hydraulic desliming, (4) reagent conditioning of ore flowing from the hydraulic desliming operations, using various depressants, such as, starch and polyacrylamides, (5) separation of amine-coated potassium chloride grains from sodium chloride by flotation caused by froths from tallow amines, (6) separation of product crystals from process brine by centrifugation, (7) product drying at high temperatures (about 175°C or above), and finally (8) sizing the product, separating different sized particles such as coarse, standard, and suspension-grade materials.

Analysis

Elemental composition: K 52.44%, Cl 47.56%. An aqueous solution of the salt can be analyzed conveniently for potassium by various wet methods or instrumental techniques (see Potassium). Chloride ion can be determined by ion chromatography or by titration with a standard solution of silver nitrate using potassium chromate indicator.

Toxicity

Ingestion of large doses can cause irritation of the gastrointestinal tract and nausea. Potassium chloride can stop the heart beat and is a component of lethal injections.

POTASSIUM CHROMATE

[7789–00–6]
Formula: K_2CrO_4; MW 194.20
Synonyms: neutral potassium chromate; potassium chromate(VI); tarapacaite

Uses

Potassium chromate is used in enamels; rustproof metals; and leather finishes. The compound also is an indicator in argentometric titrations.

Physical Properties

Lemon-yellow rhombohedral crystals; density 2.732 g/cm^3; melts at 968°C; very soluble in water , 63 g/100mL at 20°C; aqueous solution alkaline; insoluble in alcohol.

Thermochemical Properties

$\Delta H_f°$	–335.5 kcal/mol
$\Delta G_f°$	–309.7 kcal/mol
S°	47.8 cal/deg mol
C_ρ	34.9 cal/deg mol

Preparation

Potassium chromate can be made from chrome ore (chromite, $FeO \cdot Cr_2O_3$) that contains about 45% Cr_2O_3. The ore is crushed and mixed with potassium carbonate and roasted in air or oxygen at 1,100 to 1,250°C:

$$2Cr_2O_3 + 4K_2CO_3 \rightarrow 4K_2CrO_4 + 4CO_2$$

Potassium chromate also can be prepared by heating a mixture of pure potassium dichromate and potassium carbonate in a moist atmosphere. The salt is dried and purified by recrystallization.

Also, the compound may be obtained as an intermediate in the production of potassium dichromate. The product, however, contains trace amounts of potassium sulfate which is difficult to separate.

Analysis

Elemental composition: K 40.26%, Cr 26.78%, O 32.96%. An aqueous solution of the salt is analyzed for potassium and chronium (see Potassium and Chronium). Potassium chromate may be identified by its physical properties and by x-ray methods. Also, an aqueous solution of the salt forms a red precipitate of silver chromate when treated with a solution of silver nitrate. The chromate content may be determined stoichiometrically by weighing the dry precipitate.

POTASSIUM CYANIDE

[151–50–8]
Formula KCN; MW 65.12

Uses

Potassium cyanide is used in extracting gold, silver and platinum from their ores. It also is used in electroplating baths and in making other cyanide salts and complexes.

Physical Properties

Colorless cubic crystals or white granular powder; deliquescent; density 1.52 g/cm³; melts at 634.5°C; readily dissolves in water, 50 g/100mL at 20°C, 100 g/100mL in boiling water; moderately soluble in methanol 4.9 g/100mL at 20°C; soluble in glycerol.

Thermochemical Properties

ΔH_f° (cry)	–27.0 kcal/mol
ΔH_f° (gas)	21.7 kcal/mol
ΔG_f° (cry)	–24.35 kcal/mol
ΔG_f° (gas)	15.34 kcal/mol
S° (cry)	30.71 cal/deg mol
S° (gas)	62.57 cal/deg mol
C_r (cry)	15.84 cal/deg mol
C_ρ (gas)	12.51 cal/deg mol

Preparation

Potassium cyanide is prepared by heating a mixture of potassium carbonate and carbon with ammonia at high temperatures:

$$K_2CO_3 + 4C + 2NH_3 \rightarrow 2\ KCN + 3CO\uparrow + 3H_2\uparrow$$

Also, potassium cyanide can be made by reduction of potassium amide with carbon at red heat:

$$KNH_2 + C \rightarrow KCN + H_2\uparrow$$

A preparative method similar to the Castner process for the production of sodium cyanide involves adding red-hot charcoal slowly to molten potassium in a steel vessel. The mixture is heated to about 750°C and then ammonia is introduced gradually. The fused product is pumped to a filter furnace at high tempeature where the molten potassium cyanide is filtered in a nitrogen atmosphere. The overall reaction for the process is:

$$2K + 2C + 2NH_3 \rightarrow 2KCN + 3H_2$$

A convienient method of preparing potassium cyanide is to absorb hydrogen cyanide in 50% aqueous solution of potassium hydroxide followed by evaporation of the solution in a vacuum:

$$KOH + HCN \rightarrow KCN + H_2O$$

A mixture of sodium and potassium cyanides may be obtained by reduction of potassium ferrocyanide with sodium:

$$K_4Fe\ (CN)_6 + 2Na \rightarrow 4KCN + 2\ NaCN + Fe$$

Analysis

Elemental composition: K 60.05%, C 18.44%, N 21.51%. An aqueous solution of the salt is analyzed for potassium (see Potassium) and for CN^- by a cyanide ion-selective electrode. The solution must be diluted appropriately for measurement. Alternatively, CN^- may be titrated by the pyridine-barbituric acid colorimetric method (see Hydrogen Cyanide.)

Reactions

Reactions of potassium cyanide in aqueous solutions are essentially those of cyanide ion. A few reactions are highlighted below (molecular reactions are shown formally.)

The salt in aqueous solution oxidizes to cyanate when treated with sodium hypochlorite:

$$KCN + NaOCl \rightarrow KOCN + NaCl$$

Reaction with chlorine in alkaline medium also yields cyanate:

$$KCN + Cl_2 + 2KOH \rightarrow KOCN + 2KCl + H_2O$$

Reactions with acids liberate HCN:

$$KCN + HCl \rightarrow HCN + KCl$$

Reactions with copper sulfate or copper chloride form cyanogen and metallic copper:

$$2KCN + CuSO_4 \rightarrow K_2SO_4 + Cu + C_2N_2$$

Potassium cyanide is reduced by powdered metals, such as calcium, magnesium, and aluminum when heated in the absence of air:

$$2KCN + 3Ca \rightarrow 2K + 2C + Ca_3N_2$$

Potassium cyanide forms a number of complexes. For example, in aqueous solution it reacts with silver in the presence of air or oxygen to form a silver cyanide complex:

$$8KCN + 4Ag + 2H_2O + O_2 \rightarrow 4K[Ag(CN)_2] + 4KOH$$

When an aqueous solution of potassium cyanide is boiled with sulfur, potassium thiocyanate is produced:

$$KCN + S \rightarrow KSCN$$

Toxicity

Potassium cyanide is a dangerously toxic substance. Ingestion of 100 to 150 mg can cause collapse and cessation of breathing in humans. At lower doses, the acute effects are nausea, vomiting, headache, confusion and muscle weakness (Patnaik, P.1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. pp. 292-294. New York: John Wiley & Sons). Contact with acid can liberate highly toxic vapors of hydrogen cyanide. Sodium thiosulfate and sodium sulfate have shown antidotal activity to KCN toxicity.

Disposal and Destruction

Small amounts of KCN or effluents containing cyanide can be destroyed by treatment with chlorine or hypochlorite in alkaline solution.

POTASSIUM DICHROMATE

[7778–50–9]
Formula: $K_2Cr_2O_7$; MW 294.18
Synonyms: potassium bichromate; potassium dichromate(VI)

Uses

Potassium dichromate is a strong oxidizing agent. Many of its applications involve its oxidation action. The salt is used in pyrotechnics, safety matches, bleaching wax, palm oil, pigments, dyeing and painting, printing, photolithography, waterproofing fabrics, tanning leather, and inhibiting corrosion. Other uses are in electric batteries and as a depolarizer for dry cells. Potassium dichromate is an oxidizing agent in organic synthesis and in chromic cleaning mixture for laboratory glassware.

Physical Properties

Bright orange-red triclinic or monoclinic crystals; density 2.676 g/cm^3 at 25°C; triclinic form converts to monoclinic modification at 241.6°C; melts at 398°C; decomposes at 500°C; moderately soluble in cold water, 4.9 g/100mL at 0°C; very soluble in boiling water, 102 g/100mL at 100°C; aqueous solution acidic, a 10% solution has a pH 3.57; insoluble in alcohol.

Preparation

Potassium dichromate is obtained by reacting potassium chloride with sodium dichromate as a hot concentrated solution. The salt crystallizes when the solution is cooled:

$$2KCl + Na_2Cr_2O_7 \rightarrow K_2Cr_2O_7 + 2NaCl$$

As the least soluble of four salts, $K_2Cr_2O_7$ crystallizes first from solution.

Potassium dichromate also is produced from chrome ore. Ore is roasted with potassium carbonate or hydroxide to form potassium chromate:

$$2Cr_2O_3 + 4K_2CO_3 + 3O_2 \rightarrow 4\ K_2CrO_4 + 4CO_2$$

K_2CrO_4, upon heating in air or oxygen, converts to dichromate. In acid solution at low pH, chromate ion converts to dichromate:

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

Reactions

The dichromate ion, $Cr_2O_7^{2-}$ is a strong oxidizing agent in acid solution:

$$Cr_2O_7^{2-}\ (aq) + 14H^+\ (aq) + 6e^- \rightarrow 2Cr^{3+}\ (aq) + 7H_2O(l) \quad E^\circ = +1.33V$$

The yellow solution of chromate salt on acidification turns orange due to formation of dichromate ion. Both the ions are in equilibrium, sensitive to pH change:

$$\underset{\text{(yellow)}}{2CrO_4^{2-}\ (aq)} + 2H+\ (aq) \leftrightarrow \underset{\text{(orange)}}{Cr_2O_7^{2-}\ (aq)} + H_2O(l)$$

In aqueous solution, it undergoes many redox reactions. Some of these reactions are similar to those of permanganate ion; MnO_4^-.

When concentrated sulfuric acid is added, it precipitates red crystalline chromium(Vl) oxide, CrO_3:

$$[2K^+\ (aq) + Cr_2O_7^{2-}\ (aq)] + 2H_2SO_4(l) \rightarrow [2K^+(aq) + 2HSO_4^-\ (aq)] + 2CrO_3(s)\downarrow + H_2O\ (l)$$

When heated with carbon, potassium dichromate converts to chromium(III) oxide:

$$K_2Cr_2O_7\ (s) + 2\ C\ (s) \rightarrow Cr_2O_3\ (s) + Na_2CO_3(\ s) + CO\ (g)$$

Analysis

Elemental composition: K 26.58%, Cr 35.36%, and O 38.07%. Diluted aqueous solution is analyzed for the metals potassium and chromium (see Potassium and Chromium). Also, the salt can be identified from its color and other physical properties.

POTASSIUM FERRICYANIDE

[13746–66–2]
Formula: $K_3Fe(CN)_6$; MW 329.25
Synonyms: potassium hexacyanoferrate(III); tripotassium hexakis(cyano-C)ferrate(3–); red prussiate of potash

Uses

Potassium ferricyanide is used to make pigments, as a coloring agent for blueprints, in calico printing, for dyeing wool, for staining wood, and as an etching liquid. It also is used in electroplating and for tempering iron and steel. The compound also is a mild oxidizing agent and finds limited use in preparing certain organics. In analytical chemistry it is used for standardization of sodium thiosulfate solution.

Physical Properties

Bright red lustrous crystals; density 1.89 g/cm^3; decomposes on heating; soluble in water, ~40 g/100mL at 20°C ; decomposes slowly on standing; slightly soluble in alcohol; soluble in acids with decomposition

Preparation

Potassium ferricyanide is prepared by oxidation of potassium ferrocyanide, $K_4Fe(CN)_6$. Thus, when chlorine is passed through an aqueous solution of potassium ferrocyanide, the ferricyanide separates as crystals.

Analysis

Elemental composition: K 35.62%, Fe 16.96%, C 21.89%, N 25.53%. An aqueous solution of the salt may be analyzed for potassium and iron by various instrumental methods (see Iron, and Potassium Analysis). Its concentration in aqueous solution may be measured by adding excess potassium iodide to an acidified solution and titrating the iodine liberated with a standard solution of sodium thiosulfate using starch indicator.

POTASSIUM FERROCYANIDE

[13943–58–3]
Formula: $K_4Fe(CN)_6$; MW 368.34; exists as trihydrate, $K_4Fe(CN)_6 \cdot 3H_2O$ [14459–95–1] having a molecular weight 422.39
Synonyms: potassium hexacyanoferrate(II); tetrapotassium hexakis(cyano-C)ferrate(4–); yellow prussiate of potash

Physical Properties

The trihydrate is a yellow monoclinic crystalline complex salt; density 1.85 g/cm^3; begins to lose water at 60°C; becomes anhydrous at 100°C; soluble in water, insoluble in ethanol and ether

Preparation

Potassium ferrocyanide may be prepared by the action of potassium cyanide with ferrous sulfate solution:

$$6KCN + FeSO_4 \rightarrow K_4Fe(CN)_6 + 2K^+ + SO_4^{2-}$$

The complex also may be obtained by reduction of potassium ferricyanide, $K_3Fe(CN)_6$, with a suitable reducing agent, such as sodium oxalate, $Na_2C_2O_4$, or sodium thiosulfate, $Na_2S_2O_3$.

Analysis

Elemental composition: K 42.46%, Fe 15.16%, C 19.56%, N 22.82%. An aqueous solution may be analyzed for potassium and iron by various instrumental means (see Potassium and Iron, Analysis).

POTASSIUM FLUORIDE

[7789–23–3]
Formula KF; MW 58.10

Uses

Potassium fluoride is a fluorinating agent in organic synthesis. Other applications are in making insecticide formulations, as an additive to flux for making hard solder, and to control fermentation.

Physical Properties

Colorless cubic crystals or white deliquesce powder or solid; density 2.48 g/cm^3; melts at 858°C; vaporizes at 1,505°C; soluble in water, 92 g/100mL at 18°C, very soluble in hot water; soluble in hydrofluoric acid; insoluble in alcohol.

Thermochemical Properties

$\Delta H_f°$	–135.6 kcal/mol
$\Delta G_f°$	–128.5 kcal/mol
S°	15.9 cal/deg mol
C_ρ	11.7 cal/deg mol

Preparation

Potassium fluoride is prepared by dissolving potassium carbonate in excess hydrofluoric acid. Evaporation of the solution forms crystals of potassium bifluoride. The bifluoride on heating yields potassium fluoride:

$$K_2CO_3 + 4HF \rightarrow 2KHF_2 + CO_2\uparrow + H_2O$$

$$KHF_2 \rightarrow KF + HF\uparrow$$

The salt must not be prepared in glass or porcelain vessels as HF and the aqueous solution of KF corrode glass and porcelain. Heat resistant plastic containers may be used.

Analysis

Elemental composition: K 67.30%, F 32.70%. The aqueous solution may be analyzed for potassium by various methods (see Potassium.) and for fluoride by fluoride ion selective electrodes or ion chromatography.

Toxicity

Potassium fluoride is moderately toxic by ingestion. The oral LD_{50} in guinea pigs is 250 mg/kg.

POTASSIUM FORMATE

[590–29–4]
Formula: HCOOK; MW 84.12

Use

Potassium formate is used to prepare potassium oxalate simply by heating at 360°C.

Physical Properties

Colorless rhombohedral crystals or deliquesc granules; density 1.91 g/cm^3; melts at 167.5°C; decomposes on further heating; highly soluble in water, 331 g/100mL at 18°C, much greater solubility in hot water, 657 g/100mL at 80°C; soluble in alcohol; insoluble in ether.

Thermochemical Properties

$\Delta H_f°$	–126.5 kcal/mol

Preparation

Potassium formate is produced slowly by absorption of carbon monoxide by 50 to 80 wt% aqueous solution of potassium hydroxide at 100 to 200°C and a CO partial pressure over 7 atm.

$$CO + KOH \rightarrow HCOOK$$

Potassium formate also can be made by passing pure carbon monoxide or purified producer gas (sometimes called blow gas) containing about 30% carbon monoxide under pressure through a hot solution of potassium sulfate and milk of lime:

$$K_2SO_4 + Ca(OH)_2 + 2CO \rightarrow 2HCOOK + CaSO_4$$

The solution is filtered to remove calcium sulfate.

Analysis

Elemental composition: K 46.48%, C 14.28%, H 1.20%, O 38.04%. The aqueous solution is analyzed for potassium by various methods (see Potassium). The salt is heated at 360°C and converted to oxalate. The oxalate formed may be dissolved in water and the solution may be measured quantitatively for oxalate by redox titration.

POTASSIUM HYDRIDE

[7693–26–7]
Formula: KH; MW 40.11

Uses

Potassium hydride is a reducing agent.

Physical Properties

White needle; density 1.47 g/cm^3; decomposes to its elements on heating; reacts violently with water, evolving hydrogen; insoluble in benzene, ether, and carbon disulfide.

Thermochemical Properties

$\Delta H_f°$	–13.80 kcal/mol

Preparation

Potassium hydride is prepared by passing hydrogen over potassium at high temperature:

$$2K + H_2 \rightarrow 2KH$$

Alternatively, the hydride may be made by passing hydrogen into molten potassium dispersed in oil.

Analysis

Elemental composition: K 97.48%, H 2.52%. The hydride may be decomposed cautiously in water in small amounts (the reaction is violent) and the solution analyzed for potassium (see Potassium). Hydrogen may be identified by its combustion (see Hydrogen).

POTASSIUM HYDROGEN PHTHALATE

[877–24–7]
Formula: $C_8H_5KO_4$; MW 204.22;
Structure: $HOOCC_6H_4COOK$
Synonyms: potassium biphthalate; potassium acid phthalate; acid potassium phtalate; phthalic acid potassium acid salt; KHP

Uses

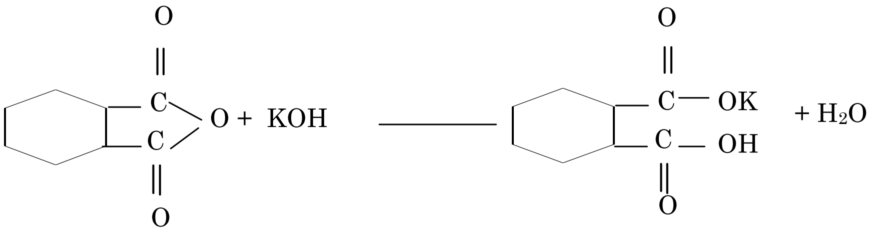
Potassium hydrogen phthalate has many uses in analytical chemistry. It is a primary standard for standardization of bases in aqueous solutions. Its equivalent weight is 204.2. It also is a primary standard for acids in anhydrous acetic acid. Other applications are as a buffer in pH determinations and as a reference standard for chemical oxygen demand (COD). The theoretical COD of a 1mg/L potassium hydrogen phthalate is 1.176mg O_2.

Physical Properties

White orthorhombic crystals; stable in air; density 1.636 g/cm^3 at 25°C; soluble in water, about 8.3g /100mL at 20°C and 33 g/100mL in boiling water; pH of 0.05M aqueous solution 4.005 at 25°C; slightly soluble in ethanol.

Preparation

Potassium hydrogen phthalate is prepared by neutralization reaction of phthalic anhydride and potassium hydroxide, followed by crystallization:



Alternatively, it is preparaed by half neutralization of phthalic acid with potassium hydroxide:

$$C_6H_4(COOH)_2 + KOH \rightarrow HOOCC_6H_4COOK + H_2O$$

Reactions

Aqueous solutions of potassium hydrogen phthalate, when refluxed with a powerful oxidizing agent such as potassium dichromate–sulfuric acid mixture, completely decompose, forming various products. Under closed refluxing conditions, $K_2Cr_2O_7$ provides all the oxygen required for the oxidation. (Patnaik, P 1997. *Handbook of Environmental Analysis*, pp.197. Boca Raton, FL: CRC Press) The reactions under closed and open refluxing conditions are:

$$2HOOCC_6H_4COOK + 10K_2Cr_2O_7 + 41H_2SO_4$$

$$\rightarrow 16\ CO_2 + 46H_2O + 11K_2SO_4 + 10Cr_2(SO_4)_3$$

$$2\ HOOCC_6H_4COOK + 15O_2 \rightarrow 16CO_2 + 4H_2O + 2KOH$$

Potassium hydrogen phthalate undergoes neutralization with alkalies:

$$HOOCC_6H_4COOK + KOH \rightarrow C_6H_4(COOK)_2 + H_2O$$

The theoretical COD for 100 mg phthalate is 117.5 mg O_2

Analysis

Elemental composition: K 30.51%, C18.75%, H 0.79%; O 49.95%. An aqueous solution of potassium hydrogen phthalate may be measured by titration against a standard solution of potassium hydroxide.

POTASSIUM HYDROXIDE

[1310–58–3]
Formula KOH; MW 56.11
Synonyms: caustic potash; potassa; potassium hydrate

Uses

Potassium hydroxide is used to make soft soap, in scrubbing and cleaning operations, as a mordant for woods, in dyes and colorants, and for absorbing carbon dioxide. Other principle uses of caustic potash are in the preparation of several potassium salts, acid-base titrations, and in orgainic sytheses. Also, KOH is an electrolyte in certain alkaline storage batteries and fuel cells.

Physical Properties

White rhombohedral deliquescent crystal; density 2.044 g/cm^3; melts at 360°C; vaporizes around 1,320°C; highly soluble in water, 107 g/100mL at 15°C and 178 g/100mL at 100°C; aqueous solution highly alkaline, pH of 0.1M solution is 13.5; soluble in alcohol and glycerol; insoluble in ether and liquid ammonia.

Thermochemical Properties

$\Delta H_f°$	–101.52 kcal/mol
$\Delta G_f°$	–90.61 kcal/mol
S°	15.51 cal/deg mol
C_ρ	18.85 cal/deg mol
ΔH_{soln}	–13.8 kcal/mol

Production

Potassium hydroxide is produced commerically by electrolysis of a saturated solution of potassium chloride in brine using mercury cells consisting of a titanium anode and mercury cathode. Potassium reacts with mercury forming the amalgam which, on treatment with water, forms potassium hydroxide and hydrogen.

Other types of electrolytic cells, although not so commonly used today, are also known. In a diaphragm type cell that separates the cell into anode and cathode compartments, an aqueous solution of potassium chloride is electrolyzed. Potassium hydroxide and hydrogen are produced at the cathode and chlorine is liberated at the anode. The solution discharged from the cell is evaporated to concentrate potassium hydroxide and precipitate potassium chloride.

Potassium hydroxide also may be made by reacting potassium superoxide with water:

$$2KO_2 + 2H_2O \rightarrow 2KOH + H_2O_2 + O_2$$

Reactions

Potassium hydroxide is a very strong base, more basic than caustic soda. It is neutralized by acids. The solution on evaporation yields the corresponding potassium salt:

$$KOH + HCl \rightarrow K^+ + Cl^- + H_2O$$

Action of bromine or iodine on a warm concentrated solution of KOH forms bromate and bromide or iodate and iodide, respectively:

$$3Br_2 + 6OH^- \rightarrow BrO_3^- + 5Br^- + 3H_2O$$

$$3I_2 + 6OH^- \rightarrow IO_3^- + 5I^- + 3H_2O$$

When carbon dioxide is passed through its aqueous solution and the solution evaporated, potassium bicarbonate is formed:

$$KOH + CO_2 \rightarrow KHCO_3$$

Reaction with carbon monoxide at 100 to 200°C at a CO pressure above 7 atm yields potassium formate:

$$KOH + CO \rightarrow HCOOK$$

Reaction with phenol in dilute methanol solution forms potassium phenoxide:

$$KOH + C_6H_5OH \rightarrow C_6H_5OK + H_2O$$

Reaction with boric acid and hydrofluoric acid forms potassium tetrafluoroborate, KBF_4:

$$KOH + H_3BO_3 + 4HF \rightarrow KBF_4 + 4H_2O$$

An alcoholic solution of potassium hydroxide reacts with an alcoholic solution of carbon disulfide to form potassium ethylxanthogenate, $C_2H_5OCS_2K$

$$KOH + C_2H_5OH + CS_2 \rightarrow C_2H_5OCS_2K + H_2O$$

Reaction with sodium borohydride forms potassium borohydride:

$$KOH + NaBH_4 \rightarrow KBH_4 + NaOH$$

Reaction with hydrofluoric acid forms potassium bifluoride:

$$KOH + 2HF \rightarrow KHF_2 + H_2O$$

Half neutralization of a phthalic anhydride solution forms potassium hydrogen phthalate.

Analysis

The normality of KOH in its aqueous solution can be determined by acid-base titration against a standard solution of HCl, H_2SO_4, or HNO_3 using a color indicator or by a pH meter. Potassium can be identified by flame test or by wet methods or instrumental analysis (see Potassium).

POTASSIUM IODATE

[7758–05–6]
Formula: KIO_3; MW 214.00

Uses

Potassium iodate is an oxiding agent in volumetric analysis. It releases iodine in KIO_3–KI solutions for iodometric titrations. It also is a topical antiseptic; and an additive to food to provide nutrient iodine.

Physical Properties

Colorless crystals or white powder; monoclinic structure; density 3.90 g/cm^3; stable at ordinary temperatures; melts at 560°C with partial decomposition, releasing oxygen; moderately soluble in cold water; 4.74 g/100mL at 0°C; greater solubility in boiling water 32.3 g/100mL at 100°C; soluble in potassium iodide solution; insoluble in alcohol and liquid ammonia

Thermochemical Properties

$\Delta H_f°$	–119.8 kcal/mol
$\Delta G_f°$	–100.0 kcal/mol
S°	36.2 cal/deg mol
C_ρ	25.4 cal/deg mol

Preparation

Potassium iodate can be produced by fusing potassium iodide with potassium chlorate, bromate or perchlorate:

$$KI + KClO_3 \rightarrow KIO_3 + KCl$$

The melt is extracted with water and potassium iodate is isolated from solution by crystallization.

Analysis

Elemental composition: K 18.27%, I 59.30%, and O 22.43%. An aqueous solution may be analyzed for potassium (see Potassium) and for IO_3^- by ion chromatography. The iodate, IO_3^- content can be measured by iodometric titration:

$$IO_3^- + 6H^+ + 5I^- \text{ (excess)} \rightarrow 3I_2 + 3H_2O$$

In strong acid solution IO_3^- oxidizes I^- liberating iodine, which can be titrated against a standard solution of sodium thiosulfate. At the end point, the blue solution decolorizes.

POTASSIUM IODIDE

[7681–11–0]
Formula: KI; MW 166.00

Occurrence and Uses

Potassium iodide is found in seaweed. Some important applications of this compound involve its use in pharmaceuticals and as a source of iodine in food, especially in animal and poultry feed. Potassium iodide is added to table salt to provide iodine in human food.

Another major use is in making photographic emulsions. In analytical chemistry, potassium iodide is used in iodometric titration with starch indicator to analyze dissolved oxygen, dissolved chlorine, sulfide, and other analytes in water.

Physical Properties

Colorless or white cubic crystals or granules; becomes yellowish when exposed to bright light due to photochemical decomposition liberating traces of free iodine; density 3.13 g/cm³; melts at 681°C; vaporizes at 1,330°C; highly soluble in water, ~140 g/100mL at 20°C; aqueous solution readily dissolves iodine; sparingly soluble in ethanol (about 2 g/100mL at 25°C) and acetone; slightly soluble in ether and ammonia.

Thermochemical Properties

$\Delta H_f°$	–78.37 kcal/mol
$\Delta G_f°$	–77.65 kcal/mol
S°	25.4 cal/deg mol
C_ρ	12.65 cal/deg mol

Preparation

Potassium iodide is made by absorption of iodine in potassium hydroxide:

$$3I_2 + 6KOH \rightarrow 5KI + KIO_3 + 3H_2O$$

Most potassium iodate, KIO_3 , is separated from the product mixture by crystallization and filtration. Remaining iodates are removed by evaporation of the solution and other processes, such as carbon reduction or thermal decompostion at 600ºC to iodide:

$$2KIO_3 \rightarrow 2KI + 3O_2$$

Another method of preparation that does not involve the formation of iodate is by treating iron turnings with iodine solution. The product, ferrosoferric iodide, $Fe_3I_8 \cdot 16H_2O$, is boiled with 15 wt% potassium carbonate solution:

$$Fe_3I_8 \cdot 16H_2O + 4K_2CO_3 \rightarrow 8\ KI + 4CO_2 + Fe_3O_4 + 16H_2O$$

A similar method is used to prepare potassium bromide, discussed earlier (see Potassium Bromide.)

Potassium iodide can be prepared by reacting hydriodic acid with potassium bicarbonate:

$$HI + KHCO_3 \rightarrow KI + CO_2 + H_2O$$

It is purified by melting in dry hydrogen.

Potassium iodide also may be obtained by various electrolytic processes.

Reactions

The reactions of potassium iodide in aqueous solutions are those of iodide ion, I^-. In iodometric titration I^- combines with iodine to form triiodide ion, I_3^-. The latter adds to β–amylose fraction of the starch to form a blue complex.

Potassium iodide dissolves iodide of certain metals to form complex anions:

$$HgI_2 + 2I^- \rightarrow [HgI_4]^{2-}$$

Analysis

Elemental composition: K 23.55%, I 76.45%. Potassium may be measured by various instrumental methods (see Potassium). Iodide ion in an aqueous solution can be measured by ion chromatography or leuco crystal violet colorimetric method (see Iodine).

POTASSIUM NITRATE

[7757–79–1]
Formula KNO_3; MW 101.10
Synonyms: saltpeter; niter

Uses

Potassium nitrate is used in explosives, blasting powders, gunpowder, matches, and fireworks. Other applications of this salt include pickling meats; tempering steel; impregnating candle wicks; freezing mixtures; preparing other potassium salts; and as a diuretic.

Physical Properties

Colorless transparent crystals or white granular or crystalline powder; rhombohedral structure; density 2.11 g/cm^3 at 20°C; melts at 334°C; decomposes at 400°C evolving oxygen; soluble in cold water, 13.3 g/100mL at 0°C; highly soluble in boiling water, 247 g/100mL at 100°C; lowers the temperature of water on dissolution; very slightly soluble in ethanol; soluble in glycerol and liquid ammonia.

Thermochemical Properties

$\Delta H_f°$	–118.22 kcal/mol
$\Delta G_f°$	–94.39 kcal/mol
C_ρ	31.80 cal/deg mol
S°	23.04 cal/deg mol

Production

Potassium nitrate may be produced by several methods. It is made commercially by reacting potassium chloride with nitric acid at high temperature. Nitrosyl chloride, a product obtained in the reaction, is converted into chlorine in this manufacturing process. Also, nitric acid is partly recycled in the process. The reactions are (Dancy, W.B. 1981. Potassium Compounds. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd. ed. Pp. 939-42. New York: Wiley Interscience):

$$3KCl + 4HNO_3 \rightarrow 3KNO_3 + Cl_2 + NOCl + 2H_2O$$

$$2NOCl + 4HNO_3 \rightarrow 6NO_2 + Cl_2 + 2H_2O$$

$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$$

Potassium nitrate also can be prepared by mixing a hot saturated solution of potassium chloride and sodium nitrate. The reaction is:

$$K^+ + Cl^- + Na^+ + NO_3^- \rightarrow NaCl\downarrow + K^+ + NO_3^-$$

Sodium chloride is less soluble than KCl, $NaNO_3$ and KNO_3. It separates out by crystallization. The remaining solution is cooled to ambient temperature. Potassium nitrate crystallizes out.

Analysis

The aqueous solution may be analyzed for potassium by various instrumental and wet methods (see Potassium) and for nitrate ion by ion chromatography or electrode method.

POTASSIUM NITRITE

[7758–09–0]
Formula: KNO_2; MW 85.10

Uses

Potassium nitrite is an antidote to cyanide poisoning. It also is a vasodilator. An important application is in the dye industry to prepare diazonium salts and azo dyes. Another use is in curing certain meat products where the salt imparts an appetizing pink color to cured meats and retards microbial growth on the meat. The commerical product is usually a nitrite-nitrate mixture, containing 85% KNO_2 and 15% KNO_3

Physical Properties

White or slight yellow prismatic granules; deliquesc; density 1.915 g/cm^3; melts at 440°C; decomposition starts at 350°C; very soluble in water, 281 g/100mL at 0°C; much more soluble in boiling water, 413 g/100mL at 100°C; aqueous solution is alkaline; slightly soluble in cold alcohol but moderately solublel in hot alcohol; very soluble in liquid ammonia; decomposes in acids, liberating brown NO_2 fumes.

Thermochemical Properties

$\Delta H_f°$	–88.39 kcal/mol
$\Delta G_f°$	–73.28 kcal/mol
S°	36.35 cal/deg mol
C_ρ	25.67 cal/deg mol

Preparation

Potassium nitrite may be prepared by fusion of nitrate with lead:

$$KNO_3 + Pb \rightarrow KNO_2 + PbO$$

The product is extracted with water and allowed to crystallize. Filtration separates nitrite from insoluble lead oxide.

Potassium nitrite also may be obtained by high temperature thermal decomposition of nitrate:

$$2KNO_3 \rightarrow 2KNO_2 + O_2\uparrow$$

Analysis

Elemental composition: K 45.94%, N 16.46%, O 37.60%. An aqueous solution of the salt may be analyzed for potassium (see Potassium). The nitrite ion may be measured by colorimetric methods. The NO_2^- is diazotized with sulfanilamide and coupled with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye. The absorbance or transmittance of the solution can be measured at 543 nm or 540 nm using a spectrophotometer or a filter photometer. Nitrite anion in the presence of nitrate can be best measured by ion chromatography using a low capacity strongly basic anion exchange separator column.

POTASSIUM OXALATE

[127–96–8]
Formula $K_2C_2O_4$; MW 166.22; forms a stable monohydrate, $K_2C_2O_4 \cdot H_2O$, MW 184.23 [6487–48–5]

Occurrence and Uses

Potassium oxalate, along with calcium oxalate, is found in leaves and roots of certain plants. It is used for cleaning and bleaching straw and for removing stains. It also is used in photography, in clinical tests, as a secondary pH standard, and in wet chemical analysis. The analytical application involves standardization of many oxidizing agents in titrimetric analysis.

Physical Properties

The monohydrate is a white crystalline solid; monoclinic structure; density 2.13 g/cm^3; loses its water at about 160°C; converts to carbonate when ignited; effloresces in warm dry air; soluble in water, 33 g/100 mL at 20°C; a 0.05m solution of $K_2C_2O_4 \cdot 2H_2O$ has a pH 1.679.

Thermochemical Properties

$\Delta H_f°$ –321.9 kcal/mol

Preparation

Potassium oxalate can be preparaed by heating potassium formate at 360°C:

$$2HCOOK \rightarrow K_2C_2O_4 + H_2$$

The salt is obtained as its monohydrate by neutralization of oxalic acid with a dilute aqueous solution of potassium hydroxide followed by crystallization:

$$H_2C_2O_4 + 2KOH \rightarrow K_2C_2O_4 + 2H_2O$$

Analysis

Elemental composition (for anhydrous $K_2C_2O_4$): K 47.05%, C 14.45%, O 38.50%. The water content of the monohydrate, $K_2C_2O_4 \cdot H_2O$ is 9.78%, which may be measured by thermogravimetric analysis. Potassium may be analyzed by AA, flame photometry or ICP/AES (see Potassium). The concentration of oxalate in the aqueous solution of the salt may be determined by titrating against a standard solution of potassium bromate in the presence of excess potassium bromide.

Toxicity

Ingestion can cause irritation of the GI tract, shock and cardiac arrhythmias.

POTASSIUM PERCARBONATE

[589–97–9]
Formula $K_2C_2O_6$; MW 198.22; stable as a monohydrate, $K_2C_2O_6 \cdot H_2O$; MW 216.23
Synonyms: potassium peroxydicarbonate; potassium perdicarbonate; peroxydicarbonic acid dipotassium salt.

Uses

Potassium percarbonate is used in photography under the name "Antihypo" for removing the last traces of thiosulfate from film and paper. It is a strong oxidizing agent in certain chemical analysis; and in microscopic identification of *tubercle bacilli*.

Physical Properties

The monohydrate consists of a white granular mass; starts melting above 200°C; soluble in water, about 15 g/100mL at 20°C; decomposes in boiling water, evolving oxygen.

Preparation

Potassium percarbonate can be prepared by electrolysis of potassium carbonate, K_2CO_3.

Analysis

Elemental composition: K 39.45%, C 12.12%, O 48.43%. An aqueous solution is analyzed for potassium. The solution is boiled and evolved oxygen is identified by its inflaming a glowing splinter. Also, evolved oxygen may be introduced into a stream of carrier gas, helium, and analyzed by GC or GC/MS. The characteristic mass for its identification by GC/MS is 32.

POTASSIUM PERCHLORATE

[7778–74–7]
Formula $KClO_4$; MW 138.55
Synonym: peroidin

Uses

Potassium perchlorate is used in explosives and pyrotechnics. It also is used in photography.

Physical Properties

Colorless crystals or white crystalline powder; rhombohedral structure; density 2.52 g/cm^3; melts around 610°C under controlled conditions; decomposes at 400°C; slightly soluble in cold water 0.75 g/100mL at 0°C, soluble in boiling water, 21.8 g/100mL at 100°C; practically insoluble in alcohol; insoluble in ether.

Thermochemical Properties

$\Delta H_f°$	–103.43 kcal/mol
$\Delta G_f°$	–72.46 kcal/mol
S°	36.1 cal/deg mol
C_ρ	26.9 cal/deg mol

Preparation

Potassium perchlorate is prepared from potassium chlorate. Potassium chlorate, on heating, melts first and then resolidifies to potassium perchlorate:

$$4KClO_3 \rightarrow 3KClO_4 + KCl$$

Potassium perchlorate is produced commercially by electrolysis of a saturated solution of potassium chlorate. Hydrogen gas is liberated at the cathode. The reaction at the anode is:

$$ClO_3^- \text{ (aq)} + H_2O \text{ (l)} \rightarrow ClO_4^- \text{ (aq)} + 2H^+ \text{ (aq)} + 2e^-$$

Reactions

On strong heating, potassium perchlorate decomposes to potassium chloride and oxygen:

$$KClO_4 \rightarrow KCl + 2O_2$$

The salt, on treatment with sulfuric acid, yields potassium bisulfate and perchloric acid:

$$KClO_4 \text{ (s)} + H_2SO_4 \text{ (l)} \rightarrow KHSO_4 \text{ (s)} + HClO_4\text{(l)}$$

In aqueous solution the reactions of potassium perchlorate are those of the ClO_4^- ion.

It is an oxidizing agent and undergoes redox reactions with reducing agents. Its oxidizing action, however, is weaker to that of potassium chlorate. Thus the salt is unable to oxidize the iodide ion to iodine in acid medium.

Analysis

Elemental composition: K 28.22%, Cl 25.59%, and O 46.19%. An aqueous solution is analyzed for potassium by AA, ICP, and other methods (see Potassium). Perchlorate ion may be analyzed by ion chromatography or a liquid–membrane electrode. Iodide, bromide, chlorate, and cyanide ions interfere in the electrode measurement. Alternatively, perchlorate ion may be measured by redox titration. Its solution in 0.5M H_2SO_4 is treated with a measured excess standard ferrous ammonium sulfate. The excess iron(II) solution is immediately titrated with a standard solution of potassium dichromate. Diphenylamine sulfuric acid may be used as an indicator to detect the end point:

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

POTASSIUM PERIODATE

[7790–21–8]
Formula: KIO_4; MW 230.00
Synonym: potassium metaperiodate

Uses

Potassium periodate is a powerful oxidizing agent in acid. It is, therefore, used as an oxidizing agent in organic synthesis and in titrimetric and colorimetric analysis based on its oxidation-reduction reactions.

Physical Properties

Colorless tetragonal crystals; density 3.618 g/cm^3; melts at 582°C; slightly soluble in water at ordinary temperatures, 0.42 g/100mL at 20°C; moderately soluble in hot water, 4.4 g/100mL at 80°C.

Thermochemical Properties

$\Delta H_f°$	–111.7 kcal/mol
$\Delta G_f°$	–86.4 kcal/mol
S°	42.0 cal/deg mol

Preparation

Potassium periodate can be prepared by oxidation of potassium iodate with a powerful oxidizing agent such as potassium permanganate, chlorine or bromine in basic solution:

$$IO_3^- + Cl_2 + 2OH^- \rightarrow IO_4^- + 2Cl^- + H_2O$$

Also, the salt may be prepared by electrolysis.

Analysis

Elemental composition: K 17.00, I 55.18%, and O 27.82%. An aqueous solution of potassium periodate is analyzed for potassium by AA, ICP, and other methods (see Potassium) and for periodate ion by ion chromatography. Alternatively, the solution is buffered with sodium bicarbonate, made slightly alkaline, and then treated with excess potassium iodide. The liberated iodine is titrated with a standard solution of sodium thiosulfate or sodium arsenite using starch indicator.

POTASSIUM PERMANGANATE

[7722–64–7]
Formula: $KMnO_4$; MW 158.03
Synonyms: permanganic acid potassium salt; chameleon mineral

Uses

Potassium permanganate is widely used as an oxidizing agent in analytical chemistry and in organic synthesis. The salt is a disinfectant in water purification. Other important applications are in bleaching a variety of materials including cotton, silk, and other fibers, fats, oils, resins, and waxes. Miscellaneous applications are in printing fabrics, tanning leathers, and photography.

Physical Properties

Dark purple rhombohedral crystal; density 2.703 g/cm^3; stable in air; decomposes at about 240°C; moderately soluble in cold water, 6.38 g/100mL at 20°C, soluble in hot water, 25 g/100mL at 65°C; decomposed by alcohol, acetone and many organic solvents causing their oxidation; also decomposed by concentrated acids.

Thermochemical Properties

$\Delta H_f°$	–200.1 kcal/mol
$\Delta G_f°$	–176.3 kcal/mol
S°	41.0 cal/deg mol
C_ρ	28.1 cal/ deg mol

Reactions

Potassium permanganate is a powerful oxidizing agent. In acid medium its oxidizing ability may be attributed to its high redox potential E° which is +1.51 V for the reaction:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O.$$

In basic solution, the redox potential for the half reaction, $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$, is + 0.60V.

All reactions of potassium permanganate in aqueous solutions are essentially those of the MnO_4^- ion. Some examples are:

In acid solution it readily oxidizes Fe^{2+} to Fe^{3+}:

$$MnO_4^- (aq) + 5Fe^{2+} (aq) + 8H^+ (aq) \rightarrow Mn^{2+} (aq) + 5Fe^{3+} (aq) + 4H_2O (l)$$

The purple color of MnO_4^- disappears when it is reduced to Mn^{2+}.

Permanganate ion oxidizes chloride ion in acid solution to chlorine gas. The net ionic equation is:

$$2MnO_4^- (aq) + 16H^+ (aq) + 10Cl^- (aq) \rightarrow 2Mn^{2+} (aq) + 5Cl_2 (g) + 8H_2O (l)$$

In basic solution MnO_4^- oxidizes sulfide to sulfate:

$$2MnO_4^- (aq) + 3SO_3{}^{2-} (aq) + H_2O (l) \rightarrow 2MnO_2 (s) + 3SO_4{}^{2-} (aq) + 2OH^- (aq)$$

and iodide to iodate:

$$2MnO_4^- (aq) + I^- (aq) + H_2O(l) \rightarrow IO_3^- (aq) + 2MnO_2(s) + 2OH^- (aq)$$

In basic solution, MnO_4^- oxidizes glycerol to carbonate. The net ionic equation and formal molecular reaction are:

$$14MnO_4^- + 20\ OH^- + C_3H_8O_3 (aq) \rightarrow 14MnO_4{}^{2-} + 3CO_3{}^{2-} + 14H_2O(l)$$

$$14KMnO_4 + 20\ KOH + C_3H_8O_3 (aq) \rightarrow 14K_2MnO_4 + 3K_2CO_3 + 14H_2O (l)$$

Potassium permanganate reacts with hydrogen peroxide in dilute sulfuric acid to form manganous sulfate, potassium sulfate, and evolving oxygen. A molecular equation for this reaction is:

$$2KMnO_4 (aq) + 5H_2O_2 (aq) + 3H_2SO_4 (aq) \rightarrow$$
$$2MnSO_4 (aq) + K_2SO_4 (aq) + 5O_2 (g) + 8H_2O (l)$$

Potassium permanganate oxidizes oxalic acid evolving carbon dioxide. This reaction is often used to standardize $KMnO_4$ solutions. A molecular equation is:

$$2KMnO_4 (aq) + 5H_2C_2O_4(aq) + 3H_2SO_4 (aq) \rightarrow$$
$$2MnSO_4(aq) + K_2SO_4 (aq) + 10CO_2(g) + 8H_2O(l)$$

Preparation

Potassium permanganate is produced from manganese ore containing at least 60% manganese dioxide, MnO_2. The finely ground ore is mixed with 50% potassium hydroxide and heated at about 350°C in rotary kilns. This converts manganese dioxide to potassium manganate:

$$MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

Potassium manganate obtained above is oxidized to the permanganate either by electrolysis or by chemical oxidation. Electrolytic oxidation is more common. Electrolytic cells have cathodes made of iron rods and nickel–plated anodes. Potassium manganate melt is extracted with water prior to its electrolysis and then electrolyzed at a cell voltage of 2.3V and current of about 1,400 amp. Permanganate is produced at the anode and water is reduced to gaseous hydrogen and hydroxyl ions at the cathode:

$$2K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + 2KOH + H_2$$

Analysis

Elemental composition: K 24.74%, Mn 34.76%, O 40.50%. The compound may be identified by its dark purple color and other physical properties, and confirmed by chemical analysis for the elements potassium and manganese by AA, ICP, and other instrumental means (see Potassium and Manganese). The concentration of permanganate ion, MnO_4^- in aqueous solution may be determined by titration with a standard solution of oxalic acid or ferrous ion (see Reactions).

POTASSIUM PERSULFATE

[7727–21–1]
Formula: $K_2S_2O_8$; MW 270.31
Synonyms: potassium peroxydisulfate; potassium perdisulfate; peroxydisulfuric acid dipotassium salt; Anthion (in photography)

Uses

Potassium persulfate is an oxidizing agent in analytical chemistry, used in the measurement of organic phosphorus in wastewaters. Some important applications are in bleaching fabrics; removal of last traces of thiosulfate from photographic negatives and paper; oxidizing certain dyes in cotton printing; and initiating copolymerization reactions.

Physical Properties

Colorless or white crystals; triclinic structure; density 2.477 g/cm^3; stable in solid crystalline form; decomposes on heating, evolving oxygen; completely decomposes at about 100°C; sparingly soluble in cold water 1.75 g/100mL at 0°C; moderately soluble at ordinary temperature, 5.29 g/100 mL at 20°C; aqueous solution acidic and unstable, decomposing slowly at room temperature and more rapidly when the solution is warmed; insoluble in alcohol.

Preparation

Potassium persulfate can be prepared by electrolysis of a mixture of potassium sulfate and potassium hydrogen sulfate at a high current density:

$$2KHSO_4 \rightarrow K_2S_2O_8 + H_2$$

Also, the compound can be prepared by adding potassium hydrogen sulfate, KHSO to an electrolyzed solution of ammonium hydrogen sulfate, NH_4HSO_4

POTASSIUM PHOSPHATE, DIBASIC

[7758–11–4]
Formula: K_2HPO_4; MW 174.18
Synonyms: dipotassium hydrogen phosphate; dipotassium phosphate; potassium hydrogen phosphate.

Uses

The salt is a buffering agent in antifreeze solutions. Other applications are in fertilizers; nondairy creams; and culturing of antibiotics.

Physical Properties

White amorphous powder; deliquesces; decomposes on heating; converts to pyrophosphate when ignited; very soluble in water, 167 g/100mL at 20°C; very soluble in alcohol; aqueous solution slightly alkaline.

Preparation

Dipotassium phosphate is prepared by partial neutralization of phosphoric acid with potassium hydroxide, followed by crystallization:

$$H_3PO_4 + 2KOH \rightarrow K_2HPO_4 + 2H_2O$$

Analysis

Elemental composition: K 44 89%, P 17.79%, H 0.58%, and O 36.74%. An aqueous solution may be analyzed for potassium by various methods (see Potassium) and for phosphorus by colorimetry (see Phosphorus).

POTASSIUM PHOSPHATE, MONOBASIC

[7778–77–0]
Formula: KH_2PO_4; MW 136.09
Synonyms: potassium dihydrogen phosphate; potassium biphosphate; monopotassium phosphate; potassium acid phosphate.

Uses

The monobasic salt is a buffering agent for pH measurement and a pharmaceutical buffer. The monobasic and the dibasic salts mixed to form potassium tripolyphosphate [13845–36–8], a surfactant in laundry detergents.

Physical Properties

Colorless crystals or white granular powder; tetragonal structure; deliquesces; density 2.338 g/cm^3; melts at 252.6°C; soluble in water 33 g/100mL at 25°C; pH 4.4–4.7; insoluble in alcohol.

Preparation

Monopotassium phosphate may be prepared by partial neutralization of phosphoric acid with potassium hydroxide in equimolar amounts:

$$H_3PO_4 + KOH \rightarrow KH_2PO_4 + H_2O$$

Analysis

Elemental composition: K 28.73%, P 22.76%, H 1.48%, and O 47.03%. Potassium content of the salt can be measured by various instrumental methods (see Potassium). The phosphorus content of the salt can be measured in its aqueous solution by colorimetric methods (see Phosphorus).

POTASSIUM PHOSPHATE, TRIBASIC

[7778–53–2]
Formula: K_3PO_4; MW 212.27
Synonyms: tripotassium phosphate; potassium orthophosphate

Uses

The tribasic salt is a water softener; emulsifier; and a nutrient for yeast production and wine fermentation.

Physical Properties

Colorless orthorhombic crystals; deliquescent; density 2.564 g/cm^3 at 17°C; melts at 1,380°C; very soluble in water, 90 g/100mL at 20°c; aqueous solutions strongly alkaline; insoluble in alcohol.

Preparation

The tribasic salt is produced by complete neutralization of phosphoric acid with potassium hydroxide, followed by evaporation and crystallization:

$$H_3PO_4 + 3KOH \rightarrow K_3PO_4 + 3H_2O$$

Analysis

Elemental composition: K 55.25%, P 14.59%, O 30.15%. The salt is dissolved in water for potassium analysis (see Potassium) and colorimetric determination of phosphate ion (see Phosphoric Acid).

POTASSIUM SORBATE

[24634–61–5]
Formula: $CH_3CH{=}CHCH{=}CHCOOK$; MW 150.22
Synonyms: potassium 2, 4–hexadienoate; sorbic acid potassium salt; 2, 4–hexadienoic acid potassium salt.

Uses

The compound is an inhibitor of yeast and mold growth in water.

Physical Properties

Colorless or white crystalline solid; density 1.36 g/cm^3; decomposes at 270°C; soluble in water, 58 g/100 g solution; moderately soluble in alcohol.

Preparation

Potassium sorbate is prepared by reacting potassium hydroxide with sorbic acid, followed by evaporation and crystallization:

$$CH_3CH{=}CHCH{=}CHCOOH + KOH \rightarrow CH_3CH{=}CHCH{=}CHCOOK + H_2O$$

Analysis

Elemental composition: K 26.03%, C 47.97%, H 4.70%, and O 21.30%. The salt is dissolved in water and analyzed for potassium by various methods (see Potassium). A diluted alcoholic solution may be analyzed by GC/MS. The characteristic masses for this compound are 111, 112.

POTASSIUM SULFATE

[7778–80–5]
Formula: K_2SO_4; MW 174.25
Synonyms: sal polychrestum; arcanum duplicatum

Occurrence and Uses

Potassium and sodium sulfates and their double sulfates with calcium and magnesium occur naturally in various salt lakes. Potassium sulfate also occurs in certain volcanic lava. Its double salt with magnesium occurs in nature, as the mineral langbeinite.

Potassium sulfate is used in fertilizers as a source of potassium and sulfur, both of which are essential elements for plant growth. Either in simple form or as a double salt with magnesium sulfate, potassium sulfate is one of the most widely consumed potassium salts in agricultural applications. It is preferred over potassium chloride for certain types of crops; such as, tobacco, citrus, and other chloride–sensitive crops. Some other applications include making gypsum cements; to make potassium alum; in the analysis of Kjeldahl nitrogen; and in medicine.

Physical Properties

Colorless or white crystals or white granules or powder; rhombohedral structure; bitter taste; density 2.66 g/cm^3; melts at 1,069°C; vaporizes at 1,689°C; moderately soluble in water, 12 g/100mL at 25°C and 24g/100mL at 100°C; slightly soluble in glycerol; insoluble in alcohol, acetone, and carbon disulfide.

Thermochemical Properties

$\Delta H_f°$	–343.6 kcal/mol
$\Delta G_f°$	–315.8 kcal/mol
S°	42.0 cal/deg mol
C_ρ	31.4 cal/deg mol

Production

Potassium sulfate is produced by various methods, selection of process depending on availability and cost of raw materials.

The salt may be obtained from its naturally occurring mineral, langbeinite, $K_2SO_4 \cdot 2MgSO_4$. The ore first is crushed and washed with water to separate sodium chloride. After that, magnetite is separated from the washed langbeinite by magnetic separation. After the separation of these two major impurities, the purified double salt is treated with an aqueous solution of potassium chloride to obtain potassium sulfate:

$$K_2SO_4 \cdot 2MgSO_4 + 4KCl \rightarrow 3K_2SO_4 + 2MgCl_2$$

The solution is filtered to remove insoluble residues and the products are separated from their aqueous mixture by crystallization.

Potassium sulfate also is produced from the mineral kieserite, $MgSO_4 \cdot H_2O$ by treatment with potassium chloride. The intermediate double salt obtained reacts further with potassium chloride to form potassium sulfate:

$$MgSO_4 \cdot H_2O + 2KCl + 4H_2O \rightarrow K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + MgCl_2$$

$$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + 2KCl \rightarrow 2K_2SO_4 + MgCl_2$$

Potassium sulfate is separated from the more soluble magnesium chloride by crystallization.

Also, potassium sulfate can be made by two other processes in which no naturally occurring mineral is employed. In the Mannheim process, the salt is produced by action of sulfuric acid on potassium chloride:

$$2KCl + H_2SO_4 \rightarrow K_2SO_4 + 2HCl$$

In Hargreaves process, which is a slight variation of the Mannheim method, potassium sulfate is made by heating a mixture of potassium chloride, sulfur dioxide, air and water:

$$4KCl + 2SO_2 + 2H_2O + O_2 \rightarrow 2K_2SO_4 + 4HCl$$

Analysis

Elemental composition: K 44.87%, S 18.40%, and O 36.73%. Potassium content may be determined by analyzing an appropriately diluted aqueous solution for the metal by AA, ICP, or other instrumental methods (see Potassium). The sulfate concentration may be measured by ion chromatography or gravimetry following precipitation with barium chloride.

POTASSIUM THIOCYANATE

[333–20–0]
Formula: KSCN; MW 97.18
Synonyms: potassium sulfocyanate; potassium rhodanide

Uses

Potassium thiocyanate is used in dyeing and printing textiles; to make artificial mustard oil; as a slimicide in paper production; for controlling microbial growth in cooling water; and in the preparation of organic thiocyanates. The salt also is used in analytical chemistry in Volhard titration.

Physical Properties

Colorless rhombohedral crystals; deliquesces; density 1.886 g/cm^3 at 15°C; melts at 173.2°C, the color of the fused salt changing from brown to green and then blue; turns white again on cooling; decomposes at about 500°C; very soluble in water, 177 g/100mL at 0°C and 217 g/100mL at 20°C; solution cools upon dissolution; aqueous solution neutral; readily dissolves in acetone and liquid ammonia; moderately soluble in hot alcohol.

Thermochemical Properties

$\Delta H f°$	–47.84 kcal/mol
$\Delta G f°$	–42.62 kcal/mol
S°	29.70 cal/deg mol
C_ρ	21.16 cal/deg mol

Preparation

Potassium thiocyanate may be made by adding caustic potash to a solution of ammonium thiocyanate, followed by evaporation of the solution.

$$NH_4SCN + KOH \rightarrow KSCN + NH_4OH$$

Also, the compound can be prepared by heating potassium cyanide with sulfur:

$$KCN + S \rightarrow KSCN$$

Reactions

The reactions of potassium thiocyanate in aqueous solution are essentially those of the thiocyanate anion. Its reaction with ferric ammonium sulfate, applied in Volhard titration, results in the formation of ferric thiocyanate, $Fe(SCN)_3$. Similarly, in titration against sliver nitrate, it forms insoluble silver thiocyanate, AgSCN.

Potassium thiocyanate reacts in aqueous solution of ethylene oxide to form ethylene sulfide, C_2H_4S.

Reactions with trialkylboranes yield the corresponding alkyl thiocyanate, RSCN.

Analysis

Elemental composition: K 40.23%, S 33.00%, C 12.36%, N 14.41%. Potassium can be measured in an aqueous solution by flame photometry, AA, or ICP/AES (see Potassium). Thiocyanate anion can be measured by Volhard titration against a standard solution of silver nitrate in the presence of ferric ammonium sulfate. The color of the solution turns red at the end point.

POTASSIUM TRIIODO MERCURATE(II)

[22330–18–3]
Formula: $KHgI_3$; MW 620.40
Synonyms: potassium mercuriiodide; mercuric potassium iodide. Its aqueous solution also is known as Channing's solution or Thoulet's solution.

Uses

The compound is prepared and marketed only in aqueous solution. It is used mostly as a disinfectant and a topical antiseptic. Also, it is used to make Nessler's reagent for analyzing ammonia, and as an analytical reagent for alkaloids.

Physical Properties

Yellow, deliquescent crystals; melts at 150°C; very soluble in water and alcohol; soluble in potassium iodide solution, acetic acid and ether.

Preparation

The commercial product is made and sold as an aqueous solution by dissolving 1g mercuric iodide and 0.8g potassium iodide in 100mL water:

$$HgI_2 + KI \rightarrow KHgI_3 \text{ (or } KI \bullet HgI_2\text{)}$$

Toxicity

The complex salt or its aqueous solution is toxic by ingestion.

PRAESODYMIUM

[7440–10–0]
Symbol Pr; atomic number 59; atomic weight 140.908; a lanthanide–series rare earth element; belongs to the cerium group of rare earths; electron configuration [Xe] $4f^36s^2$; partially filled *f* subshell; valence states +3, +4; most stable oxidation state +3; electrode potential E°/V (aq) for $Pr^{3+} + 3e^- \leftrightarrow Pr$ is –2.35 V; atomic radius 1.828 Å; first ionization potential 5.46 eV; one naturally–occurring isotope, Pr–141; twenty–nine artificial radioactive isotopes known in the mass range 124, 126–140 and 142–154; the longest–lived isotope Pr–143, $t_{1/2}$ 13.57 day, and the shortest–lived isotope Pr–124, $t_{1/2}$ 1.2 second.

History, Occurrence, and Uses

Mosander extracted from the mineral lanthana a rare earth fraction, named didymia in 1841. In 1879, Boisbaudran separated a rare earth oxide called samaria (samarium oxide) from the didymia fraction obtained from the mineral samarskite. Soon after that in 1885, Baron Auer von Welsbach isolated two other rare earths from didymia. He named them as praseodymia (green twin) and neodymia (new twin) after their source didymia (twin). The name praseodymium finally was assigned to this new element, derived from the two Greek words, *prasios* meaning green and *didymos* meaning twin.

Praseodymium occurs in nature associated with other rare earths in a relatively high abundance. It is more abundant than some common metals such as silver, gold, or antimony. The average concentration of this metal in the earth's crust is estimated to be 8.2 mg/kg.

Praesodymium is a component of didymium glass used in welder's goggles. Its salts are used as colorants for glasses and enamels. When in glass, they produce an intense yellow color. Its oxide, praesodymium oxide, is one of the most refractory substances known and is a core material for carbon arcs used in lighting and projection. The Misch metal that contains about 5% praesodymium is used to make cigarette lighters.

Physical Properties

Pale yellow metal; attains a green oxide coating on exposure to air; exhibits two crystalline modifications; (1) an alpha form, that has a hexagonal close–packed structure, a density of 6.773 g/cm^3 and a molar volume 20.82 cc/mol, and (2) a beta form that has an open body–centered cubic structure having a density of 6.64 g/cm^3 and a molar volume of 21.20 cc/mol. The alpha form transforms to beta at 792°C.

Praesodymium metal melts at 931°C; vaporizes at 3,510°C; paramagnetic at ambient temperatures; magnetic susceptibility at 25°C 5.32×10^{-6} emu/mol; electrical resisitivity 68.0×10^{-6} ohm–cm at 25°C and 132×10^{-6} ohm–cm at 820°C (beta–form); hardness on Vickers scale, 43 kg/mm^2 (for alpha–form); Young's modulus 3.25×10^{11} dynes/cm^2 (based on sound velocity measurements); Poisson's ratio 0.305; thermal neutron absorption cross section 11.6 barns.

Thermochemical Properties

ΔH_f° (cry)	0.0
ΔH_f° (gas)	84.99 kcal/mol
ΔG_f° (gas)	76.70 kcal/mol
S° (cry)	17.5 cal/deg mol
S° (gas)	45.4 cal/deg mol
C_ρ (cry)	6.50 cal/deg mol
C_ρ (gas)	5.11 cal/deg mol
ΔH_{fus}	1.65 kcal/mol
ΔH_{vap}	85.3 kcal/g atom
$\Delta H_{transformation\ (alpha \rightarrow beta)}$	0.76 kcal/mol
Coefficient of thermal expansion	4.8×10^{-6}/°C
Thermal conductivity	0.125 W/cm/K

Preparation

Praesodymium may be recovered from its minerals monazite and bastanasite. The didymia extract of rare earth minerals is a mixture of praesodymia and neodymia, primarily oxides of praesodymium and neodymium. Several methods are known for isolation of rare earths. These are applicable to all rare earths including praesodymium. They include solvent extractions, ion–exchange, and fractional crystallization. While the first two methods form easy and rapid separation of rare earth metals, fractional crystallization is more tedious. Extractions and separations of rare earths have been discussed in detail earlier (see Neodymium and Cerium).

Praesodymium metal can be obtained from its anhydrous halides by reduction with calcium. The metal also may be prepared by electrolysis of fused praesodymium chloride at elevated temperatures (about 1,000°C). Alternatively, an eutectic mixture of praesodymium chloride, potassium chloride, and sodium chloride may be electrolyzed. In such electrolysis graphite is the anode and tungsten the cathode.

Compounds

Several compounds of praesodymium are known, mostly in +3, some in +4, and a few in other oxidation states. Its salts containing practically all anions are known. The metal reacts rapidly with dry oxygen forming praesodymium sesquioxide, Pr_2O_3 [12036–32–7], a white hexagonal solid of density 6.9 g/cm^3 and melting at 2,300°C. All Pr halide salts are known: namely fluoride, PrF_3 [13709–46–1], chloride, $PrCl_3$ [10361–79–2], heptahydrate $PrCl_3 \cdot 7H_2O$ [10025–90–8], bromide, $PrBr_3$ [13536–53–3], and iodide, PrI_3 [13813–23–5]. All halides are green to light green in color. The chloride, bromide and iodide salts are all hygroscopic and soluble in water and alcohol. The insoluble fluoride has a density of 6.3 g/cm^3 and melts at 1,395°C. Reaction with nitric acid produces the nitrate salt which crystallizes as light green hexahydrate, $Pr(NO_3)_3 \cdot 6H_2O$ [14483–17–1]. Praesodymium also forms binary compounds at varying nonstoichiometric compositions when heated with many nonmetals and metalloid elements at elevated temperatures. They include the sulfide, Pr_2S_3 [12038–13– 0], density 5.1 g/cm^3 and melting at 1,765°C; nitride PrN [25764–09–4] of density 7.46 g/cm^3; boride PrB_6 [12008–27–4], black cubic crystals of density 4.84 g/cm^3 and melting at 2,610°C; silicide $PrSi_2$ [12066–83–0] of density 5.46 g/cm^3 and melting at 1,712°C; and the telluride Pr_2Te_3 [12038–12–9] of density 7.09 g/cm^3 and melting at 1,500°C.

Praesodymium salts containing oxo anions such as sulfate, hydroxide, carbonate, silicates, oxalate, thiosulfate, chromate, molybdate, and borate are known.

Analysis

Praesodymium salts can be identified nondestructively by x–ray diffraction. The metal can be analyzed by atomic absorption or emission spectroscopy. The water insoluble oxide and other compounds may be digested with aqua regia, diluted, and analyzed by AA or ICP.

PROMETHIUM

[7440–12–2]
Symbol: Pm; atomic number 61; atomic weight 145; a lanthanide series inner–transition metal; electron configuration [Xe]$4f^56s^2$; partially filled *f* orbitals; valence states +3; ionic radius Pm^{3+} 0.98Å; all isotopes of promethium are radioactive; twenty-two isotopes in the mass range 134–155; longest–lived isotope Pm–145, $t_{1/2}$ 17.7 year; shortest–lived isotope Pm–140, $t_{1/2}$ 9.2 sec.

History, Occurrence, and Uses

The discovery of this element is credited to J.A. Marinsky and L.E. Glendenin who, in 1945, identified its long-lived isotope Pm–147 ($t_{1/2}$ 2.64 years) in the fission products of uranium. They named the element after Prometheus, who according to Greek mythology stole fire from heaven. The element was first isolated from fission product wastes by G.W. Parker and P.M. Lantz in 1948. It first was recovered from natural sources by O. Erametsa in 1965. An amount less than 0.5 g was recovered from 20 tons of rare earths.

Promethium does not occur in metallic form in nature. Minute quantities are associated with other rare earths. It also is detected in uranium fission products. It is probably the rarest of the lanthanide elements.

Promethium has very limited applications. It is used in phosphor lights to produce signals. Also, it is used as a beta particle source for thickness gages, nuclear batteries, and portable x–ray units.

Physical Properties

Silvery–white metal; density 7.22 g/cm^3; because of radioactivity, the metal and its salts luminesce in the dark giving a pale blue or greenish glow; melts at 168±6°C; vaporizes at 2,460°C; insoluble in water.

Production

Promethium–147, the isotope used commercially, is isolated from fission product wastes. The radioactive materials must be handled safely in a glove box. The metal complexes either with ethlenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA) and is isolated by elution from Dowex 50.

The metal may be obtained from its fluoride salt, promethium(III) fluoride by heating with lithium metal in a double tantalum crucible at 700 to 800°C in vacuum and then increasing the temperature to 1,100°C.

Compounds

Promethium forms all its compounds in +3 oxidation state. Several compounds have been prepared and are well characterized. A few typical examples are pink hexagonal fluoride, PmF_3, density 6.72 g/cm^3; lavender hexagonal chloride, $PmCl_3$, density 4.19 g/cm^3 and yellow hydrated chloride $PmCl_3 \cdot xH_2O$; the orthorhombic coral–red bromide salt, $PmBr_3$, density 5.45 g/cm^3; the oxide salt, Pm_2O_3 exhibiting three allotropic modifications, colors ranging from pink to coral–red with crystal systems hexagonal, monoclinic, and cubic structures; a hexagonal purple–pink hydroxide, $Pm(OH)_3$, density 5.1 g/cm^3; a garnet–red phosphate salt, $PmPO_4$, with a monoclinic crystal system and density 5.62 g/cm^3; and a hexagonal formate salt, $Pm(HCOO)_2$ that has a pale–lavender appearance (Weigel, F., Promethium,.pp 576–580 in *The Encyclopedia of Chemical Elements*, ed. C.A. Hampel, 1968. New York: The Reinhold Book Corp.)

Analysis

Promethium is identified by x–ray emission spectra, spark spectrum, and other spectroscopic methods. At extremely low concentrations, the element can be measured by ICP–MS. Also promethium and its salts can be detected from their pale–blue or greenish glow in the dark due to their radioactivity. Highly sensitive beta probes can be used for monitoring radioactive Pm–147.

Hazard

All isotopes of promethium and their salts present radiation hazard from exposure to beta and gamma rays.

PROTACTINIUM

[7440–13–3]
Symbol: Pa; atomic number 91; atomic weight 231.04; an actinide series radioactive element; an inner–transition metal; electron configuration [Rn]$5f^26d^17s^2$; valence states +4 and +5; atomic radius 1.63Å (for coordination number 12); twenty–two isotopes are known in the mass range 215–218,

221–238; all are radioactive; longest–lived isotope Pa–231, $t_{1/2}$ 32, 500 years.

History, Occurrence, and Uses

In 1913 Fajans and Gohring identified the first isotope of this element, a metastable isotope having a mass 234, Pa–234m, a short–lived member of uranium–238 decay series. They named it brevium. In 1918, two independent groups, namely Hahn and Meitner and Soddy, Cranston, and Fleck simultaneously identified a longer–lived isotope Pa–231, a member of the uranium–235 decay series. The isotope Pa–234 in its ground state was discovered by Hahn and Meitner in 1921. The element derived its name from the Greek word *protos*, which means 'first.' Protactinium 231 occurs in the ore pitchblende at about 0.1ppm abundance. Certain ores of pitchblende have a higher abundance of this isotope, about 3ppm. Pa–231 also is found naturally in uranium and radium wastes. No commercial application of protactinium isotopes is known.

Physical Properties

Shiny white metal with bright metallic luster; hard and malleable; body–centered tetragonal structure; density 15.37 g/cm^3 (calculated); melts below 1,600°C; vapor pressure $3.88x10^{-2}$ torr at about 1,930°C (calculated); superconducting below 1.4°K

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	145.0 kcal/mol
$\Delta G_f°$ (cry)	0.0
$\Delta G_f°$ (gas)	134.6 kcal/mol
S° (cry)	12.4 cal/deg mol
S° (gas)	47.3 cal/deg mol
C_{ρ} (gas)	5.48 cal/deg mol
Coefficient of linear expansion (0 to 700°C)	$9.9x10^{-6/}$°C (calculated)

Production

Protactinium-233 is produced by the beta decay of the short–lived thorium-233. Thorium-233 is obtained by neutron capture of natural thorium-232. The nuclear reactions are as follows:

$$^{232}_{90}Th + ^{1}_{0}n \longrightarrow ^{223}_{90}Th + \gamma$$

$$^{233}_{90}Th + ^{1}_{0}n \xrightarrow{\beta^-} ^{233}_{91}Pa$$

To synthesize Pa-233, thorium nitrate is irradiated with neutron. Pa-233 formed, as shown above, is dissolved in 3M nitric acid. The solution is heated. A manganous salt and permanganate are added to this solution. Manganese dioxide, MnO_2, is precipitated. Pa-233 co-deposits onto this precipitate. The precipitate is washed with water. It is then dissolved in 6M hydrochloric acid.

Pa-233 is extracted into diisopropyl ketone. The solvent extract containing Pa-233 is washed with 6M HCl for the removal of trace manganese salts and impurities. From the diisopropyl ketone extract, protactinium-233 is re-extracted into an HCl–HF mixture solution containing 6M HCl and 0.1M HF.

Protactinium-231 can be recovered from the residues of uranium refining by various chemical processes. One such recovery process is highlighted below (Maddock, A.G. 1968. Protactinium. In *The Encyclopedia of Chemical Elements*, ed. C.A. Hampel, pp 580–585. New York: Reinhold Book Corp).

The isotope Pa–231 is extracted with a mixture of 8M HCl and 0.1M HF from the uranium refining residues. Protactinium converts to its fluoride, PaF_4. Addition of boric acid or aluminum converts PaF_4 into a complex, which is extracted into diisopropyl ketone. The organic solution is washed and the Pa–complex is re-extracted into HCl–HF mixture. After repeated extractions, the diisopropyl ketone solution is treated with oxalic acid to reduce any iron salts present as contaminants. The solution is then treated with potassium hydrogen fluoride, KHF_2 , to precipitate protactinium as K_2PaF_7. The precipitate is filtered and dissolved in sulfuric acid. Treatment with hydrogen peroxide forms a precipitate of protactinium peroxide, thus separating it from niobium. Peroxide on ignition forms diprotactinium pentoxide, Pa_2O_5.

Other reagents can be employed to recover protactinium from uranium refining residues or wastes. For example, treatment with 4M phosphoric or iodic acid precipitates protactinium as phosphate or iodate which is soluble in HF.

Protactinium-231, similar to Pa-233, also can be synthesized by neutron bombardment of thorium–230:

$$^{230}_{90}Th + ^{1}_{0}n \longrightarrow ^{231}_{90}Th + \gamma$$

$$^{231}_{90}Th + ^{1}_{0}n \xrightarrow{\beta^-} ^{231}_{91}Pa$$

Compounds

The two oxidation states of protactinium are +4 and +5. In solution, Pa^{4+} is oxidized to Pa^{5+} by atmospheric oxygen. The chemistry of pentavalent protactinium is quite similar to that of niobium and tantalum. In acid medium, several metal ions at high concentrations co-precipitate protactinium. When heated with hydrogen at 300°C, protactinium forms a hydride that probably has a composition PaH_3. A few selected compounds of protactinium include the black cubic oxide PaO_2 and the white hexagonal pentoxide Pa_2O_5; the tetragonal oxide sulfide PaOS of pale yellow color; the tan colored monoclinic fluoride, PaF_4 and the white tetragonal pentafluoride, PaF_5; the greenish–yellow tetragonal chloride, $PaCl_4$; and the pale yellow monoclinic pentachloride, $PaCl_5$; a black orthorhombic pentaiodide, PaI_5; and an orange red orthorhombic pentabromide, $PaBr_5$. A number of other salts and complexes are known.

Analysis

Protactinium is separated by solvent extraction and anion exchange processes by using sulfate solutions. After chemical separation, the protactinium salts are ignited to a pentoxide, Pa_2O_5 , which may be converted into an arsenazo(III) complex. The absorbance of the solution is measured at 630 nm with a spectrophotometer. Protactinium-231 is an alpha emitter and also forms photons at 300 KeV, which can be measured by various radioactive counters and spectrophotometric techniques. Protactinium also can be measured by neutron activation analysis.

Toxicity

Protactinium is a very dangerous substance to work with. It is highly toxic and presents a radiation hazard (alpha emitter). The Pa-231 isotope is a long–lived alpha–emitter which is not excreted out readily. Exposure can cause cancer.

RADIUM

[7440–14–4]
Symbol Ra; atomic number 88; atomic weight 226; a Group II (Group 2) alkaline-earth element resembling chemically to barium; a radioactive element; electron configuration [Rn]$7s^2$; valence state +2; four naturally-occurring isotopes: radium-223, a member of the uranium-235 series, $t_{1/2}$ 11.6 days; radium-224, a member of the thorium series, $t_{1/2}$ 3.6 days; radium-226, a member of the uranium-238 series, $t_{1/2}$ 1,600 years; radium-228, a member of the thorium series, $t_{1/2}$ 1.9 year; while the isotopes Ra-233, -224, and -226 are alpha emitters, Ra-228 is a beta–emitter; the total number of isotopes including the above four naturally-occurring isotopes are twenty-nine, having mass numbers 206 to 234.

History, Occurrence, and Uses

Radium was discovered in 1898 by Marie Curie, collaborating with her husband Pierre Curie and G. Bemont. They recovered this element from the naturally–occurring uranium ore, pitchblende. Tons of pitchblende were extracted to obtain less than 500mg of radium. Radium repeatedly was concentrated, first into the barium fraction of their residues and then separated from barium by fractional crystallization. Marie Curie named the new element radium. This name was originally assigned to its isotope Ra–226. However, radium currently refers to all isotopes of the element having atomic number 88. She purified a radium salt to determine its atomic weight. This was done by dissolving radium sulfate in sodium carbonate solution and then converting the radium carbonate formed as its chloride by dissolving in hydrochloric acid. Repeated fractionation gave pure radium chloride, $RaCl_2$, from which Mme Curie derived an atomic weight of 225.18. This value closely agreed with the atomic weight 225.97 obtained several years later by Honigschmid, using other methods.

Radium occurs in small quantities in all uranium minerals. It is a daughter element of uranium, i.e., one of its radioactive disintegration products. The mineral carnotite, found in the USA, contains about 10mg radium per ton. Radium has been detected in many groundwaters in the USA.

Radium salts have several applications. Historically, it was used in cancer treatment for destroying malignant tumors. At present, such use has been considerably reduced, replaced by readily available and low cost radioisotopes such as cobalt–60. Its gamma radiation is used for irradiating metals to detect any fractures in welding. Radium, in minute proportion, is mixed with phosphors (substances that emit light when irradiated) and used to make luminous paints and watch dials. Radium compounds are used to remove static electricity from textile products. Its gamma rays ionize the air, making the air able to remove static electricity from surfaces.

Radium-226 also is a source material to produce radon–222 in several radiotherapy treatments. Radon-222, the first daughter of radium-226, is safer to use because of its much shorter half-life of 3.8 days. Curie (Ci), the internationally adopted unit for radioactivity, is based on the emanation of alpha particles by radium-226. This unit is equal to the number of alpha particles emitted by 1g of radium in any form per second. One curie is equal to 3.70×10^{10} alphas/sec.

Recovery

Radium is an intermediate member of the uranium decay series. Therefore, it is present in all uranium minerals. Its abundance in uranium is calculated to be about 0.33ppm.

Uranium mineral first is digested with hot nitric acid. All uranium and radium compounds dissolve in the acid. The solution is filtered to separate insoluble residues. The acid extract is then treated with sulfate ions to separate radium sulfate, which is co-precipitated with the sulfates of barium, strontium, calcium, and lead. The precipitate is boiled in an aqueous solution of sodium chloride or sodium hydroxide to form water-soluble salts. The solution is filtered and the residue containing radium is washed with boiling water. This residue also contains sulfates of other alkaline earth metals. The solid sulfate mixture of radium and other alkaline earth metals is fused with sodium carbonate to convert these metals into carbonates. Treatment with hydrochloric acid converts radium and other carbonates into chlorides, all of which are water-soluble. Radium is separated from this solution as its chloride salt by fractional crystallization. Much of the barium, chemically similar to radium, is removed at this stage. Final separation is carried out by treating radium chloride with hydrobromic acid and isolating the bromide by fractional crystallization.

Radium in hydrochloric acid solution may be separated effectively by ion exchange methods using cation exchange-resin columns. A weak HCl solution is passed through the column. The absorbed metals on the ion-exchange column are eluted with ethylenediaminetetraacetic acid (EDTA) at pH 6.25 or with ammonium citrate at pH 7.8. With either eluant, radium is eluted last, after removing barium and then lanthanum, calcium, magnesium, and other metals.

Reactions

The chemistry of radium is very similar to its Group IIA alkaline-earth analog barium. The metal forms a number of salts in its +2 valence state, the only valence state typical of all alkaline earth metals. The few salts that are of commercial use include chloride, $RaCl_2$, bromide $RaBr_2$, and sulfate, $RaSO_4$.

Analysis

Gross alpha and gross beta activity can be determined by various radioactive counters, such as internal proportional, alpha scintillation, and Geiger counters. Radium in water can be measured by co-precipitating with barium sulfate followed by counting alpha particles. Radium-226 can be measured from alpha counting of radon-222. Various methods are well documented (APHA, AWWA, and WEF•1998. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington DC: American Public Health Association).

Hazard

The radiation from radium can cause cancer in the lung, osteogenic sarcoma, blood dyscrasias and injury to skin. Inhalation, ingestion, skin contact or body exposure to radium and all its salts must be avoided.

RADON

[10043–16–4]
Symbol: Rn; atomic number 86; atomic weight 222; a radioactive noble gas element; heaviest of the noble gases; electron configuration $1s^22s^22p^63s^2\,3p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}6s^26p^6$; valence 0; one of the intermediates of uranium-238 series; first daughter of radium-226; eighteen isotopes are known; all radioactive; the longest–lived isotope Rn-222, $t_{1/2}$ 3.823 day.

History, Occurrence, and Uses

Three isotopes of radon were discovered around 1900. Rutherford found that thorium continuously produced a radioactive gas, which was swept away by air. He called this gaseous radioactive product “thorium emanation.” Dorn, around the same time, found that radium also evolved a gaseous radioactive daughter known as “radium emanation.” A third gas was found among products of actinium decay by Debierne in 1900. This was termed “actinium emanation.” All the three emanations were isotopes of element 86. They were thoron, radon, and actinum, respectively, corresponding to their atomic masses of 220, 222, and 219. The name radon was adopted for the entire element 86 in 1923. The spectrum of radium emanation (Rn-222) appeared similar to that of argon, krypton, and xenon. The gas is chemically inert like other noble gases. The element was assigned an atomic number 86 and placed as a noble gas below xenon in the Periodic Table.

Radon occurs in deep earth gases. Many products are emitted continuously from uranium deposits in the earth's crust. Trace concentrations of radon are found in its groundwaters, in the basements of many houses, and in household air. Radon diffuses partially from radium salts and deposits its radioactive decay products on surrounding objects.

Radon is a radiation source for treating cancer. It is safer than radium-226 because of its much shorter half-life. Its solution in petroleum jelly is used in some ointments for treating certain skin diseases. The non-medical uses of radon include its application as a gaseous tracer to detect leaks; to measure flow rates; as a source of neutron in radon–beryllium mixtures; to ionize gases to promote radon-induced chemical reactions such as oxidation, decomposition, and polymerization; to measure reaction rates, and in other kinetic studies; and as a point source of gamma rays in radiography to inspect welding and castings of metals.

Physical Properties

Colorless gas; density about 9.73 g/L at STP; liquefies at –61.8°C; density of liquid radon 4.4g/mL at –62°C; solidifies at –71°C to an opaque crystalline solid; density of solid radon 4.0 g/cm^3; critical temperature 104.4°C; critical pressure 62.4 atm; viscosity 2.13×10^{-4} poise at 0°C (estimated); strongly absorbed onto surfaces; dissolves in water, 230 mL/L at 20°C; slightly soluble in alcohol and other organic solvents .

Thermochemical Properties

$\Delta H_f°$	0.0
$\Delta H_f°$ (Rn^+)	249.3 kcal/mol
$\Delta G_f°$	0.0
S°	42.1 cal/deg mol
C_ρ	4.97 cal/deg mol

Production

Radon can be isolated from radium by several methods. An aqueous solution of radium salt such as radium bromide is heated, liberating radon. Radioactive bombardment then decomposes water to oxygen and hydrogen. Radon is separated from the gaseous mixture by condensation in tiny tubes placed in liquid air. The tubes then are sealed by melting. A gold or platinum coating is applied to form the "radon seeds" used in radiation therapy.

Alternatively, a slightly acid solution of a soluble radium salt such as chloride or bromide is placed in a soft-glass vessel behind lead shielding. The solution is boiled. Radon is pumped out as needed and frozen into a cold trap at –95°C. Hydrogen and oxygen are the main impurities generated from radiolytic decomposition of water. They are recombined by sparking or applying a hot wire. Carbon dioxide, water vapor, acid vapor, and hydrocarbon impurities are removed by various chemical methods.

Radon can be obtained from radium salts in the solid phase too. At ordinary temperatures, certain mixtures containing radium salts such as radium mixed with barium, radium palmitates, or gels of radium mixed with iron(III) hydroxide or aluminum(III) hydroxide efficiently release radon. Although any radium salt would emit radon, the latter can diffuse very slowly at room temperature through the walls of the container vessels. However, when a radium salt is heated above 600°C radon diffuses rapidly through the solid container vessels and escapes.

Radon also may be separated from gas streams by adsorption on activated charcoal or silica gel. At temperatures colder than dry ice, charcoal is an excellent adsorbent. Radon may be desorbed by heating the adsorbent in vacuum at 350°C.

Analysis

Radon-222 may be transported with a carrier gas into an ionization chamber and its alpha particles counted. Short-lived isotopes in a carrier gas stream are measured this way using a flow-type ionization chamber.

Hazard

Exposure to radon can cause lung cancer.

RHENIUM

[7440–15–5]
Symbol: Re; atomic number 75; atomic weight 186.21; a Group VIIB (Group 7) transition metal of manganese triad; electron configuration $[Xe]4f^{14}5d^{5}6s^{2}$; valence states –1, +1, +2, +3, +4, +5, +6, +7; most common valence state, +7; two naturally occurring isotopes: Re-185 (37.40%), Re-187 (62.60%); Re-187 is radioactive with $t_{1/2}$ 4.5×10^{10} year; twenty–seven artificial radioisotopes in the mass range, 162–170, 172, 174–184, 186, 188–192.

History, Occurrence, and Uses

The element was discovered in 1925 by Walter Noddack, Ida Tacke Noddack, and O. Berg. They detected it by x–ray examination of platinum ores. X–ray studies also showed its occurrence in columbite and other minerals. It was named after the German river Rhine, called Rhenus in Latin. In 1929, Walter and Ida Noddack produced 1g of rhenium metal from 660 kg of Norwegian molybdenite.

Rhenium does not occur alone in nature in elemental form. It is found in trace quantities in a number of minerals such as columbite, gadolinite, molybdenite, tantalite, wolfranite, and many platinum ores. Its average concentration in earth's crust is 0.0007mg/kg.

Rhenium is used in tungsten and molybdenum-based alloys. It is used for filaments for ion gages in mass spectrometers. Rhenium-tungsten alloys are used in thermocouples to measure temperatures up to 2,200°C. Rhenium wire is used in flash bulbs for photography. Rhenium compounds also are used as catalysts in hydrogenation and hydrocracking reactions in petroleum refining.

Physical Properties

Metallic appearance in massive form, black to metallic color in powdered state or in electrodeposited form; hexagonal crystal system; density 20.53 g/cm^3; hardness (Brinell) 250; melts at 3,180°C; vaporizes at 5,627°C (estimated); vapor pressure $4.6x10^{-5}$ torr at 2,500°C; electrical resistivity 19.14 microhm –cm; modulus of elasticity $67x10^6$ psi at 20°C; specific magnetic susceptibility $0.369x10^{-6}$; thermal neutron absorption cross section 86 barns/atom; superconductivity transition temperature 1.7°K; insoluble in water and hydrochloric acid; soluble in dilute nitric acid and hydrogen peroxide; slightly soluble in sulfuric acid.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	184.0 kcal/mol
$\Delta G_f°$ (cry)	0.0
$\Delta G_f°$ (gas)	173.2 kcal/mol
S° (cry)	8.81 cal/deg mol
S° (gas)	45.13 cal/deg mol
C_ρ (cry)	6.09 cal/deg mol
C_ρ (gas)	4.97 cal/deg mol
Thermal conductivity (at 25°C)	0.480 W/cm/K
ΔH_{fus}	14.45 kcal/mol
Coefficient of linear expansion (20–1,000°C)	$6.6–6.8x10^{-6}$/°C

Production

Rhenium is usually recovered from the molybdenite ore, MoS_2. Such ores contain rhenium in concentrations ranging from 0.002 to 0.02%. The ore is roasted to produce flue dusts and effluent gases that contain rhenium and that serve as a raw material in making rhenium. Flue dusts and gases are leached and scrubbed with water. Rhenium oxide, Re_2O_7 and anhydride of perrhenic acid, $HReO_4$, dissolve in water. The solution becomes acidic because of perrhenic acid. The solution is treated with solid potassium chloride. This precipitates potassium perrhenate, $KReO_4$, which is purified by repeated crystallization. At the boiling point of water, the solubility of potassium perrhenate is about 14g/100g and at ordinary temperatures, it is below 1g/100g. Thermal dissociation of potassium perrhenate in the presence of hydrogen at elevated temperatures forms rhenium. Instead of potassium salt of perrhenic acid, the equivalent ammonium salt can be used. Ammonium perrhenate is heated with pure dry hydrogen at 700 to 800°C:

$$2NH_4ReO_4 + 7H_2 \rightarrow 2Re + 8H_2O + 2NH_3$$

Rhenium is obtained as a metal powder. It is cooled to ambient temperature under a stream of nitrogen. The metal powder also may be pressed into bars in vacuum at 1,200°C.

Reactions

In compact or massive form, rhenium is stable at ordinary temperatures. When heated in oxygen or air at 350°C or above, it oxidizes to yellow heptoxide, Re_2O_7. Rhenium also forms two other oxides, the red trioxide, ReO_3, and the black dioxide, ReO_2.

Rhenium reacts with all halogens including iodine to yield halides in several valence states from +1 to +6. Such halides include dark red hexagonal trichloride, $ReCl_3$, dark green pentachloride, $ReCl_5$, green hexafluoride, ReF_6, and the greenish black crystalline tribromide, $ReBr_3$.

The metal forms a dimeric pentacarbonyl $[Re(CO)_5]_2$ which decomposes at 250°C. Also, it forms a yellow rhombohedral pentacarbonyl iodide, $ReI \cdot 5CO$, soluble in benzene and which decomposes at 400°C.

Rhenium forms two sulfides when heated with sulfur. These are the disulfide, obtained as black leaflets, having formula ReS_2 and a density 7.51 g/cm^3 and the heptasulfide, Re_2S_7, a black powdery material of density 4.87 g/cm^3.

Rhenium is attacked by neither hydrochloric acid nor by cold sulfuric or hydrofluoric acid. However, oxidizing acids, such as nitric acid or hot sulfuric acid, vigorously react with the metal forming perrhenic acid, $HReO_4$. The metal is oxidized by hydrogen peroxide in ammoniacal solution forming ammonium perrhenate, NH_4ReO_4.

Rhenium combines with phosphorus, arsenic, silicon, selenium, and tellurium at elevated temperatures forming binary compounds. The metal, however, is stable in hydrogen and nitrogen at high temperatures.

Analysis

Rhenium can be analyzed by various instrumental techniques that include flame-AA, ICP-AES, ICP-MS, as well as x-ray and neutron activation methods. For flame-AA analysis the metal, its oxide, or other insoluble salts are dissolved in nitric acid or nitric-sulfuric acids, diluted, and aspirated directly into nitrous oxide-acetylene flame. Alternatively, rhenium is chelated with 8–hydroxyquinoline, extracted with methylisobutyl ketone and measured by flame-AA using nitrous oxide-acetylene flame.

RHODIUM

[7440-16-6]

Symbol Rh; atomic number 45; atomic weight 102.906; a Group VIII (Group 9) noble metal placed between cobalt and iridium; electron configuration $[Kr]4d^85s^1$; valence states +2, +3, +4, +5, +6; most stable valence state +3; atomic radius 1.34Å ; ionic radius Rh^{3+}, 0.67Å (CN 6); standard electrode potential, $Rh^{3+} + 3e^- \leftrightarrow Rh$, $E° = 0.578V$; one naturally-occurring isotope, Rh-103; twenty-five artificial radioactive isotopes in the mass range 92-102, 104-117; the longest-lived radioisotope, Rh-101, $t_{1/2}$ 3.3 year.

History, Occurrence, and Uses

Rhodium was discovered by W. H. Wollaston in 1803-04 in the aqua regia extract of native platinum. After removal of platinum as diammonium platium hexachloride, $(NH_4)_2PtCl_6$, from the aqua regia extract, the resulting filtrate contained two new metals, palladium and rhodium. The element was named rhodium, derived from the Greek word *rhodon* for the beautiful rose color of its chloro salt and its aqueous solution.

Rhodium occurs in nature in trace quantities, always associated with other platinum metals. It is found in native form. Its average abundance in the earth's crust is estimated to be 1mg/kg. Rhodium is used as a precious metal for making jewelry and decorative. Other important applications of this metal or its compounds are in making glass for mirrors or filtering light; in catalytic reactions to synthesize a number of products; as an alloying element for platinum; as a hardening agent for platinum and palladium at high temperatures; in electrical contact plates in radio- and audio-frequency circuits. Rhodium alloyed with platinum is used in thermocouples. A 10% Rh-Pt alloy was introduced by LeChatelier in 1885 for use in thermocouples. Also, rhodium alloys are used in laboratory crucibles, electrodes, optical instruments, furnace linings, and making glass fibers.

Physical Properties

Grayish-white metal; face-centered cubic crystals; density 12.41 g/cm^3; hardness, annealed 100-120 Vickers units; melts at 1,964°C; vaporizes at 3,695°C; electrical resistivity 4.33 microhm–cm at 0°C; tensile strength, annealed 50 tons/in^2; Young's modulus, annealed 2.3×10^4 tons/in^2; magnetic susceptibility 0.99×10^{-6} cm^3/g; thermal neutron absorption cross section 156 barns; insoluble in water; soluble in concentrated sulfuric or hydrochloric acid under boiling conditions; the metal in massive form is slightly soluble in aqua regia, but in small quantities or in thin plates it partially dissolves in aqua regia; forms solid solutions with platinum, palladium and iridium.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	133.1 kcal/mol
$\Delta G_f°$ (cry)	0.0
$\Delta G_f°$ (gas)	122.1kcal/mol
S° (cry)	7.53 cal/deg mol
S° (gas)	44.4 cal/deg mol
C_ρ(cry)	5.97 cal/deg mol
C_ρ(gas)	5.02 cal/deg mol
ΔH_{fus}	5.15 kcal/mol
Coefficient of linear expansion (20–100°C)	8.3×10^{-6}/°C
Thermal conductivity (0–100°C)	1.50 W/cmK

Reactions

At ordinary temperatures rhodium is stable in air. When heated above 600°C, it oxidizes to Rh_2O_3, forming a dark oxide coating on its surface. The gray crystalline sesquioxide has a corundom-like crystal structure. The sesquioxide, Rh_2O_3 , decomposes back to its elements when heated above

1,100°C. However, on further heating the metal starts to lose its weight similar to platinum, probably due to loss of its volatile oxide RhO_2 dissolved in the metal. The molten metal readily absorbs gaseous oxygen.

The metal in powder form absorbs hydrogen when heated. When heated with carbon monoxide under pressure rhodium forms carbonyl, $Rh_4(CO)_{12}$.

The metal combines with halogens at elevated temperatures. When heated with fluorine at 500 to 600°C, it forms a trifluoride, RhF_3, a red rhombohedral crystalline powder insoluble in water, dilute acids, or alkalis. Also, a blue tetrafluoride, RhF_4, is formed as a minor product. When heated with chlorine gas above 250°C, the brown-red trichloride, $RhCl_3$, forms. It is hygroscopic, decomposing at 450°C.

Rhodium is attacked by fused caustic soda or caustic potash. Also, fused sodium or potassium cyanide and sodium bisulfate attack the metal.

Recovery

The recovery of rhodium from the raw ores usually involves a series of lengthy steps. Rhodium may be obtained as one of the by-products from refining nickel by the Monod process. In this process the residue from refining nickel is leached with acid to form concentrates of the precious metals. Also, rhodium and other noble metals are derived from the anode slimes that accumulate in the electrolytic refining of copper and nickel. The precious metal concentrates obtained from such nickel refining are first treated with acids as appropriate to remove base metals. The solution is filtered and the precious metals in the residue are separated by treatment with aqua regia. While gold, platinum and palladium dissolve in aqua regia, rhodium remains mostly undissolved along with ruthenium, osmium, iridium, and silver. This residue, containing rhodium, is smelted with a mixture of lead carbonate, soda ash, borax, and carbon to produce slag. The smelting converts lead to an alloy that contains silver and precious metals. The alloy is treated with dilute nitric acid. Silver passes into the solution as soluble silver nitrate. The insoluble residue containing rhodium and other noble metals is fused with sodium bisulfate at 500°C in a silica vessel. Rhodium is converted to its water-soluble sulfate and separated from other noble metals that remain in insoluble residue when the fused mass is treated with water. The insoluble residue is filtered from the aqueous solution of rhodium sulfate. The solution is treated with caustic soda to precipitate rhodium as its hydroxide, $Rh(OH)_3$. The hydroxide is washed and dissolved in hydrochloric acid. Impurity metals are removed by precipitation in the presence of nitrite. Addition of cobalt nitrite forms a nitrite complex of rhodium, $CoRh(NO_2)_6$, which remains in solution over a wide range of pH. Impurity metals are precipitated as their hydrous oxides under varying pH conditions. After the removal of impurity metals, ammonia is added to the solution whereupon rhodium precipitates as ammonium hexanitrorhodite, $(NH_4)_3Rh(NO_2)_6$. This complex is dissolved in hydrochloric acid. The solution containing chlororhodite, $RhCl_6^{3-}$, is passed through a column of cation exchange resin to remove trace impurity metals, such as lead, copper and iron. Boiling purified chlororhodite solution with formic acid precipitates rhodium black. This is reduced with hydrogen to form high purity rhodium powder.

Wollaston's earliest method involved recovery of rhodium from native platinum. Pt was digested with aqua regia. Rhodium in bulk form is slightly soluble in aqua regia. However, when present as a minor constituent in platinum alloys, the metal may be extracted with aqua regia. Platinum was precipitated from aqua regia extract as ammonium hexachloroplatinate, $(NH_4)_2PtCl_6$. Addition of mercurous cyanide, $Hg_2(CN)_2$, to the filtrate separated palladium as yellow palladium cyanide, $Pd(CN)_2$. Excess mercurous cyanide in the remaining solution was decomposed by evaporating the solution with hydrochloric acid. The residue was treated with ethanol. A dark red solid residue that remained after alcohol treatment was a double chloride, sodium chlororhodite, $Na_3RhCl_6 \cdot 18H_2O$. Heating this rhodium complex with hydrogen decomposed the double chloride forming sodium chloride, hydrogen chloride and rhodium metal:

$$2Na_3RhCl_6 + 3H_2 \rightarrow 6NaCl + 6HCl + 2Rh$$

Sodium chloride was removed by leaching with water. Rhodium powder was left as residue.

Analysis

Rhodium may be analyzed by flame atomic absorption spectrophotometry using the direct air-acetylene flame method. The metal, its oxide and insoluble salts may be solubilized by digesting with sulfuric acid–hydrochloric acid mixture. Rhodium also may by analyzed by ICP-AES and ICP/MS techniques. ICP/MS is the most sensitive method. Also, it may be analyzed by neutron activation analysis.

RHODIUM CHLORIDE

[10049-07-7]
Formula: $RhCl_3$; MW 209.26; forms a trihydrate $RhCl_3 \cdot 3H_2O$
Synonyms: rhodium trichloride; rhodium(III) chloride

Uses

Rhodium chloride is used to prepare other rhodium salts.

Physical Properties

Brownish–red powder; deliquescent; decomposes on heating at 450 to 500°C; sublimes at 800°C; insoluble in water, water-solubility, however, depends on the method of preparation; soluble in alkali hydroxide or cyanide solutions; soluble in aqua regia

The trihydrate is a dark red powder; deliquescent; loses water at 100°C; very soluble in water; soluble in alcohol and hydrochloric acid; insoluble in ether.

Thermochemical Properties

$\Delta H_f°$ –71.5 kcal/mol

Preparation

Rhodium trichloride is prepared by heating rhodium with chlorine gas at 250°C:

$$2Rh + 3Cl_2 \rightarrow 2RhCl_3$$

Also, the chloride salt may be obtained by treating the yellow hydrous oxide, $Rh_2O_3 \cdot 5H_2O$, with hydrochloric acid. The solution is carefully evaporated to form a dark red and water-soluble salt, rhodium trichloride tetrahydrate, $RhCl_3 \cdot 4H_2O$. Heating the tetrahydrate in a stream of hydrogen chloride gas at 180°C forms the anhydrous salt, $RhCl_3$.

Analysis

Elemental composition: Rh 49.17%, Cl 50.83%. Rhodium is analyzed in an aqueous solution (or after dissolving in water) by AA or other techniques. Insoluble chloride is extracted with aqua regia, diluted, and analyzed to determine the rhodium content using various instrumental techniques. The chloride may be decomposed at elevated temperatures and liberated chlorine identified by color and other physical properties. Chlorine may be measured quantitatively by dissolving in an acidified solution of potassium iodide and titrating liberated iodine with a standard solution of sodium thiosulfate, using starch indicator.

RHODIUM SESQUIOXIDE

[12036-35-0]
Formula Rh_2O_3; MW 253.81; forms tri- and pentahydrates, $Rh_2O_3 \cdot 3H_2O$ and $Rh_2O_3 \cdot 5H_2O$
Synonym: rhodium(III) oxide

Uses

Rh_2O_3 is used to make rhodium metal and its various salts. Also, the oxide is a catalyst for hydrogenation.

Physical Properties

Gray crystalline solid or amorphous powder; corundum-type structure; density 8.20 g/cm^3; decomposes at about 1,100 to 1,150°C; insoluble in water, acids, or aqua regia.

The pentahydrate $Rh_2O_3 \cdot 5H_2O$ is a yellow precipitate; soluble in acids; partially dissolves in hot water; ignites to form anhydrous oxide.

The trihydrate $Rh_2O_3 \cdot 3H_2O$ is a black precipitate; insoluble in acids.

Thermochemical Properties

$\Delta H_f°$ –82.0 kcal/mol

C_p 24.8cal/deg mol

Preparation

Rhodium sesquioxide is obtained by heating rhodium metal to red heat in air.

$$4Rh + 3O_2 \rightarrow 2Rh_2O_3$$

Alternatively, Rh_2O_3 may be prepared by igniting rhodium nitrate, $Rh(NO_3)_3$.

Treating the sesquioxide with alkali first forms a yellow precipitate of pentahydrate, $Rh_2O_3 \cdot 5H_2O$, soluble in acid and excess alkali. In excess alkali a black precipitate of trihydrate, $Rh_2O_3 \cdot 3H_2O$ is obtained. The trihydrate is insoluble in acids.

Analysis

Elemental composition (Rh_2O_3): Rh 81.09%, O 18.91%. The oxide may be solubilized by treatment with alkali to form hydrated oxide, which may be dissolved in acid and diluted for analysis of rhodium metal by AA or ICP. The oxide may be characterized by x-ray diffraction, physical properties, and reaction with strong alkali to form yellow precipitate of pentahydrate, and in excess alkali a black precipitate of the trihydrate.

RUBIDIUM

[7440-17-7]
Symbol Rb; atomic number 37; atomic weight 85.468; a Group I (Group 1) alkali metal element; electron configuration [Kr] $5s^1$; valence +1; atomic radius 2.43Å; ionic radius, Rb^+ 1.48Å; atomic volume 55.9 cc/g-atom at 20°C; ionization potential 4.177 V; standard electrode potential $Rb^+ + e^- \leftrightarrow Rb$, $E° = -2.98V$; two naturally-occurring isotopes, Rb-85 (72.165%) and Rb-87 (27.835%); Rb-87 radioactive, a beta emitter with a half-life 4.88×10^{10} year; twenty-seven artificial radioactive isotopes in the mass range 74–84, 86, 88–102.

History, Occurrence, and Uses

Rubidium was discovered in 1861 by Kirchoff and Bunsen. They observed new lines in the dark red spectral region of a sample extract of mineral lepidolite. The element got its name from the Latin word *rubidus*, which means dark red. Bunsen later succeeded in preparing metallic rubidium in low yield by heating rubidium hydrogen tartrate with carbon. The metal was obtained in higher yield by Hevesy and later by Beketov, Hevesy electrolyzing a melt of rubidium hydroxide and Beketov reducing the hydroxide with aluminum at red heat.

Rubidium is widely distributed in nature. Its abundance in the earth's crust is estimated to be 90 mg/kg. Rubidium occurs at trace levels in many potassium minerals. Often it is associated with cesium. Some rubidium-containing minerals are lepidolite, leucite, petalite, feldspars, pollucite, beryl, and amazonite. The metal is never found as a major constituent in any mineral. Rubidium also occurs in many rocks such as basalts, granites and clay shales. Rubidium is found in seawater at an average concentration of 0.12 mg/L.

Rubidium metal and its salts have very few commercial applications. They are used in research involving magnetohydrodynamics and thermoionic experiments. Rubidium is used in photocells. The metal also is a getter of oxygen in vacuum tubes. The beta-emitter rubidium –87 is used to determine age of some rocks and minerals. Radioisotopes of rubidium have been used as radioactive tracers to trace the flow of blood in the body. The iodide salt treats goiters. Rubidium salts are in pharmaceuticals as soporifics, sedatives, and for treating epilepsy.

Physical Properties

Silvery-white metal; body-centered cubic crystals; ductile; soft and very light (the fourth lightest metallic element); Mohs hardness 0.3; density 1.522 g/cm^3 at 18°C; melts at 39.3°C; density of the liquid metal 1.472 g/mL at 39°C; vaporizes at 689°C producing a blue vapor; vapor pressure 1 torr at 294°C and 10 torr at 387°C; electrical resistivity 11.6 microhm-cm at 0°C and 13.1 mirohm-cm at 25°C; viscosity 0.484 centipoise at 100°C; magnetic susceptibility 0.09×10^{-6} cgs units at 18°C; thermal neutron absorption cross section 0.73 barns; reacts violently with water

Thermochemical Properties

$\Delta H_f°$(cry)	0.0
$\Delta H_f°$(gas)	19.34 kcal/mol
$\Delta G_f°$(gas)	12.69 kcal/mol
S°(cry)	18.36 cal/deg mol
S°(gas)	40.66 cal/deg mol
C_ρ(cry)	7.43 cal/deg mol
C_ρ(gas)	4.97 cal/deg mol
ΔH_{fus}	0.52 kcal/mol
Thermal conductivity (at 27°C)	0.582 W/cmK
Coefficient of linear expansion (at 20°C)	90×10^{-6}/°C

Production

Rubidium is recovered from its ore lepidolite or pollucite. Mineral lepidolite is a lithium mica having a composition: $KRbLi(OH,F)Al_2Si_3O_{10}$. The ore is opened by fusion with gypsum (potassium sulfate) or with a mixture of barium sulfate and barium carbonate. The fused mass is extracted with hot water to leach out water-soluble alums of cesium, rubidium, and potassium. The solution is filtered to remove insoluble residues. Alums of alkali metals are separated from solution by fractional crystallization. Solubility of rubidium alum or rubidium aluminum sulfate dodecahydrate, $RbAl(SO_4)_2•12H_2O$ falls between potassium and cesium alum.

Alternatively, the mineral is opened by prolonged heating with sulfuric acid. Often calcium fluoride (fluorspar) is added for removal of silicon. Alkali metals are converted into water-soluble sulfates. After filtering residual solid, the solution is treated with ammonium or potassium carbonate or carbon dioxide. Lithium precipitates as lithium carbonate. Alkali metal carbonates are converted back to alums and separated by fractional crystallization.

Rubidium alum obtained by either method above is decomposed by treatment with alkali solutions for removal of aluminum and sulfate. Aluminum is precipitated as aluminum hydroxide. Addition of barium hydroxide to the filtrate removes sulfate, precipitating barium sulfate. Evaporation of the solution crystallizes rubidium as hydroxide.

Rubidium also may be recovered by the chlorostannate method. In this method the alkali metal carbonate solution obtained from the mixed alum is treated with carbon dioxide. Most potassium is precipitated as bicarbonate, $KHCO_3$. Addition of hydrochloric acid converts the carbonates to chlorides. The chlorides are converted to chlorostannates by carefully adding stoichiometric quantities of stannic chloride at pH just below 7:

$$2RbCl + SnCl_4 \rightarrow Rb_2SnCl_6$$

Cesium chlorostannate, Cs_2SnCl_6, more insoluble than the rubidium salt, precipitates before any rubidium starts to precipitate. Under such controlled addition of stannic chloride, potassium chloride remains in solution in chloride form. Rubidium chlorostannate complex, on thermal decomposition, forms rubidium chloride, RbCl.

Rubidium metal may be obtained from its carbonate, hydroxide or chloride by reduction with magnesium or calcium at high temperatures in the presence of hydrogen:

$$Rb_2CO_3 + 3Mg \rightarrow 2Rb + 3MgO + C$$

$$2RbOH + Mg \rightarrow 2Rb + Mg(OH)_2$$

$$2RbCl + Ca \rightarrow 2Rb + CaCl_2$$

Rubidium is a flammable solid. It is stored in dry hexane, isooctane or other saturated hydrocarbon liquids. Alternatively, the metal may be packaged and stored in well-sealed borosilicate glass ampules or stainless-steel containers under vacuum or an inert atmosphere.

Reactions

Rubidium is a highly reactive metal, more reactive than sodium or potassium. Most reactions are similar to sodium or potassium (see Potassium). The metal ignites spontaneously in air forming oxides. It is coated rapidly with a gray-blue oxide film. It forms four oxides, Rb_2O, Rb_2O_2, Rb_2O_3, and Rb_2O_4. It reacts violently with water to form rubidium hydroxide, RbOH:

$$2Rb + 2H_2O \rightarrow 2RbOH + H_2$$

Reaction with dilute mineral acids can proceed with explosive violence, releasing hydrogen.

Rubidium combines with hydrogen and nitrogen forming hydride, RbH and nitride, Rb_3N, respectively.

Analysis

Rubidium and its salts may be analyzed by flame AA, flame photometric and ICP/AES methods. Rb metal imparts a deep red color to flame.

Hazard

As a highly reactive metal, its contact with water or acids can produce violent reactions. Skin contact can cause serious burns.

RUBIDIUM CARBONATE

[584-09-8]
Formula Rb_2CO_3; MW 230.945; readily forms a monohydrate, $Rb_2CO_3 \cdot H_2O$

Uses

Rubidium carbonate is used in special glass and in fiber optics. It enhances stability and durability of glass, reducing its conductivity. It also is used in the preparation of Rb metal and other rubidium salts.

Physical Properties

Colorless crystals or white powder; monoclinic structure; very hygroscopic; melts at 837°C; decomposes above 900°C; very soluble in water

Thermochemical Properties

$\Delta H_f°$	–271.5 kcal/mol
$\Delta G_f°$	–251.2 kcal/mol
S°	43.3 cal/deg mol
C_ρ	28.1 cal/deg mol

Preparation

Rubidium carbonate is an intermediate in recovery of rubidium from lepidolite. The mineral, on prolonged heating with concentrated sulfuric acid, converts to alums.

The mixed alum solution, on treatment with ammonia or potassium carbonate, forms carbonates of potassium, rubidium and cesium. Rubidium carbonate is separated from other alkali metal carbonates by fractional crystallization (see Rubidium)

The carbonate salt also may be obtained by passing carbon dioxide through a solution of rubidium hydroxide in a fluorocarbon or nickel container. The solution is evaporated to yield the product carbonate.

Also, the salt may be prepared by adding ammonium carbonate to a solution of rubidium hydroxide. The solution is evaporated to dryness to expel ammonia.

Analysis

Rubidium may be analyzed in an aqueous solution of rubidium carbonate by AA, ICP-AES or other methods (see Rubidium). Carbonate anion, CO_3^{2-} may be measured quantitatively by ion chromatography. Additionally, CO_3^{2-} may be tested by treating Rb salt with a dilute acid. Liberation of CO_2 with effervescence that turns lime water milky is a qualitative test.

RUBIDIUM CHLORIDE

[7791-11-9]
Formula RbCl; MW 120.91

Uses

Rubidium chloride is used in preparing rubidium metal and many rubidium salts. Also, it is used in pharmaceuticals as an antidepressant and as a density-gradient medium for centrifugal separation of viruses, DNA, and large particles. Other applications are as an additive to gasoline to improve its octane number and as a catalyst.

Physical Properties

Colorless cubic crystals; refractive index 1.493 at 35°C; density 2.80 g/cm^3 at 25°C; density of liquid melt 2.088 g/mL at 750°C; melts at 718°C; vaporizes at 1,390°C; readily dissolves in water, solubility 77 g/100mL at 0°C and 139 g/100mL at 100°C; sparingly soluble in methanol, 1.41g/100mL at 25°C.

Thermochemical Properties

$\Delta H_f°$	–104.05 kcal/mol
$\Delta G_f°$	–97.5 kcal/mol
S°	22.9 cal/deg mol
C_ρ	12.5 cal/deg mol

Preparation

Rubidium chloride is prepared by adding hydrochloric acid to a solution of rubidium carbonate or hydroxide. The solution is evaporated to obtain well-defined colorless cubic crystals of rubidium chloride

$$RbOH + HCl \rightarrow RbCl + H_2O$$

$$Rb_2CO_3 + 2HCl \rightarrow 2RbCl + H_2O + CO_2$$

Analysis

Elemental analysis: Rb 70.68%, Cl 29.32%. Aqueous solution of rubidium chloride may be analyzed for rubidium by AA or ICP and for the chloride anion by ion chromatography or titration with a standard solution of silver nitrate using potassium chromate as indicator.

RUBIDIUM HYDROXIDE

[1310-82-3]
Formula RbOH; MW 102.475
Synonym: rubidium hydrate

Uses

Rubidium hydroxide is used as a catalyst in oxidative chlorination. It also may be used as a powerful base, stronger than caustic potash, in many preparative reactions. The compound holds promising applications as an electrolyte in storage batteries for use at low temperatures.

Physical Properties

Grayish-white orthogonal crystals; hygroscopic; density 3.2 g/cm^3; melts at 301°C; very soluble in water (100 g/100 mL at 15°C), the solution highly alkaline; soluble in ethanol.

Thermochemical Properties

$\Delta H_f°$	–96.6 kcal/mol

Preparation

Rubidium hydroxide may be obtained as an intermediate in recovering rubidium metal from mineral lepidolite (see Rubidium). In the laboratory it may be prepared by adding barium hydroxide to a solution of rubidium sulfate. The insoluble barium sulfate is separated by filtration:

$$Rb_2SO_4 + Ba(OH)_2 \rightarrow 2RbOH + BaSO_4$$

Preparation should be in nickel or silver containers because rubidium hydroxide attacks glass. The solution is concentrated by partial evaporation. The commercial product is usually a 50% aqueous solution.

Reactions

Rubidium hydroxide is a stronger base than caustic soda or caustic potash. Its reactions are similar to theirs. Neutralization occurs with acids. Rubidium hydroxide absorbs carbon dioxide forming rubidium carbonate.

Analysis

Rubidium may be analyzed by various instrumental methods (see Rubidium). The strength of solution may be measured by titration against a standard solution of strong acid using a color indicator or a potentiometer.

Toxicity

The compound or its aqueous solution is highly corrosive. Skin or eye contact can cause serious injury.

RUBIDIUM SULFATE

[7488-54-2]
Formula Rb_2SO_4; MW 267.00

Physical Properties

White orthogonal crystal; density 3.6 g/cm^3; melts at 1,050°C; very soluble in water, 36 g/100g at 0°C and 82 g/100g at 100°C.

Thermochemical Properties

$\Delta H_f°$	–343.1 kcal/mol
$\Delta G_f°$	–314.7 kcal/mol
S°	47.2 cal/deg mol
C_ρ	32.1 cal/deg mol

Preparation

Rubidium sulfate can be prepared by neutralization of a solution of rubidium hydroxide or carbonate with sulfuric acid:

$$2RbOH + H_2SO_4 \rightarrow Rb_2SO_4 + 2H_2O$$

$$Rb_2CO_3 + H_2SO_4 \rightarrow Rb_2SO_4 + H_2O + CO_2$$

Alternatively, Rb sulfate may be obtained by treating a hot solution of rubidium aluminum sulfate (rubidium alum) with ammonia solution. Aluminum hydroxide precipitates. The product mixture is filtered. The filtrate on evaporation crystallizes rubidium sulfate.

Analysis

An aqueous solution of the salt may be analyzed for rubidium by AA, ICP-AES and flame photometry, and for sulfate anion by ion chromatography. Rb sulfate in solution also may be measured by gravimetry after adding barium chloride to precipitate sulfate as barium sulfate, $BaSO_4$.

RUTHENIUM

[7440-18-8]
Symbol: Ru; atomic number 44; atomic weight 101.07; a Group VIII (Group 9) noble metal; electron configuration [Kr]$4d^75s^1$; valence states 0, +1, +2, +3, +4, +5, +6, +7, +8; most stable valence states +2, +3, +4; atomic radius 1.34Å; ionic radius, Ru^{8+} 0.36Å (for a coordination number 8); seven naturally-occurring stable isotopes: Ru-96 (5.53%), Ru-98 (1.89%), Ru-99 (12.71%), Ru-100 (12.61%), Ru-101 (17.01%), Ru-102 (31.62%), Ru-104 (18.72%); twenty artifi-

cial radioactive isotopes in the mass range 89-95, 97, 103, 105-115; longest-lived isotope Ru-106,$t_{1/2}$ 1.02 year; shortest-lived isotope Ru-114, $t_{1/2}$ 0.57 second

History, Occurrence, and Uses

Ruthenium was recognized as a new element by G.W. Osann in 1828. He found it in insoluble residues from aqua regia extract of native platinum from alluvial deposits in the Ural mountains of Russia. He named it *Ruthen* after the Latin name *Ruthenia* for Russia. The discovery of this element, however, is credited to Klaus who in 1844 found that Osann's ruthenium oxide was very impure and isolated pure Ru metal from crude platinum residues insoluble in aqua regia.

Ruthenium occurs in nature natively, found in minor quantities associated with other platinum metals. Its abundance in the earth's crust is estimated to be 0.001 mg/kg, comparable to that of rhodium and iridium.

Ruthenium alloyed to platinum, palladium, titanium and molybdenum have many applications. It is an effective hardening element for platinum and palladium. Such alloys have high resistance to corrosion and oxidation and are used to make electrical contacts for resistance to severe wear. Ruthenium–palladium alloys are used in jewelry, decorations, and dental work. Addition of 0.1% ruthenium markedly improves corrosion resistance of titanium. Ruthenium alloys make tips for fountain pen nibs, instrument pivots, and electrical goods. Ruthenium catalysts are used in selective hydrogenation of carbonyl groups to convert aldehydes and ketones to alcohols.

Physical Properties

Hard silvery-white metal; hexagonal close-packed crystal structure; density 12.41 g/cm^3 at 20°C; melts at 2,334°C; vaporizes at 4,150°C; electrical resistivity 7.1 microhm-cm at 0°C; hardness (annealed) 200-350 Vickers units; Young's modulus 3.0×10^4 tons/in^2; magnetic susceptibility 0.427 cm^3/g; thermal neutron absorption cross section 2.6 barns; insoluble in water, cold or hot acids, and aqua regia; can be brought into aqueous phase by fusion of finely divided metal with alkaline hydroxides, peroxides, carbonates and cyanides.

Thermochemical Properties

$\Delta H_f°$(cry)	0.0
$\Delta H_f°$(gas)	153.6 kcal/mol
$\Delta G_f°$(cry)	0.0
$\Delta G_f°$(gas)	142.4 kcal/mol
S°(cry)	6.82 cal/deg mol
S°(gas)	44.55 cal/deg mol
C_ρ(cry)	5.75 cal/deg mol
C_ρ(gas)	5.14 cal/deg mol
ΔH_{fus}	9.22 cal/deg mol
Thermal conductivity (at 27°C)	1.17 W/cmK
Coefficient of linear expansion (at 25°C)	6.4×10^{-6}/°C

Production

Ruthenium is derived from platinum metal ores. Method of production depends on the type of ore. However, the extraction processes are similar to those of other noble metals (see Platinum, Rhodium and Iridium). Ruthenium, like Rhodium, may be obtained from accumulated anode sludges in electrolytic refining of nickel or copper from certain types of ores. Also, residues from refining nickel by Mond carbonyl process contain ruthenium and other precious metals at very low concentrations. The extraction processes are very lengthy, involving smelting with suitable fluxes and acid treatments.

Metals, such as gold, platinum, and palladium, are separated by digesting refining residues with aqua regia. These metals are soluble in aqua regia, leaving ruthenium, rhodium, iridium, osmium, and silver in the insoluble residue.

The treatment of this insoluble residue may vary. In one typical process, residue is subjected to fusion with sodium peroxide. Ruthenium and osmium are converted to water-soluble sodium ruthenate and osmate, which are leached with water. The aqueous solution is treated with chlorine gas and heated. The ruthenate and the osmate are converted to their tetroxides. Ruthenium tetroxide is distilled out and collected in hydrochloric acid. The tetroxide is converted into ruthenium chloride. Traces of osmium are removed from ruthenium chloride solution by boiling with nitric acid.

Nitric acid converts osmium to volatile osmium tetroxide but forms a nitrosyl complex with ruthenium that remains in the solution. After removal of trace osmium, the solution is treated with ammonium chloride. This precipitates ruthenium as crystals of ammonium chlororuthenate, NH_4RuCl_6. The precipitate is washed, dried, and ignited to form ruthenium black. This is reduced with hydrogen at 1,000°C to form very pure ruthenium powder.

Reactions

When heated in air at 500 to 700°C, ruthenium converts to its dioxide, RuO_2, a black crystalline solid of rutile structure. A trioxide of ruthenium, RuO_3, also is known; formed when the metal is heated above 1,000°C. Above 1,100°C the metal loses weight because trioxide partially volatilizes.

Ruthenium also forms a tetroxide, RuO_4, which, unlike osmium, is not produced by direct union of the elements.

Halogens react with the metal at elevated temperatures. Fluorine reacts with ruthenium at 300°C forming colorless vapors of pentafluoride, RuF_5, which at ordinary temperatures converts to a green solid. Chlorine combines with the metal at 450°C to form black trichloride, $RuCl_3$, which is insoluble in water. Ru metal at ambient temperature is attacked by chlorine water, bromine water, or alcoholic solution of iodine.

Ruthenium is stable in practically all acids including aqua regia. Fusion with an alkali in the presence of an oxidizing agent forms ruthenate, RuO_4^{2-} and perruthenate, RuO_4^-.

When finely-divided Ru metal is heated with carbon monoxide under 200 atm pressure, ruthenium converts to pentacarbonyl, $Ru(CO)_5$, a colorless liquid that decomposes on heating to diruthenium nonacarbonyl, $Ru_2(CO)_9$, a yellow crystalline solid.

Ruthenium reacts with cyclopentadiene in ether to form a sandwich complex, a yellow crystalline compound, bis(cyclopentadiene) ruthenium(0), also known as ruthenocene.

Analysis

Ruthenium and its compounds are analyzed by flame AA method using nitrous oxide-acetylene flame. ICP-AES, ICP/MS, and neutron activation analysis are also applicable. The metal or its insoluble compounds may be solubilized by fusion with alkali and leached with water.

RUTHERFORDIUM

[53850-36-5]

Symbol Rf; atomic number 104; atomic weight 261; a man-made radioactive element; first transactinide element; a Group IV B (Group 4) element below hafnium in titanium subgroup; electron configuration $[Rn]6d^27s^2$; valence +4

The element was discovered in 1964 by the scientists at the Joint Nuclear Research Institute at Dubna, USSR, by accelerating neon ions of 113 to 115 MeV energy. They obtained an isotope of this new element having mass 260. The group proposed the name Kurchatovium for this new element in honor of Soviet physicist Igor Kurchatov. Attempts to synthesize this element by Ghiorso and group at Berkeley, California by the above method were not successful. In 1969, Ghiorso and his team obtained three isotopes of element 104 by bombardment of Californium-249 with high energy carbon-12 and carbon-13. The isotopes had mass 257, 258 and 259. The element is currently named Rutherfordium in honor of Ernest Rutherford.

Synthesis

The element was prepared first by bombardment of plutonium-242 with high energy neon ions:

$$^{242}_{94}\text{Pu} + ^{20}_{10}\text{Ne} \xrightarrow{113\text{-}115\text{MeV}} ^{260}_{104}\text{Rf} + 4\,^{1}_{0}\text{n}$$

Rutherfordium-257, -258 and -259 were produced by Ghiorso and his group by bombarding californium-249 with high energy carbon-12 and carbon-13 isotopes:

$$^{249}_{98}\text{Cf} + ^{12}_{6}\text{C} \xrightarrow{71\text{ MeV}} ^{257}_{104}\text{Rf} + 4\,^{1}_{0}\text{n}$$

$$^{249}_{98}\text{Cf} + ^{13}_{6}\text{C} \xrightarrow{69\text{ MeV}} ^{259}_{104}\text{Rf} + 3\,^{1}_{0}\text{n}$$

$$^{249}_{98}\text{C}f + ^{12}_{6}\text{C} \xrightarrow{69\text{ MeV}} ^{258}_{104}\text{R}f + 3\,^{1}_{0}\text{n}$$

The isotope Rf-257 has a half-life of 4.7 sec. It is an alpha-emitter decaying to nobelium-253. The isotopes Rf-258 and Rf-259 have the half-life of 12ms and 3.4 sec., respectively.

Rutherfordium is chemically similar to hafnium, the element above it in the same subgroup. The element has no commercial application.

SAMARIUM

[7440-19-9]

Symbol: Sm; atomic number 62; atomic weight 150.36; a lanthanide series inner transition element; a rare earth metal; electron configuration $[Xe]4f^66s^2$; partially-filled *f* orbitals; valence states +2, +3; atomic radius 1.804Å; ionic radius of Sm^{3+} 1.08Å (for coordination number 8); seven naturally-occurring isotopes: Sm-144 (3.11%), Sm-147 (15.02%), Sm-148 (11.31%), Sm-149 (13.81%), Sm-150 (7.41%), Sm-152 (26.72%), Sm-154 (22.72%); the isotopes 147, 148, 149 radioactive; twenty-two artificial radioactive isotopes in the mass range 131,133–143, 145–146, 151, 153, 155–160; longest-lived radioactive isotopes are naturally-occurring Sm-149, $t_{1/2}$ 10^{16} year and Sm-148, $t_{1/2}$ 7×10^{15} year; shortest-lived isotope Sm-131, $t_{1/2}$ 1.2 seconds

History, Occurrence, and Uses

The discovery of samarium is credited to Boisbaudran, who in 1879 separated its oxide, "samaria" from Mosander's "didymia," the mixture of rare earth oxides from which cerium and lanthanum were isolated earlier. Demarcay in 1901 first identified samaria to be a mixture of samarium and europium oxides. The element got its name from its mineral, samarskite. The mineral, in turn, was named in honor of the Russian mine official Col. Samarki.

Samarium occurs in nature widely distributed but in trace quantities, always associated with other rare earth metals. The two most important minerals are (i) monazite, which is an orthophosphate of thorium and the rare earths; and (ii) bastanasite, which is a rare earth fluocarbonate. The samarium content of these ores is about 2%, as oxide. It also is found in precambrian granite rocks, shales, and certain minerals, such as xenotime and basalt. Its abundance in the earth's crust is estimated to be 7.05 mg/kg.

Samarium salts are used in optical glass, capacitors, thermoionic generating devices, and in sensitizers of phosphors. The metal is doped with calcium fluoride crystals for use in lasers. It also is used along with other rare earths for carbon-arc lighting. Its alloys are used in permanent magnets.

Recovery

Samarium ore usually is digested with concentrated sulfuric or hydrochloric acid. The extraction process is similar to other lanthanide elements. Recovery of the metal generally consists of three basic steps. These are (1) opening the ore, (2) separation of rare earths first to various fractions and finally to their individual compounds, usually oxides or halides, and (3) reduction of the oxide or halide to pure metal. Although recovery of samarium involves mostly the same processes as other rare earth metals, the final reduction steps are quite different from most other metals. Commercial processes vary, depending on type and chemical nature of the ore, end product, purity desired, and cost. One such classical recovery process using monazite as the starting material is briefly mentioned below (Silvernail, W.L. Samarium. In *The Encyclopedia of Chemical Elements*, ed. C.A. Hampel, 1968. pp 616–620. New York: Reinhold.) At present, separation of rare earths is by methods based on ion exchange and solvent extraction.

The monazite sand is heated with sulfuric acid at about 120 to 170°C. An exothermic reaction ensues raising the temperature to above 200°C. Samarium and other rare earths are converted to their water-soluble sulfates. The residue is extracted with water and the solution is treated with sodium pyrophosphate to precipitate thorium. After removing thorium, the solution is treated with sodium sulfate to precipitate rare earths as their double sulfates, that is, rare earth sulfates-sodium sulfate. The double sulfates are heated with sodium hydroxide to convert them into rare earth hydroxides. The hydroxides are treated with hydrochloric or nitric acid to solubilize all rare earths except cerium. The insoluble cerium(IV) hydroxide is filtered. Lanthanum and other rare earths are then separated by fractional crystallization after converting them to double salts with ammonium or magnesium nitrate. The samarium–europium fraction is converted to acetates and reduced with sodium amalgam to low valence states. The reduced metals are extracted with dilute acid. As mentioned above, this fractional crystallization process is very tedious, time-consuming, and currently rare earths are separated by relatively easier methods based on ion exchange and solvent extraction.

Metallic samarium is obtained by heating the oxide, Sm_2O_3 with lanthanum turnings or cerium in slight excess amounts in a tantalum crucible under high vacuum. The metal is recovered by condensation of its vapors at 300 to 400°C. The metal cannot be obtained by reduction of its halides, SmF_3 or $SmCl_3$, or by heating with calcium or barium. In such reduction, trihalides are reduced to dihalides, but not to the metal.

Physical Properties

Hard yellow metal; exhibits two crystals forms: an alpha form having a rhombohedral crystal structure at ordinary temperatures; the alpha form converts to a body-centered cubic beta form at 917°C; density 7.52 g/cm^3 (alpha form) and 7.40 g/cm^3 (beta form) melts at 1,074°C; vaporizes at 1,791°C; ignites in air at 150°C; electrical resistivity 94 microhm-cm at 25°C; thermal neutron absorption cross section 5,600 barns; insoluble in water; soluble in acid.

Thermochemical Properties

$\Delta H_f°$(cry)	0.0
$\Delta H_f°$(gas)	49.4 kcal/mol
$\Delta G_f°$(cry)	0.0

ΔG_f°(gas)	41.3 kcal/mol
S°(cry)	16.6 cal/deg mol
S°(gas)	43.7 cal/deg mol
C_ρ(cry)	7.06 cal/deg mol
C_ρ(gas)	7.26 cal/deg mol
ΔH_{fus}	2.06 kcal/mol
ΔH_{subl} (at 25°C)	49.3 kcal/mol

Reactions

Samarium is stable in dry air at ordinary temperatures. However, it oxidizes in moist air forming an oxide coating. The metal ignites in air at about 150°C. It reacts with hydrogen, nitrogen, phosphorus, sulfur and carbon at elevated temperatures forming binary compounds. Samarium burns in halogen vapors at about 200°C forming halides.

Samarium reduces several metal oxides to metals. Such metal oxides include iron, zinc, lead, chromium, manganese, tin, and zirconium. When heated with carbon monoxide, it forms samarium oxide and carbon.

Samarium forms salts both in +3 and +2 oxidation states. The trivalent salts are more prevalent. Among the trivalent salts, the sesquioxide, Sm_2O_3 [12060-58-1], is commercially important. Other trivalent compounds include the pale yellow triclinic nitrate hexahydrate, $Sm(NO_3)_6 \cdot 6H_2O$, the yellow chromate octahydrate, $Sm_2(CrO_4)_3 \cdot 8H_2O$; the greenish yellow triclinic trichloride hexahydrate, $SmCl_3 \cdot 6H_2O$ [13456-55-9]; white crystalline oxalate decahydrate, $Sm_2(C_2O_4)_3 \cdot 10H_2O$; light yellow monoclinic sulfate octahydrate, $Sm_2(SO_4)_3 \cdot 8H_2O$ [13456-58-2]; violet orthorhombic molybdate, $Sm_2(MoO_4)_3$; and the pale yellow trihydroxide, $Sm(OH)_3$.

The divalent compounds of samarium primarily are halides, the reddish-brown crystalline dichloride, $SmCl_2$ [13874-75-4]; the dark-brown diiodide, SmI_2 [32248-43-4]; and the dark brown dibromide, $SmBr_2$ [50801-97-3]. Samarium also forms a difluoride, SmF_2 [15192-17-3]. The trivalent salts of these halogens are more stable than their divalent counterparts.

Analysis

Samarium may be analyzed by spectrographic and spectrophotometric methods. In solution, the trivalent samarium shows sharp and intense absorption bands at 362.5, 347.5 and 402.0 nm. Trace analysis may be carried out most accurately by flame AA, ICP-AES, ICP/MS and neutron activation analysis. ICP/MS is the most sensitive method. The metal and its insoluble salts may be solubilized by digestion with acids and diluted appropriately for most instrumental measurements.

SAMARIUM SESQUIOXIDE

[12060-58-1]
Formula Sm_2O_3; MW 348.72
Synonyms: samarium(III) oxide, samarium oxide; samaria

Uses

Samarium sesquioxide is used in optical and infrared absorbing glass to absorb infrared radiation. Also, it is used as a neutron absorber in control rods for nuclear power reactors. The oxide catalyzes dehydration of acyclic primary alcohols to aldehydes and ketones. Another use involves preparation of other samarium salts.

Physical Properties

Yellowish-white powder; density 8.347g/cm³; insoluble in water; dissolves readily in mineral acids.

Thermochemical Properties

$\Delta H_f°$	–435.7 kcal/mol
$\Delta G_f°$	–414.6 kcal/mol
S°	36.1cal/deg mol
C_ρ	27.4cal/deg mol

Preparation

Samarium sesquioxide may be prepared by two methods; (1) thermal decomposition of samarium carbonate, hydroxide, nitrate, oxalate or sulfate:

$$Sm_2(CO_3)_3 \rightarrow Sm_2O_3 + 3CO_2$$

$$2Sm(OH)_3 \rightarrow Sm_2O_3 + 3H_2O$$

or (2) by burning the metal in air or oxygen at a temperature above 150°C:

$$4Sm + 3O_2 \rightarrow 2Sm_2O_3$$

Reactions

Samarium sesquioxide dissolves in mineral acids, forming salts upon evaporation and crystallization:

$$Sm_2O_3 + 6HCl \rightarrow 2SmCl_3 + 3H_2O$$

$$Sm_2O_3 + 6HNO_3 \rightarrow 2Sm(NO_3)_3 + 3H_2O$$

$$Sm_2O_3 + 3H_2SO_4 \rightarrow Sm_2(SO_4)_3 + 3H_2O$$

Salts obtained upon crystallization are the hydrated salts, $SmCl_3 \cdot 6H_2O$, $Sm(NO_3)_3 \cdot 6H_2O$ and $Sm_2(SO_4)_3 \cdot 8H_2O$

The oxide is reduced to metallic samarium by heating with a reducing agent, such as hydrogen or carbon monoxide, at elevated temperatures:

$$Sm_2O_3 + 3H_2 \rightarrow 2Sm + 3H_2O$$

Analysis

Elemental composition: Sm 86.24%, O 13.76%. The oxide may be dissolved in a mineral acid, diluted, and analyzed by flame AA or ICP-AES. Also the oxide can be characterized nondestructively by x-ray diffraction.

SCANDIUM

[7440-20-2]
Symbol Sc; atomic number 21; atomic weight 44.956; a Group III B (Group 3) transition metal; electron configuration $[Ar]3d^14s^2$; valence state +3; atomic radius 1.62Å; ionic radius Sc^{3+} 0.75Å (for coordination number 6); ionization potential ($Sc \rightarrow Sc^{3+}$) 24.76 eV; one naturally-occurring isotope scadium-45; fifteen artificial radioactive isotopes in the mass range 40–44 and 46–55; the longest–lived radioisotope Sc-46, $t_{1/2}$ 83.8 days; shortest-lived isotope Sc-40, $t_{1/2}$ 0.18 second,

History, Occurrence, and Uses

The existence of scandium was predicted in 1871by Mendeleev, who placed it under boron in Group III of his Periodic Table. He called it *ekaboron*. Five years later Lars Nilson of Sweden discovered this new element while examining the ore euxenite. Nilson named this element scandium after his homeland Scandinavia. Metallic scadium was preparaed first by Fisher, Brunger, and Grieneisen in 1937 by an electrolytic process.

Scadium occurs in nature, very widely dispersed in low concentrations. It is found in most soils and numerous minerals in very minute quantities. The principal minerals are wolframite, euxenite, wiikite, bazzite, cassiterite, gadolinite, and throtveitite. Its abundance in the earth's crust is estimated to be 22 mg/kg. The element also has been detected in the sun and other stars.

The metal is used to produce high intensity lights. Its iodide is added to mercury vapor lamps to form very bright indoor lights. Radioactive scadium-46 is used as a tracer for crude oil.

Physical Properties

Silvery white metal; soft and light; turns slightly yellow when exposed to air; density 2.99 g/cm^3; exhibits two allotropic modifications: a hexagonal close-packed structure stable up to 1,335°; transforms to body-centered cubic form above 1,335°C, having a density 3.19 g/cm^3; melts at 1,541°C; vaporizes at 2,831°C; electrical resistivity 56.2×10^{-6} ohm-cm; thermal neutron absorption cross section 24 ± l barns; decomposes in water.

Thermochemical Properties

$\Delta H_f°$(cry	0.0
$\Delta H_f°$(gas)	90.3 kcal/mol
$\Delta G_f°$ (cry)	0.0
$\Delta G_f°$ (gas)	80.3 kcal/mol
S°(cry)	8.28 cal/deg mol

S°(gas)	41.8 cal/deg mol
C_ρ(cry)	6.10 cal/deg mol
C_ρ(gas)	5.28 cal/deg mol
ΔH_{fus}	3.37 kcal/mol
Thermal conductivity(at 27°C)	0.158 W/cmK
Coefficent of linear expansion (at 25°C)	10.2×10^{-6}/°C

Recovery

Scandium mostly is extracted from its ore thortveitite, $(Sc,Y)_2Si_2O_7$, which has the highest scandium content among the ores. The scandium content in this ore usually varies between 30 to 40% as Sc_2O_3. The ore also contains about 46% SiO_2, 9.5% heavy rare earths, 5% Al_2O_3, 3% Fe_2O_3, 1.5% light rare earths, and smaller amounts of oxides of manganese, calcium, magnesium, thorium, hafnium, and zirconium.

The ore thortveitite is crushed and powdered. It is mixed with a large excess of ammonium hydrogen fluoride and heated at about 400°C for several hours in a platinum container under a stream of dry air. Silica is converted to volatile silicon tetrafluoride and swept out with dry air. Scandium oxide is converted to scandium trifluoride, ScF_3:

$$Sc_2O_3 + 6NH_4HF_2 \rightarrow 2ScF_3 + 6NH_4F + 3H_2O$$

All other metals also are converted to their fluorides. The fluoride mixture is heated at 1,400°C in a tantalum crucible in an inert atmosphere. This produces a scadium-rich alloy phase constituting about 70% Sc and calcium fluoride slag:

$$2ScF_3 + 3Ca \rightarrow 3CaF_2 + 2Sc$$

Treatment with hydrochloric acid dissolves scandium and other metals. The solution is treated with sodium thiocyanate and extracted with ether. Scandium converted to its oxide Sc_2O_3 is separated from the solvent extract by ion exchange.

The ore thortveitite may be cracked by fusion with sodium carbonate or by heating with hydrofluoric acid. In a series of steps, scandium is precipitated as hydroxide or oxalate, which on thermal decomposition forms lower yield of oxide. This recovery, however, is tedious and is now obsolete.

Scandium also is obtained as a by-product of processing uranium ores, although they contain only traces of the metal.

In most recovery processes, scandium oxide is converted to its fluoride salt. The fluoride salt is the end product. The fluoride is converted to metallic scandium by heating with calcium in a tantalum crucible at elevated temperatures. A similar reduction is carried out with most rare earths. The metal is purified by distillation at 1,650 to 1,700°C under high vacuum in a tantalum crucible.

Scandium also may be produced by electrolysis of scadium chloride in a molten salt bath. The first preparation of the metal was carried out by this electrolysis using an eutectic melt of lithium and potassium chlorides with scandium chloride at 700 to 800°C. Electrolysis methods usually yield impure metal containing mostly iron, silicon and other impurities.

Reactions

Scandium reacts with oxygen forming its only oxide, Sc_2O_3. The reaction is slow on bulk metal at ordinary temperatures but rapid above 500°C.

The metal reacts with water liberating hydrogen. The reaction is slow at ambient temperatures:

$$2Sc + 6H_2O \rightarrow 2Sc(OH)_3 + 3H_2$$

Scandium metal reacts rapidly with most acids liberating hydrogen and forming salts upon evaporation of the solution. Scandium, however, is not attacked by 1:1 mixture of concentrated nitric acid and 48% hydrofluoric acid. A similar behavior is exhibited by yttrium and heavy rare earth metals.

Scandium forms all its compounds in 3+ oxidation state. This is the only valence known for the metal. These compounds include the oxide, Sc_2O_3; hydroxide, $Sc(OH)_3$; chloride, $ScCl_3$; fluoride, ScF_3; sulfate, $Sc_2(SO_4)_3$, and the nitrate salt, $Sc(NO_3)_3$.

SELENIUM

[7782-49-2]

Symbol Se; atomic number 34; atomic weight 78.96; a Group VI A (Group 16) metallic element in the oxygen group of elements; electron configuration $[Ar]3d^{10}4s^24p^4$; valence states –2, +4, +6; atomic radius 1.19Å; ionic radius, Se^{4+} 0.50Å (for CN 6); Se^{6+} 0.42Å (for CN 6); six naturally-occurring isotopes: Se-74 (0.89%), Se-76 (9.36%), Se-77 (7.64%), Se-78 (23.79%), Se-80 (49.61%), Se-82 (8.74%); nineteen radioactive isotopes in the mass range 65, 67–73, 75, 79, 81, 83–89, 91

History, Occurrence, and Uses

Selenium was discovered by Berzelius and Gahn in1817 while investigating the lead chamber process for making sulfuric acid. They initially believed that the bottom of the lead chamber generating an offensive odor was due to presence of tellurium, a sulfur group element that was discovered thirty-five years earlier. Further studies indicated a new element, the chemical properties of which were very similar to tellurium. This new element was named selenium, derived from the Greek word *selene*, meaning moon. The name followed *tellus*, the Latin word for earth given to tellurium which chemically resembled the new element. Willoughby Smith in 1873 discovered photoresistivity in this metal; i.e., as the intensity of light exposure on the metal increased, its current resistance decreased.

Selenium is a very rare element. The metal does not occur in nature in free elemental form. Its abundance in the earth's crust is about 0.05 mg/kg. It occurs in certain copper ores and sometimes with native sulfur. Some selenium containing minerals are eucairite, CuAgSe; clausthalite, PbSe; naumannite, Ag_2Se; crookesite, $(CuTlAg)_2Se$; and zorgite, PbCuSe.

Selenium has many industrial uses, particularly electronic and solid-state applications, which have increased phenomenally in recent years. This is attributed to its unique properties: (1) it converts light directly to electricity (photovoltaic action); (2) its electrical resistance decreases with increased illumination (photoconductivity); and (3) it is able to convert alternating current to direct current.

Selenium is used in photoelectric cells, solar cells, and as a rectifier in radio and television sets. It also was used historically in exposure meters in photography and as an ingredient of toning baths. It is used in photocopying documents. In the glass industry it is incorporated to pigments to color pink, orange, and ruby-red glass. Other applications are as a metallic base in preparing electrodes for arc light; as an additive to stainless steel; in chrome plating bath for inducing microcracks for corrosion control; in vulcanization of rubber; as a catalyst; and as a flame-proofing agent for electric switchboard cables.

Although a toxic metal, selenium in trace amounts is a nutritional element. Trace amounts added to cattle food are effective against muscular dystrophy in sheep and cattle.

Physical Properties

Selenium exists in several allotropic forms. Three distinct forms are (1) amorphous (2) crystalline and (3) metallic:

Amorphous forms exhibit two colors, occurring as a red powder of density 4.26g/cm^3 that has a hexagonal crystal structure and a black vitreous solid of density 4.28g/cm^3. The red amorphous selenium converts to the black form on standing. Amorphous selenium melts at 60 to 80°C; insoluble in water; reacts with water at 50°C when freshly precipitated; soluble in sulfuric acid, benzene and carbon disulfide.

Crystalline selenium exhibits two monoclinic forms: an alpha form constituting dark red transparent crystals, density 4.50 g/cm^3. The alpha form converts to a metastable beta form of hexagonal crystal structure when heated to about 170°C. Both the crystalline forms are insoluble in water; soluble in sulfuric and nitric acids; very slightly soluble in carbon disulfide. Also, both the crystalline forms convert into gray metallic modification on heating.

The gray metallic form of selenium is its most stable modification. It constitutes lustrous gray to black hexagonal crystals; density 4.18 g/cm^3 at 20°; melts at 217°C; soluble in sulfuric acid and chloroform; very slightly soluble in carbon disulfide; insoluble in alcohol.

All forms of selenium vaporize at 684.8°C.

Thermochemical Properties

$\Delta H_f°$(cry) (hexagonal, black)	0.0
$\Delta H_f°$(cry) (monoclinic, black)	1.6 kcal/mol
$\Delta H_f°$(amorphous, glassy)	1.2 kcal/mol

$\Delta H_f°$(gas)	54.3 kcal/mol
$\Delta G_f°$(cry)	0.0
$\Delta G_f°$(gas)	44.7 kcal/mol
S°(cry) (hexagonal,black)	10.1cal/deg mol
S°(gas)	42.2cal/deg mol
C_ρ(cry) (hexagonal,black)	6.06cal/deg mol
C_ρ(gas)	4.98cal/deg mol

Production

Selenium is recovered from anode muds or slimes in electrolytic refining of copper. Anode mud is treated with sulfuric acid and roasted. Selenium is converted to its dioxide, which vaporizes and is collected in a wet scrubber system.

Alternatively, raw anode slimes are aerated with hot dilute sulfuric acid to remove copper. Slimes are then mixed thoroughly with sodium carbonate and roasted in the presence of sufficient air. Sodium selenate formed is leached with water. Hydrochloric acid is added to this selenate solution. Treatment with sulfur dioxide precipitates elemental selenium. Alternatively, the selenate solution is evaporated to dryness. Sodium selenate is reduced to sodium selenide by heating with carbon at high temperatures. Sodium selenide is leached with water. Air is blown over the solution. Selenide is oxidized to elemental selenium which precipitates.

In another process known as soda-niter smelting, a slight variation of the above method, after removal of copper anode slimes are mixed with sodium carbonate and silica and charged to the furnace. First, slags are removed. To the molten mass, caustic soda and potassium nitrate are added. Selenium and tellurium separate into the slags. The slags are cooled, crushed, and leached with water. Sulfuric acid is added. This precipitates tellurium as dioxide. Sulfur dioxide is then passed through the solution precipitating elemental selenium.

Selenium obtained by the above methods is about 99% pure. High purity metal may be obtained by refining this commercial grade material. Commercial grade selenium is distilled to form highly purified metal. Another refining method involves melting the crude metal and bubbling hydrogen through it. Hydrogen selenide so formed is decomposed at 1,000°C. A third method involves oxidizing selenium to its dioxide and reducing the latter with ammonia at 600 to 800°C.

Selenium was recovered earlier from flue dusts from lead and copper sulfide ores. This process is now obsolete and no longer used.

Reactions

The chemical properties of selenium fall between sulfur and tellurium. Thus, selenium reacts with oxygen similarly to sulfur, forming two oxides, selenium dioxide, SeO_2 and trioxide, SeO_3. The metal combines with halogens forming their halides. With nonmetals, selenium forms binary compounds exhibiting oxidation states +4 and +6.

Selenium reacts with electropositive metals and hydrogen forming selenides, where its oxidation state is –2. Thus, it combines with sodium to form sodium selenide, Na_2Se. When the metal is heated with hydrogen below 250°C, the product is hydrogen selenide, H_2Se.

The metal is not attacked by hydrochloric acid, nor does it react with dilute nitric and sulfuric acids. High purity selenium reacts slowly with concentrated nitric acid. The crude metal, however, dissolves in cold concentrated nitric acid.

When fused with caustic soda or caustic potash, sodium selenate, or potassium selenate, Na_2SeO_4, or K_2SeO_4 is obtained.

Molten selenium combines with most metals forming selenides. Such metal selenides include Ag_2Se, Cu_2Se, HgSe, ZnSe, CdSe, PbSe, FeSe, $FeSe_2$, and Sb_2Se_3.

Selenium dissolves in sulfur and tellurium in all proportions.

Analysis

Selenium is converted to its volatile hydride by reaction with sodium borohydride, and the cold hydride vapor is introduced to flame AA for analysis. Alternatively, selenium is digested with nitric acid and 30% H_2O_2, diluted and analyzed by furnace-AA spectrophotometer. The metal also may be analyzed by ICP-AES or ICP/MS. The wavelengths most suitable for its measurements are 196.0 nm for flame- or furnace-AA and 196.03 nm for ICP-AES. Selenium also may be measured by neutron activation analysis and x-ray fluorescence.

Selenite in aqueous solution can be measured by colorimetric or fluorometric methods. Selenite reacts with 2, 3-diaminonaphthalene to form a brightly colored fluorescent derivative that is extracted with hexane. The absorbance can be measured by a spectrophotometer at 480 nm, or the fluorescence may be measured by a fluorometer at 525 nm.

Toxicity

Although an essential nutrient metal at trace concentrations, selenium is highly toxic at moderate concentrations. Some of its compounds, such as hydrogen selenide, are very toxic. Exposure to Se metal fumes can cause severe irritation of eyes, nose and throat. The metal is listed by the US EPA as one of the priority pollutant metals in the environment.

SELENIUM DIOXIDE

[7446-08-4]
Formula SeO_2; MW 110.96
Synonyms: selenium oxide; selenious anhydride

Uses

Selenium dioxide is used to make other selenium compounds and as an oxidizing agent.

Physical Properties

White tetragonal crystals; acidic taste; leaves a burning sensation; density 3.95 g/cm^3; sublimes at 315°C forming greenish yellow vapors with a sour and pungent odor; melts at 340 to 350°C; vapor pressure 12.5 torr at 70°C; soluble in water, 38.4 g/100mL at 14°C; highly soluble in hot water 82.5 g/100mL at 65°C; soluble in benzene; moderately soluble in ethanol and acetone 6.7 and 4.4g/100mL solvent, respectively, at 15°C; sparingly soluble in acetic acid (1.11g/100mL at 14°C).

Thermochemical Properties

$\Delta H_f°$ (cry)	–53.86 kcal/mol
$\Delta H_f°$ (aq)	–52.97 kcal/mol

Preparation

Selenium dioxide is obtained by burning selenium metal in oxygen:

$$Se + O_2 \rightarrow SeO_2$$

Selenium also forms a trioxide, SeO_3. In excess oxygen the product mixture may contain both dioxide and trioxide. The trioxide is unstable.

Selenium dioxide may be prepared by heating selenium with oxygen and nitrogen dioxide. Presence of excess oxygen would oxidize nitrogen dioxide to pentoxide, instead converting selenium dioxide to trioxide:

$$2Se + 3O_2 + 4NO_2 \rightarrow 2SeO_2 + 2N_2O_5$$

Selenium dioxide also may be produced by oxidation of selenium by nitric acid. The overall reaction may be written as follows:

$$Se + 2HNO_3 \rightarrow SeO_2 + H_2O + NO_2 + NO$$

Reactions

Selenium dioxide is reduced to selenium metal when heated with carbon and other reducing agents.

When heated with ammonia, selenium dioxide forms selenium, nitrogen and water:

$$3SeO_2 + NH_3 \rightarrow 3Se + 2N_2 + 6H_2O$$

Ammonia reacts with selenium dissolved in ethanol to form ammonium ethyl selenite, $NH_4(C_2H_5)SeO_3$.

Reaction with nitric acid forms selenic acid:

$$Se + 2HNO_3 \rightarrow H_2SeO_4 + 2NO$$

Selenium dioxide is reduced by hydrazine to black amorphous selenium:

$$SeO_2 + N_2H_4 \rightarrow Se + N_2 + 2H_2O$$

Hydroxylamine hydrochloride reduces selenium dioxide to reddish-brown amorphous selenium:

$$SeO_2 + 4NH_2OH\cdot HCl \rightarrow Se + 2N_2 + 6H_2O + 4HCl$$

The dioxide rapidly absorbs hydrogen halides, forming selenium oxyhalides:

$$SeO_2 + HBr \rightarrow SeOBr_2 + H_2O$$

Reaction with thionyl chloride yields selenium oxychloride:

$$SeO_2 + SOCl_2 \rightarrow SeOCl_2 + SO_2$$

Analysis

Elemental composition: Se 71.16% O 28.84%. Aqueous solution may be analyzed for selenium metal by flame or furnace-AA or ICP-AES. A benzene or acetone solution may be analyzed directly by GC/MS. The characteristic mass ions for its identification should be 112, 110, 108, 80, and 78.

Toxicity

The compound is toxic by ingestion. Symptoms of the poisoning effects of selenium dioxide are similar to those of selenium metal. Selenium dioxide vapors are highly irritating to eyes, nose and respiratory tract.

SELENIUM HEXAFLUORIDE

[7783-79-1]
Formula SeF_6; MW 192.95

Uses

The hexafluoride is a gaseous insulator in electrical works.

Physical Properties

Colorless gas; refractive index 1.895; density 3.25 g/L at –28°C; liquefies at –34.5°C; freezes at –50.8°C; sublimes at –63.8°C; insoluble in water

Thermochemical Properties

$\Delta H_f°$	–267.0 kcal/mol
$\Delta G_f°$	–243.0 kcal/mol
S°	75.0cal/deg mol
C_ρ	26.4cal/deg mol

Preparation

Selenium hexafluoride is prepared by passing fluorine gas over finely divided selenium in a copper vessel:

$Se + 3F_2 \rightarrow SeF_6$

Analysis

Elemental composition: Se 40.92%, F59.08%. The gas may be dissolved in nitric acid and dilute hydrofluoric acid and the solution appropriately diluted and analyzed for selenium (see Selenium). The hexafluoride may be decomposed with ammonia at 200°C and product selenium analyzed by AA, and gaseous products nitrogen and hydrogen fluoride diluted with helium and analyzed by GC-TCD or GC/MS. Alternatively, selenium hexafluoride diluted with helium is introduced onto the GC injector port and analyzed by GC/MS. Molecular ions have masses 194, 192, 196, and 190.

SELENIUM OXYCHLORIDE

[7791-23-3]
Formula $SeOCl_2$; MW 165.85
Synonym: selenyl chloride

Uses

Selenium oxychloride is a solvent for synthetic phenolic resins and many other substances.

Physical Properties

Pale yellow or colorless liquid; corrosive; refractive index 1.651 at 20°C; density 2.42 g/mL at 22°C; freezes at 8.5°C; boils at 176.4°C; decomposes at 176.4°C; decomposes in water forming hydrochloric acid and selenious acid; soluble in carbon disulfide, carbon tetrachloride, chloroform, benzene, and toluene.

Preparation

Selenium oxychloride may be prepared by several methods: (1) by passing chlorine gas into a suspension of selenium dioxide in carbon tetrachloride, (2) by heating thionyl chloride, $SOCl_2$, with selenium dioxide, (3) by dehydration of dichloroselenious acid, $H_2Se(Cl_2)O_2$, and (4) by fusion of selenium dioxide, selenium, and calcium chloride.

Analysis

Elemental composition: Se 47.60%, Cl 42.75%, O 9.65%. The compound is decomposed by water and the solution analyzed for selenium (see Selenium). The oxychloride may be mixed with a suitable organic solvent such as toluene or methylene chloride, diluted appropriately with the solvent, and analyzed by GC/MS. The characteristic mass ions (molecular ions) for identification are 166, 164, 170, and 168. Other mass ions are 80, 78, 150, and 148.

Toxicity

The oxychloride is a strong irritant to skin. Eye contact can damage vision.

The compound is highly toxic by ingestion and inhalation.

SILICON

[7440-21-3]
Symbol Si; atomic number 14; atomic weight 28.086; a Group IV (Group 14) carbon family element; electron configuration $[Ne]3s^23p^2$; valence +4; atomic radius 1.173Å; electronegativity 1.8; three naturally-occurring stable isotopes: Si-28(92.23%), Si-29(4.67%), Si-30 (3.10%); twelve artificial radioactive isotopes in the mass range 24–27, 31–38; longest-lived radioisotope Si-32, a beta-emitter with a half-life 160 years.

History, Occurrence, and Uses

Gay Lussac and Thenard in 1809 obtained very impure amorphous silicon by passing silicon tetrafluoride over heated potassium. Berzelius in 1823 prepared elemental silicon in high purity by the same method. He also obtained silicon by heating potassium fluosilicate with potassium metal. Deville produced crystalline silicon in 1854 by electrolysis of a molten mixture of impure sodium aluminum chloride containing 10% silicon and a small quantity of aluminum.

Silicon is the second most abundant element on earth after oxygen. It occurs in nature combined with oxygen in various forms of silica and silicates. Silicates have complex structures consisting of SiO_4 tetrahedral structural units incorporated to a number of metals. About 90% of the earth's crust is made up of silica and naturally-occurring silicates. Silicon is never found in nature in free elemental form. Among all elements silicon forms the third largest number of compounds after hydrogen and carbon. There are well over 1,000 natural silicates including clay, mica, feldspar, granite, asbestos, and hornblende. Such natural silicates have structural units containing orthosilicates, SiO_4^{4-}, pyrosilicates $Si_2O_7^{6-}$ and other complex structural units, such as, $(SiO_3)_n^{2n-}$ that have hexagonal rings arranged in chains or pyroxenes $(SiO_3^{2-})_n$ and amphiboles, $(Si_4O_{11}^{6-})_n$ in infinite chains. Such natural silicates include common minerals such as tremolite, $Ca_2Mg_5(OH)_2Si_8O_{22}$; diopside, $CaMg(SiO_3)_2$; kaolin, $H_8Al_4Si_4O_{18}$; montmorillonite, $H_2Al_2Si_4O_{12}$; talc, $Mg_3[(OH)_2\ SiO_{10}]$; muscovite (a colorless form of mica), $H_2KAl_3(SiO_4)_3$; hemimorphite, $Zn_4(OH)_2Si_2O_7 \cdot H_2O$; beryl, $Be_3Al_2Si_6O_{18}$; zircon, $ZrSiO_4$; benitoite, $BaTiSi_3O_9$; feldspars, $KAlSi_3O_8$; zeolites, $Na_2O \cdot 2Al_2O_3 \cdot 5SiO_2 \cdot 5H_2O$; nephrite, $Ca(Mg,Fe)_3(SiO_3)_4$; enstatite, $(MgSiO_3)_n$; serpentine, $H_4Mg_3Si_2O_9$; jadeite, $NaAl(SiO_3)_2$; topaz, $Al_2SiO_4F_2$; and tourmaline, $(H,Li,K,Na)_9\ Al_3(BOH)_2Si_4O_{19}$. Many precious gemstones are silicate based. Such gems include beryl, emerald, aquamarine, morganite, topaz, tourmaline, zircon, amazon stone and moonstone.

Silica, the other most important class of silicon compounds, exists as sand, quartz, flint, amethyst, agate, opal, jasper, and rock crystal. It is discussed separately under Silicon Dioxide. Silicates and silica have many applications in numerous fields. They are used in making cements and concretes for building materials, glasses and glasswares, ceramics, pigments, adsorbents, paper boards, fillers, detergents, precious gems, catalysts, and water-softeners. Ferrosilicon, an important alloy of iron and silicon, is used as an alloying agent in the manufacture of steel and as a reducing agent in the preparation of magnesium, chromium and other metals. Silicones, or the organosilicon oxide polymers consisting of the structural unit $-R_2Si-O-$ are used as lubricants; and in making rubbers, plastics, electrical coatings, adhesives, paints and varnishes; and as water repellents for textiles, papers and concrete.

Elemental silicon has some of the most important applications in this electronic age. One of the major applications is in computer chips. The single crystals of crystalline silicon are used for solid-state or semiconductor devices.

Silicon of hyperpurity, doped with trace elements, such as boron, phosphorus, arsenic, and gallium is one of the best semiconductors. They are used in transistors, power rectifiers, diodes and solar cells. Silicon rectifiers are most efficient in converting a-c to d-c electricity. Hydrogenated amorphous silicon converts solar energy into electricity.

Physical Properties

Exists in two allotropic modifications. Crystalline silicon is made up of grayish-black lustrous needle-like crystals or octahedral platelets; cubic structure; Amorphous silicon is a brown powder. Other physical properties are: density 2.33g/cm^3 at 25°C; melts at 1,414°C; high purity liquid silicon has density 2.533 g/cm^3 at its melting point; vaporizes at 3,265°C; vapor pressure 0.76 torr at 2,067°C; Mohs hardness 6.5. Brinell hardness 250; poor conductor of electricity; dielectiric constant 13; critical temperature 4°C; calculated critical pressure 530 atm; magnetic susceptibility (containing 0.085%Fe) 0.13×10^{-6}; insoluble in water; dissolves in hydrofluoric acid or a mixture of hydrofluoric and nitric acids; soluble in molten alkalies.

Thermochemical Properties

$\Delta H_f°$(cry)	0.0
$\Delta H_f°$(amor)	1.0 kcal/mol
$\Delta H_f°$(gas)	108.9 kcal/mol
$\Delta G_f°$(cry)	0.0
$\Delta G_f°$(gas)	98.3 kcal/mol
S°(cry)	4.50 cal/deg mol
S°(gas)	40.12 cal/deg mol
C_ρ(cry)	4.78 cal/deg mol
C_ρ(gas)	5.32 cal/deg mol
ΔH_{fus}	12.08 kcal/mol
Thermal conductivity(at 25°C)	0.835 W/cmK
Coefficient of linear expansion (at 25°C)	3.0×10^{-6}/°C

Production

Elemental silicon is produced commercially by heating silica with carbon (coke) in an electric furnace using carbon electrodes:

$$SiO_2 + C \rightarrow Si + CO_2$$

The product obtained is about 96 to 98% purity. Repeated leaching forms about 99.7% purified product. Alternatively, lower grade silicon is converted to its halide or halosilane, which is then reduced with a high purity reducing agent. Hyperpure silicon for semiconductor applications can be made by several methods. Such processes include reduction of silicon tetrachloride with highly pure zinc:

$$SiCl_4 + 2Zn \rightarrow Si + 2ZnCl_2$$

or by reducing trichlorosilane with hydrogen at 1,150°C using a silicon filament on which deposition of silicon occurs:

$$SiHCl_3 + H_2 \rightarrow Si + 3HCl$$

or by heating silane or silicon tetraiodide to elevated temperatures:

$$SiH_4 \rightarrow Si + 2H_2$$

$$SiI_4 \rightarrow Si + 2I_2$$

or by reducing silicon tetrafluoride with sodium:

$$SiF_4 + 4Na \rightarrow Si + 4\ NaF$$

Several processes are known to achieve growth of single crystals of silicon for semiconductors. One such method developed in 1918 is known as Czocharlski process or Teal-Little method. The process involves dipping a single crystal "seed" into molten silicon held at the melting point. The seed is properly oriented by rotation and the molten silicon is allowed to freeze gradually over it and the seed is slowly withdrawn. The growth rate is controlled by melt temperature and heat losses from the crystal. Growth rates are usually in the range of 2.5 cm/hour but can vary with diameter. Crystals of varying sizes have been produced by this method. The common sizes of crystals usually range between 75 to 125 mm in diameter and about 100 cm long. Pure quartz crucibles or silicon pedestals are employed to carry out single crystal's growth.

Reactions

Elemental silicon is relatively stable in most substances at ordinary temperatures. Silicon shows similarity with other elements of its group, especially with germanium in many chemical properties. It forms tetravalent compounds with tetrahedral geometry almost exclusively. However, only in silicon monoxide, SiO, is its valence +2. Also, unlike carbon, silicon does not form unsaturated double or triple bond compounds. Silicon dissolves in germanium in all proportions but is not miscible with tin or lead. When heated with carbon at elevated temperatures in an electric furnace, silicon carbide, SiC, or carborundum is obtained. The carbide, however, is made in commercial scale from silica. The Si–Si bond having bond energy 42.5 kcal/mol is weaker than the C–C bond, which has a bond energy 58.6 kcal/mol. The latter is comparable to Si–C bond (57.6 kcal/mol). Similarly Si–H bond (energy 75.1 kcal/mol) is weaker than the C–H bond (87.3 kcal/mol). On the other hand Si–O bond (89.3 kcal/mol) is stronger than the C–O bond (70.0 kcal/mol).

Silicon forms two oxides, silica or the dioxide, SiO_2, and a divalent monoxide, SiO. The latter is obtained by heating silica with elementary silicon at 1,450°C in vacuum. Silicon sublimes as its monoxide, which on rapid cooling forms light brown amorphous SiO:

$$SiO_2 + Si \rightarrow 2\,SiO$$

At ordinary temperatures, the metal surface is coated with a very fine thin amorphous film of its dioxide, about 2 to 3 nm thick. Silicon combines with oxygen forming innumerable silicates. A few silicates have been mentioned above.

Silicon combines with halogens at elevated temperatures forming silicon tetrahalides. With chlorine, reaction occurs at 450°C forming silicon tetrachloride, $SiCl_4$. The tetrahalides also are obtained when silicon is heated with anhydrous hydrogen chloride, bromide and iodide:

$$Si + 4HCl \rightarrow SiCl_4 + 2H_2$$

With hydrogen fluoride, the products are fluosilicic acid, H_2SiF_6, and hydrogen:

$$Si + 6HF \rightarrow H_2SiF_6 + 2H_2$$

When heated with nitrogen at a temperature above 1,300°C, silicon nitride is produced:

$$3Si + 2N_2 \rightarrow Si_3N_4$$

With hydrogen, a series of silanes having a general formula Si_nH_{2n+2} are obtained. Silicon forms binary silicides with several metals when heated at very high temperatures.

Silicon reacts with strong bases forming silicates and liberating hydrogen. Silicon is attacked by hydrofluoric acid if there is no oxide layer over it. However, since the metal has a very thin oxide film over its surface, a mixture of nitric and hydrofluoric acid is effective in dissolution of the metal. While nitric acid dissolves the oxide layer, the metal is then attacked by hydrofluoric acid.

Analysis

Silicon can be identified from its line spectra. Trace quantities of the metal can be measured accurately by flame-AA using nitrous oxide-acetylene flame. Silica, silicates, or other silicon compounds may be digested with concentrated nitric acid, diluted and analyzed. ICP-AES, ICP/MS and neutron activation method also may be applied.

Toxicity

Inhalation of silica dusts or silicate mineral dusts can cause silicosis and other lung diseases.

SILICON CARBIDE

[409-21-2]
Formula SiC; MW 40.097
Synonym: carborundum

Uses

Silicon carbide is widely used as an abrasive in grinding and cutting glasses; in polishing glass and sharpening stones. It is used in the manufacture of porcelain, refractory brick, furnace linings, and emery paper. The compound also is used in semiconductor technology.

Physical Properties

Greenish blue to black crystalline solid; hexagonal or cubic crystals; diamond-like structure; density 3.217g/cm^3; exceedingly hard, Mohs hardness 9.5; sublimes at about 2,700°C; dielectric constant 7.0; electron mobility >100 cm^2/volt–sec; hole mobility >20cm^2/volt-sec; band gap energy 2.8 eV; insoluble in water and acids; solubilized by fusion with caustic potash.

Preparation

Silicon carbide is prepared by heating fine silica with carbon (coke) and a little salt and sawdust in an electric furnace.

Analysis

Elemental composition: Si 70.03%, C 29.97%. The carbide can be characterized by its physical properties and by x-ray crystallography. Silicon content may be determined by flame-AA after solubilizing the carbide by fusion with potassium hydroxide and extracting water–soluble potassium silicate with water.

SILICON DIOXIDE

[7631-86-9]
Formula SiO_2; MW 60.085
Synonym: silica

Occurrence and Classifications

Silicon dioxide occurs almost everywhere on earth. It is one of the most important and abundant oxides on earth, constituting about 60% weight of the earth's crust as silica itself or in combination with other metal oxides in silicates. It commonly is found as sand in the vast ocean and river shores, their beds, deserts, rocks, and minerals.

Silicon dioxide exists in several structural forms: polymorphic crystalline silica, synthetic quartz crystals, amorphous silica, and vitreous silica. This classification is not complete as there are other forms of silica synthesized for specialized applications. Various forms of silica are mentioned briefly below.

Crystalline Silica: Three principal polymorphic forms exist at atmospheric pressure. These are quartz, tridymite, and cristobalite. Quartz is stable below 870°C. It transforms to tridymite form at about 870°C. Tridymite is stable up to 1,470°C and transforms to cristobalite at 1,470°C. High cristobalite melts around 1,723°C. Other than these three polymorphs, there are also three high pressure phases of crystalline silica: keatite, coesite, and stishovite.

Quartz occurs in granite, sand, crystals, and sandstone. Quartz also has several crystalline varieties such as purple amethyst, colorless rock crystal, and yellow citrine. Flint, agate, and chert, etc. are other forms of quartz. Quartz is an excellent insulator. It does not break under temperature changes because of its low coefficient of expansion. Fused quartz transmits ultraviolet light.

Quartz exhibits two slightly varying atomic arrangements. One is the beta- or high quartz that consist of linked tetrahedral-forming helixes in which the hexagonal unit cell contains three SiO_2 units and in which Si—O bond distance is 1.62Å. The density of high quartz at 600°C is 2.53g/cm^3. The other form, known as the low, or alpha quartz, has a density of 2.65 g/cm^3 at 0°C. Here the Si—O bond distance differs slightly, measured as 1.597 and 1.617Å. Low quartz is the most common form of silica. It exhibits piezoelectric properties for which it has a high commercial value. Thermal inversion of quartz occurs around 573°C in which one form converts to the other form by slight displacement of atoms in their structural arrangements. The presence of impurities can affect the inversion temperature. Quartz also is optically active; individual crystals are either levorotatory or dextrorotatory.

Tridymite is another form of crystalline silica stable between 870 and 1,470°C at atmospheric pressure. It is found in volcanic rocks and has been identified in many stony meteorites. Tridymite also exists in various forms. It has six different modifications that undergo thermal inversions from one to another. Its density at 200°C is about 2.22 g/cm^3. The hexagonal unit cell contains four SiO_2 units. The Si—O bond distance is 1.52Å.

Cristobalite is the third crystalline silica form stable at high temperature. It exists between 1,470 to 1,723°C. A metastable form may exist below 1,470°C. Cristobalite has three-layer sequences of SiO_4. The oxygen atoms of the tetrahedral SiO_4 have cubic close-packed structure. Cristobalite is found in some volcanic rocks.

Three high pressure crystalline silica have been made in polymorph phases. One of them, keatite has a tetragonal structure with twelve SiO_2 units in the unit cell. Keatite has been prepared by crystallization of amorphous precipitated silica from dilute sodium or potassium hydroxide solutions at 380 to 585°C and 345 to 1,180 atm pressure in a hydrothermal bomb. It transforms to cristobalite when heated at 1,620°C for a few hours. Coesite is the second most dense phase of silica. Its density is 3.01 g/cm^3. Coesite is prepared by heating a mixture of sodium metasilicate and diammonium hydrogen phosphate at 500 to 800°C at 15,000 to 35,000 atm. It also can be made by oxidizing silicon with silver carbonate under pressure.

Stishovite is the most dense phase of silica. Its density is 4.35 g/cm^3. It has a rutile-type crystal structure in which the silicon atom is octahedrally surrounded by six oxygen atoms. Four Si—O bonds are 1.76Å and two 1.81Å. Stishovite has been prepared similarly to coesite but at temperatures between 1,200 to 1,400°C and a pressure above 150,000 atm. Both the coesite and stishovite are found in nature in certain meteorite craters resulting from meteorite impacts.

In addition to the above crystalline phases silica also exists in a few microcrystalline forms. Such micro crystalline or cryptocrystalline silicas occur in nature and include diatomaceous earth, flint, and chert. They are mostly of biogenic origin forming from compaction of amorphous silica over geologic time.

Amorphous Silica: The term amorphous silica refers to aggregate of small particles with high specific surface area. They lack crystal structure and do not form a sharp x-ray diffraction pattern. They are known in several forms such as colloidal silica, precipitated silica, silica gels, and fumed silica. The surface of such amorphous silica may contain silanol (SiOH) groups or can be anhydrous.

Amorphous silica in nature may originate from aquatic organisms, secreted as amorphous solid in the form of shells, plates, or skeletons. Amorphous silica also is found in volcanic ash or in precipitated material from the hot supersaturated waters of hot springs.

Amorphous silica can be hydrated up to about 14% or made anhydrous. They usually contain siloxane (–Si–C–Si–) or silanol (–Si–O–H) bonds. At the surface there may be silane (–Si–H) or organic silicon (–Si–O–R or – Si–C–R) bonds. Hydrated amorphous silica is made by polymerization of silicic acid in water in slightly acidic solution at a low temperature. At ambient temperature, such hydrated silica is stable and does not lose water below 60°C. Amorphous silica is broadly categorized into vitreous silica or glass, silica M and microamorphous silica. Vitreous silica is made by fusing quartz. Silica M is prepared by irradiating amorphous or crystalline silica with high-speed neutrons. It is a dense form of amorphous silica and is thermally unstable. When heated at 930°C for several hours, silica M converts to quartz.

Microamorphous silica is made of particles with diameters less than 1µm. They have very high surface areas, usually greater than 3m^2/g. These microamorphous silica are an aggregation of colloidal ultimate particles that broadly include sols, gels, powder, and porous glass. An important class of microamorphous silica constitutes what is known as microparticulate silica. These are the silicas precipitated from aqueous solution such as sol and gel or that are formed at high temperatures by condensation from vapor phase, such as pyrogenic silica.

Pyrogenic silica is made by vaporizing sand at 2,000°C and then cooling the vapors, or oxidizing silicon tetrachloride vapors at high temperatures. It has a SiO_2 content above 99.7% and density of 2.16 g/cm^3. The ultimate particle size is in the range 1 to 100 nm. When heated at 105°C, the weight loss is between 0.5 to 2.5%. There is no additional loss in the weight when the material is further heated at 1,200°C.

Silica sol is a stable dispersion of fine particles, while gel has a three-dimensional continuous structure. SiO_2 content in sol range between 10–50%, while that in dry silica gels is between 96.5 to 99.6%. Density of dry gels is 2.22 g/cm^3 and sols 2.20 to 2.30 g/cm^3. Weight loss in sols at 105°C is between 50–80%.

Silica gel is a rigid, continuous three-dimensional network of spherical colloidal particles. If the pores are filled with water it is known as hydrogel. The surface of silica gel consists of silanol (Si—O—H) groups or siloxane (Si—O—Si) groups. It also may have an organic surface. Silica gels are precipitated from water. When dried below 150°C, silanol surfaces are developed. When heated at 300 to 1,000°C, the silanol surfaces dehydrate to form siloxane surface. Silica gels are made by many ways. One method involves mixing sodium silicate with a strong mineral acid. This forms a silica hydrosol. It is set to a rigid mass, which is broken up mechanically to form hydrogel particles. Hydrogel is washed and then dried. The final gel properties, such as, density, hardness, surface area, and pore volume depend on silica concentration, temperature, pH, gelling time, and rate of drying. Hydrolysis of silicon tetrachloride, ethyl silicate and other silicon compounds also produces gels. These gels are dense, having very small pore size, and are of high purity.

Vitreous Silica: Vitreous silica is a glass form of silica composed of SiO_2. It may be transparent, translucent, or opaque. It has a number of abnormal and anomalous properties in thermal expansion, viscosity, bulk density, compressibility, and elasticity. These properties depend on thermal history and preparation method. Vitreous silica exhibits high resistance to chemical attack. At ambient temperature, it is not attacked by any chemical except hydrofluoric acid.

Transparent vitreous silica is made by electric melting of natural quartz minerals such as sand in vacuum. It also may be made by fusing quartz in flame or by vapor phase hydrolysis or oxidation of pure silicon compounds by heating electrically or using a flame or plasma. Translucent form is made by fusion of high purity quartz sand crystals.

Uses

The largest amount of silica is used in building materials. It is the main constituent of ceramics, such as refractory silica bricks. It also is the basic raw material of all types of glasses. Vitreous silica is used to make laboratory glassware, mirrors, prisms, cells, windows, and other optical devices. Synthetic quartz, because of its piezoelectric properties, is used in electrical oscillators, filters, transducers, and many consumer products, such as electronic watches.

Amorphous silica is used as a pigment and filler in paints and coatings. It also is used as an abrasive, absorbent and catalyst support. Silica gel is a common desiccant and adsorbent. It is used in analytical chemistry as a packing material in chromatography columns and in clean-up of organic extracts to remove interference in trace analysis of organic pollutants.

Precipitated silica is used to produce molecular sieves, as an anti-caking agent, and as filler for paper and rubber. Hydrophobic silica is a defoaming agent.

SILICON HYDRIDES

Silicon forms a series of hydrides known as silanes, formula Si_nH_{2n+2}, where *n* is the number of silicon atoms in the molecule. This general formula for the silicon hydrides is similar to the C_nH_{2n+2} for the alkane class of hydrocarbons. The names, synonyms, CAS Registry numbers, formulas, and molecular weights of the first four hydrides are given below:

Name	Synonyms	CAS No.	Formula	MW
silane	silicane, monosilane, silicon tetrahydride	[7803-62-5]	SiH_4	32.12
disilane	disilicane	[1590-87-0]	Si_2H_6	62.22
trisilane	trisilicane, trisilanepropane	[7783-26-8]	Si_3H_8	92.32
tetrasilane	tetrasilicane, tetrasilane butane	[7783-29-1]	Si_4H_{10}	122.42

Uses

Silane is used to produce hyperpure silicon for semiconductors. Also, it is used to prepare other silcon compounds. Higher silanes do not have any practical applications.

Physical Properties

Silane: Colorless gas; repulsive odor; density 1.44 g/L; liquefies at –111.8°C; freezes at –185°C; decomposes slowly in water; insoluble in alcohol, ether, chloroform and silicon tetrachloride; soluble in caustic potash solution.

Disilane: Colorless gas; density 2.865 g/L; liquefies at –14.5°C; liquid density 0.686 g/mL at –20°C; freezes at –132.5°C; slowly decomposes in water;

soluble in alcohol, benzene, and carbon disulfide.

Trisilane: Colorless liquid; density 0.743 g/mL at 0°C; freezes at –117.4°C; boils at 52.9°C; vapor density 4.15 g/L at atmospheric pressure; decomposes in water; decomposes in carbon tetrachloride.

Tetrasilane: Colorless liquid; density 0.79 g/mL at 0°C; freezes at –108°C; boils at 84.3°C; vapor density 5.48 g/L at STP; decomposes in water.

Thermochemical Properties

Silane:	ΔH_f°	8.2 kcal/mol
	ΔG_f°	13.6 kcal/mol
	S°	48.9 cal/deg mol
	C_ρ	10.2 cal/deg mol
Disilane	ΔH_f°	19.2 kcal/mol
	ΔG_f°	30.4 kcal/mol
	S°	65.1 cal/deg mol
	C_ρ	19.3 cal/deg mol
Trisilane	ΔH_f° (liq)	22.1 kcal/mol
	ΔH_f° (gas)	28.9 kcal/mol

Preparation

Silicon hydrides can be prepared by several methods. A few methods are outlined below. Silane and its higher homologs can be made by treating magnesium silicide, Mg_2Si with 20% hydrochloric acid in an atmosphere of hydrogen. An equation for monosilane is given below:

$$Mg_2Si + 4HCl \rightarrow SiH_4 + 2MgCl_2$$

The product mixture may contain higher silanes at over 50% yield, depending on reaction conditions.

Another preparative method involves treating magnesium silicide with ammonium bromide in liquid ammonia in a current of hydrogen. The process forms 70 to 80% yield of mono- and disilanes. The reaction is shown below:

$$Mg_2Si + 4NH_4Br \rightarrow SiH_4 + 2MgBr_2 + 4NH_3$$

Zinc, lithium, and aluminum silicides also may be used instead of magnesium silicide in the above preparations.

Silane also may be prepared by the reaction of silicon tetrachloride with lithium aluminum hydride in ether:

$$SiCl_4 + LiAlH_4 \rightarrow SiH_4 + LiCl + AlCl_3$$

Two other methods for preparing silane are treating silica gel with aluminum oxide in presence of hydrogen and by electrolysis of an aqueous solution of sodium or ammonium chloride using a silicon-aluminum alloy as the positive electrode.

Reactions

Silanes are flammable substances. Silane ignites in air spontaneously. Liquid disilane explodes in contact with air:

$$SiH_4 + O_2 \rightarrow SiO_2 + 2H_2O$$

$$2Si_2H_6 + 7O_2 \rightarrow 4SiO_2 + 6H_2O$$

Silanes do not react with water under normal conditions. In the presence of alkalies base hydrolysis readily occurs. Thus, reactions with caustic potash solution yield potassium silicate with evolution of hydrogen:

$$SiH_4 + 2KOH + H_2O \rightarrow K_2SiO_3 + 4H_2$$

$$Si_2H_6 + 4KOH + 2H_2O \rightarrow 2K_2SiO_3 + 7H_2$$

Silane reacts explosively with halogens at ordinary temperatures forming halogenated silane derivatives. Reaction is vigorous to moderate at very low temperatures:

$$SiH_4 + Cl_2 \rightarrow ClSiH_3 + HCl$$

$$ClSiH_3 + Cl_2 \rightarrow Cl_2SiH_2 + HCl$$

Silane forms halo derivatives with hydrogen halides. The reaction occurs moderately at ordinary temperature catalyzed by aluminum halides:

$$SiH_4 + 3HCl \xrightarrow{Al_2Cl_6} SiHCl_3 + 3H_2$$

Silane reacts with alkali metals dissolved in a solvent such as 1,2-dimethoxyethane to form the metal derivative $MSiH_3$ and hydrogen or metal hydride:

$$SiH_4 + K \rightarrow KSiH_3 + \tfrac{1}{2}H_2$$

$$SiH_4 + 2K \rightarrow KSiH_3 + KH$$

Reaction with methanol in the presence of copper catalyst yields tetramethoxysilane, $Si(OCH_3)_4$, trimethoxysilane, $SiH(OCH_3)_3$, and dimethoxysilane, $SiH_2(OCH_3)_2$

Analysis

Silanes are hydrolyzed in basic solution (e.g., KOH solution) (see Reactions). The silicate solution is analyzed for silicon by flame-AA. Hydrogen evolved from such base hydrolysis of silanes is measured quantitatively to determine the number of silicon atoms and hydrogen atoms in silane. Thus, one molecule of mono-, di-, tri-, and tetrasilanes liberate 4, 7, 10, and 13 molecules of H_2 respectively (i.e., for each Si—Si and Si—H bond present in the silane, one molecule of H_2 is liberated).

Hazard

Silanes are pyrophoric substances igniting and exploding spontaneously in air. They also liberate toxic hydrogen chloride gas. The gaseous monosilane and the vapors of higher silanes are irritants to the respiratory tract. Chronic exposure to low concentration can cause pulmonary edema.

SILICON TETRACHLORIDE

[10026-04-7]
Formula $SiCl_4$; MW 169.90; bond energy 91.06 kcal/mol
Synonym: tetrachlorosilane

Uses

Silicon tetrachloride was first prepared by Berzelius in 1823. It is used widely in preparing pure silicon and many organosilicon compounds such as silicone. It also is used to produce smoke screens in warfare.

Physical Properties

Colorless fuming liquid; suffocating odor; density 1.52 g/mL; freezes at –68.9°C; boils at 57.7°C; vapor pressure 235 torr at 25°C; critical temperature 235°C; critical pressure 35.45 atm; critical volume 326 cm^3/mol; decomposes in water forming silicic acid and HCl; soluble in benzene, toluence, chloroform, and ether.

Thermochemical Properties

$\Delta H_f°$ (liq)	–164.2 kcal/mol
$\Delta H_f°$ (gas)	–157.0 kcal/mol
$\Delta G_f°$ (liq)	–148.1 kcal/mol
$\Delta G_f°$ (gas)	–147.5 kcal/mol
S° (liq)	57.3 cal/deg mol
S° (gas)	79.0 cal/deg mol
C_ρ (liq)	34.7 cal/deg mol
C_ρ (gas)	21.6 cal/deg mol
ΔH_{fus}	1.82 kcal/mol
ΔH_{vap}	6.86 kcal/mol

Preparation

Silicon tetrachloride is prepared by heating silicon dioxide and carbon in a stream of chlorine:

$$SiO_2 + C + 2Cl_2 \rightarrow SiCl_4 + CO_2$$

Also, the compound may be prepared by heating silicon with chlorine or dry hydrogen chloride:

$$Si + 2Cl_2 \rightarrow SiCl_4$$

$$Si + 4HCl \rightarrow SiCl_4 + 2H_2$$

Reactions

Silicon tetrachloride decomposes in water forming silicic acid (precipitated silica) and hydrochloric acid:

$$SiCl_4 + 3H_2O \rightarrow H_2SiO_3 + 4HCl$$

Reactions with alcohols yield esters of orthosilicic acid. For example, with ethanol the product is tetraethyl orthosilicate or tetraethoxysilane, $Si(OC_2H_5)_4$:

$$SiCl_4 + 4C_2H_5OH \rightarrow Si(OC_2H_5)_4 + 4HCl$$

An important class of organosilicon compounds known as silicones that are used as lubricants, resins, elastomers, and antifoaming agents in high-vacuum diffusion pumps are synthesized from silicon tetrachloride. Silicon tetrachloride reacts with Grignard reagents, RMgCl to form monoalkyltrichlorosilanes, $RSiCl_3$, dialkyldichlorosilanes, R_2SiCl_2, trialkylmonochlorosilanes, R_3SiCl, and tetraalkylsilanes, R_4Si:

$$SiCl_4 + RMgCl \rightarrow RSiCl_3 + MgCl_2$$

$$SiCl_4 + 2RMgCl \rightarrow R_2SiCl_2 + 2MgCl_2$$

$$SiCl_4 + 3RMgCl \rightarrow R_3SiCl + 3MgCl_2$$

$$SiCl_4 + 4RMgCl \rightarrow R_4Si + 4MgCl_2$$

The alkylchlorosilanes on hydrolysis form various types of silicones. For example, hydrolysis of trialkylmonochlorosilanes yields sylil ethers, $R_3SiOSiR_3$, which form silicones:

$$2R_3SiCl + H_2O \rightarrow R_3SiOSiR_3 + 2HCl$$

Silicon tetrachloride reacts with diethylzinc to form tetraethylsilane. This compound was synthesized by Friedel and Crafts in 1863, the first organosilicon compound:

$$SiCl_4 + 2Zn(C_2H_5)_2 \rightarrow Si(C_2H_5)_4 + 2ZnCl_2$$

Silicon tetrachloride reacts with alkyl chloride and sodium to form the same tetraalkylsilane:

$$SiCl_4 + 4C_2H_5Cl + 8Na \rightarrow Si(C_2H_5)_4 + 8NaCl$$

Silicon tetrachloride reacts with acetic anhydride to form silicon tetraacetate (tetraacetoxysilane). This reaction was discovered by Friedel and Ladenburg in 1867:

$$SiCl_4 + 4(CH_3CO)_2O \rightarrow (CH_3COO)_4Si + 4CH_3COCl$$

Silicon tetraacetate can also be made by the reaction of silicon tetrachloride with sodium acetate. In general any carboxylate salt of silicon can be prepared from silicon tetrachloride by this reaction:

$$SiCl_4 + 4CH_3COO\ Na \rightarrow (CH_3COO)_4Si + 4NaCl$$

Ladenburg in 1873 synthesized phenyltrichlorosilane, $C_6H_5SiCl_3$ by heating silicon tetrachloride with diphenylmercury:

$$SiCl_4 + (C_6H_5)_2\ Hg \rightarrow C_6H_5SiCl_3 + C_6H_5HgCl$$

Silicon tetrachloride undergoes addition with olefinic and acetylenic unsaturated hydrocarbons. In these addition reactions, one chlorine atom adds to one carbon atom of the double or triple bond while the rest of the unit —$SiCl_3$ attaches to the other carbon atom forming a silicon—carbon bond:

$$SiCl_4 + H_2C{=}CH_2 \rightarrow ClCH_2{-}CH_2SiCl_3$$

$$SiCl_4 + HC{\equiv}CH \rightarrow ClCH{=}CHSiCl_3$$

Silicon tetrachloride is reduced to metallic silicon when heated with sodium, potassium, and a number of metals:

$$SiCl_4 + Mg \rightarrow Si + MgCl_2$$

It reacts with carbon monoxide to form a compound with a silicon carbon bond:

$$SiCl_4 + CO \rightarrow ClC({=}O)SiCl_3$$

Reaction with excess amine forms amine derivatives of silicon:

$$SiCl_4 + HN(CH_3)_2 \rightarrow Si[N(CH_3)_2]_4 + 4HN(CH_3)_2 \cdot HCl$$

Analysis

Elemental composition: Si 16.52%, Cl 83.48%. The compound may be added slowly to water and decomposed. The aqueous solution may be analyzed for silicon (see Silicon). An aliquot of the solution may be measured for chloride ion by titration with a standard solution of silver nitrate or by ion chromatography. Also, the concentration of HCl in the solution may be determined by titration against a standard solution of NaOH. Silicon tetrachloride may be dissolved in a suitable organic solvent and the solution analyzed by GC/MS.

Toxicity

The vapors are very toxic and irritating to the eyes, throat, and mucous membrane.

SILICON TETRAFLUORIDE

[7783-61-1]
Formula SiF_4; MW 104.08
Synonym: tetrafluorosilane

Uses

Unlike silicon tetrachloride, the tetrafluoride has minor applications. The compound is used in preparation of other silicon compounds. It also is an intermdiate in gravimetric analysis of silica.

Physical Properties

Colorless gas; very pungent odor; fumes heavily in moist air; density of the gas 4.69 g/L; heavier than air, density in air 3.5 (air = 1); sublimes at –95.7°C; solidifies at –90.2°C (under pressure); critical pressure 50atm; decomposes in water forming silicic acid and hydrofluoric acid.

Thermochemical Properties

$\Delta H_f°$	–386.0 kcal/mol
$\Delta G_f°$	–375.9 kcal/mol
S°	67.5 cal/deg mol
C_ρ	17.6 cal/deg mol

Preparation

Silicon tetrafluoride is prepared by heating silica with dilute hydrofluoric acid at high temperatures:

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

Also, the tetrafluoride may be obtained by heating the elements:

$$Si + 2F_2 \rightarrow SiF_4$$

Reactions

See Silicon Tetrachloride Reactions

Analysis

Elemental composition: Si 26.97%, F 73.03%. The gas is bubbled slowly through water to decompose into silicic acid and hydrofluoric acid. HF is analyzed for fluoride ion by fluoride-selective electrode or by ion chromatography. Silicon in the aqueous solution can be measured by AA or ICP.

Toxicity

Silicon tetrafluoride is a toxic gas. Inhalation can cause severe irritation of the respiratory tract.

SILVER

[7440-22-4]
Symbol Ag; atomic number 47; atomic weight 107.87; a Group 1B (Group 11) coinage metal positioned between copper and gold; electron configuration $[Kr]4d^{10}5s^1$ valence +1, +2; most common valence +1; atomic radius 1.442Å; ionic radius of Ag in crystals with coordination numbers 4 and 6 1.00Å and 1.15Å, respectively; ionization potential ($Ag \rightarrow Ag^+$) 7.576 eV; standard electrode potential E° for $Ag^+ + e^- \leftrightarrow Ag$ 0.800 V; two naturally-occurring stable isotopes: Ag-107 (51.84%) and Ag-109 (48.16%); twenty-nine radioactive isotopes in the mass range 94–106, 108, 110–124.

History, Occurrence, and Uses

Silver is one of the oldest metals, known since ancient times. It is a precious metal worldwide, used in ornaments, coins, and utensils. The symbol Ag for this element is derived from the Latin word, *argentum*. Silver occurs in nature in native form, commonly associated with gold. It is found in most lead and copper ores. The principal mineral of silver is argentite, Ag_2S [1332-04-3]. Some other silver minerals include pyrargyrite, Ag_3SbS_3 [15123-77-0]; proustite, Ag_3AsS_3 [15152-58-4]; polybasite, $Ag_{16}Sb_2S_{11}$ [53810-31-4]; cerargyrite, AgCl [14358-96-4]; stephanite, Ag_5SbS_4 [1302-12-1]; and tetrahedrite, $Cu_3(AsSb)S_3$. Abundance of silver in the earth's crust is estimated to be 0.075 mg/kg and its average concentration in sea water is 0.014 µg/L.

Silver and its alloys and compounds have numerous applications. As a precious metal, silver is used in jewelry. Also, one of its alloys, sterling silver, containing 92.5 weight % silver and 7.5 weight % copper, is a jewelry item and is used in tableware and decorative pieces. The metal and its copper alloys are used in coins. Silver-copper brazing alloys and solders have many applications. They are used in automotive radiators, heat exchangers, electrical contacts, steam tubes, coins, and musical instruments.

Some other uses of silver metal include its applications as electrodes, catalysts, mirrors, and dental amalgam. Silver is used as a catalyst in oxidation-reductions involving conversions of alcohol to aldehydes, ethylene to ethylene oxide, and ethylene glycol to glyoxal.

Many silver compounds, such as silver nitrate, silver chloride, and silver oxides, have wide commercial applications. The most important uses are in photography and batteries (see individual compounds).

Physical Properties

White metal with brilliant metallic luster; face–centered cubic crystals; density 10.43 g/cm³ at 20°C, and 9.18 g/cm³ at 1,100°C; melts at 961.8°C; vaporizes at 2,162°C; vapor pressure 5 torr at 1,500° C; pure metal has the highest electrical and thermal conductive of all metals, electrical resistivity of pure metal at 25°C 1.617×10^{-6} ohm-cm; elastic modulus 71GPa (10.3×10^{6} psi); Poisson's ratio 0.39 (hard drawn), 0.37 (annealed); viscosity of liquid silver 3.97 centipoise at 1,043°C; thermal neutron absorption cross section 63±1 barns; insoluble in water; inert to most acids; attacked by dilute HNO_3 and concentrated H_2SO_4; soluble in fused caustic soda or caustic potash in the presence of air.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	68.1 kcal/mol
$\Delta G_f°$ (cry)	0.0
$\Delta G_f°$ (gas)	58.8 kcal/mol
S° (cry)	10.2 cal/deg mol
S° (gas)	41.3 cal/deg mol
C_ρ (cry)	6.07 cal/deg mol
C_ρ (gas)	4.97 cal/deg mol
ΔH_{fus}	2.70 kcal/mol
ΔH_{vap}	68.0 kcal/mol
Thermal conductivity	4.29 W/cmK
Coefficient of linear expansion (at 25°C)	$18.9\text{x}10^{-6}$/°C

Production

Many processes are known for recovery of silver from its ores. These depend mostly on the nature of the mineral, its silver content, and recovery of other metals present in the ore. A few processes are briefly outlined below.

Silver is usually extracted from high-grade ores by three common processes that have been known for many years. These are amalgamation, leaching, and cyanidation. In one amalgamation process, ore is crushed and mixed with sodium chloride, copper sulfate, sulfuric acid, and mercury, and roasted in cast iron pots. The amalgam is separated and washed. Silver is separated from its amalgam by distillation of mercury.

In the cyanidation process the ore is crushed and roasted with sodium chloride and then treated with a solution of sodium cyanide. Silver forms a stable silver cyanide complex, $[Ag(CN)_2]^-$. Adding metallic zinc to this complex solution precipitates silver.

Several leaching processes are known. One such process, known as the Patera process, developed in the mid 19th century, involves roasting ore with sodium chloride followed by leaching with sodium thiosulfate solution. Silver is precipitated as silver sulfide, Ag_2S, by adding sodium sulfide to the leachate. In the Clandot process, leaching is done with ferric chloride solution. Addition of zinc iodide precipitates silver iodide, AgI. AgI is reduced with zinc to obtain silver.

The above processes are applied for extraction of silver from high-grade ores. However, with depletion of these ores, many processes were developed subsequently to extract silver from low-grade ores, especially lead, copper, and zinc ores that contain very small quantities of silver.

Low grade ores are concentrated by floatation. The concentrates are fed into smelters (copper, lead, and zinc smelters). The concentrates are subjected to various treatments before and after smelting including sintering, calcination, and leaching. Copper concentrates are calcined for removal of sulfur and smelted in a reverberatory furnace to convert into blister copper containing 99 wt% Cu. The blister copper is fire-refined and cast into anodes. The anodes are electrolytically refined in the presence of cathodes containing 99.9% copper. Insoluble anode sludges from electrolytic refining contain silver, gold, and platinum metals. Silver is recovered from the mud by treatment with sulfuric acid. Base metals dissolve in sulfuric acid leaving silver mixed with any gold present in the mud. Silver is separated from gold by electrolysis.

Lead and zinc concentrates can be treated in more or less the same manner as copper concentrates. Sintering lead concentrates removes sulfur and following that smelting with coke and flux in a blast furnace forms impure lead bullion. The lead bullion is drossed with air and sulfur and softened with molten bullion in the presence of air to remove most impurities other than silver and gold. Copper is recovered from the dross and zinc converts to its oxide and is recovered from blast furnace slag. The softened lead obtained above also contains some silver. The silver is recovered by the Parkes Process. The Parkes process involves adding zinc to molten lead to dissolve silver at temperatures above the melting point of zinc. On cooling, zinc-silver alloy solidifies, separating from the lead and rising to the top. The alloy is lifted off and zinc is separated from silver by distillation leaving behind metallic silver.

The unsoftened lead obtained after the softening operation contains silver in small but significant quantities. Such unsoftened lead is cast into anode and subjected to electrolytic refining. The anode mud that is formed adhering to these anodes is removed by scraping. It contains bismuth, silver, gold, and other impurity metals. Silver is obtained from this anode mud by methods similar to the extraction of anode mud from the copper refining process discussed earlier.

If the low–grade ore is a zinc mineral, then zinc concentrate obtained from the flotation process is calcined and leached with water to remove zinc. Silver and lead are left in leach residues. Residues are treated like lead concentrates and fed into lead smelters. Silver is recovered from this lead concentrate by various processes described above.

Reactions

At ordinary temperatures, silver is not affected by dry or moist air. At a temperature just above its melting point, silver absorbs a large volume of oxygen, which is greater than ten times its own volume. Such oxygen absorption, however, drops dramatically below its melting point and, just before solidification, absorbed oxygen is ejected violently. Solid silver also dissolves oxygen but to a much lesser extent, the volume absorbed depending on temperature.

Silver also absorbs hydrogen above 800°C. Exposure of pure silver at about 810°C alternatively to both hydrogen and oxygen gases embrittles the metal.

Silver reacts with halogens at elevated temperatures forming halides. With chlorine, the reaction occurs above 455°C, the melting point of silver chloride, to form molten silver chloride:

$$2Ag + Cl_2 \rightarrow 2AgCl$$

Silver reacts readily with hydrogen sulfide at ambient temperature forming silver sulfide:

$$Ag + H_2S \rightarrow Ag_2S + H_2$$

Most metal sulfides react with silver at room temperature, tarnishing the surface with a sulfide coating.

Silver is attacked by nitric acid at all concentrations. The reaction is exothermic producing silver nitrate with liberation of nitric oxide and nitrogen dioxide:

$$4Ag + 6HNO_3 \rightarrow 4AgNO_3 + NO + NO_2 + 3H_2O$$

Silver dissolves very slowly in hot concentrated sulfuric acid forming silver sulfate, Ag_2SO_4. Reaction with hydrochloric acid is slow and stops after initial formation of a protective layer of silver chloride on the surface.

Aqueous solutions of alkali metal cyanides attack silver in the presence of oxygen forming a double salt:

$$2Ag + 4KCN + H_2O + ½O_2 \rightarrow 2KAg(CN)_2 + 2NaOH$$

This reaction is used for extraction of silver from its ores.

Silver is tarnished by sulfur, sulfur dioxide, and mercury. It also is attacked by ozone, hydrogen peroxide, chromic acid, ferric sulfate, and permanganate solutions.

Analysis

Silver metal and its contents in silver alloys and salts can be measured at trace levels by various instrumental techniques such as flame- and furnace-AA, ICP-AES, ICP/MS and x-ray fluorescence methods. It is solubilized by digestion with nitric acid prior to analysis. The AA measurement may be carried out at the wavelength 328.1 nm and ICP analysis at 328.07 nm. ICP/MS is the most sensitive technique while x-ray fluorescence is relatively less sensitive. Silver also can be measured by neutron activation analysis.

Toxicity

All water-soluble silver salts are toxic and ingestion can cause severe poisoning (see Silver Nitrate). Silver is listed by the US EPA as one of the priority pollutant metals in the environment.

SILVER ACETYLIDE

[7659-31-6]
Formula Ag_2C_2; MW 239.76; Structure $AgC{\equiv}CAg$
Synonym: silver(I) acetylide

Uses

Silver acetylide is used in explosives. It is a powerful detonator.

Physical Properties

White powder; unstable; explodes when subjected to heat or shock.

Preparation

Silver acetylide is prepared by passing acetylene through a silver salt solution.

Hazard

The compound presents severe explosion hazard when shock or heat is applied.

SILVER BROMIDE

[7785-23-1]
Formula $AgBr$; MW 187.77

Uses

Silver bromide is used in photographic film and plates. It also is used in photochromic glass. In medicine it is used as a topical anti-infective and astringent agent.

It occurs as the mineral bromyrite.

Physical Properties

Yellow cubic crystals or powder; refractive index 2.253; darkens on exposure to light; Mohs hardness 2.5; density 6.47g/cm^3; melts at 432°C; vaporizes at 1,502°C; insoluble in water, alcohol, and most acids; slightly soluble in dilute ammonia and ammonium carbonate solutions; sparingly soluble in concentrated ammonia solution (0.33 g/100mL 10% ammonia solution at 12°C);

soluble in alkali cyanide solutions.

Thermochemical Properties

$\Delta H_f°$	–24.0 kcal/mol
$\Delta G_f°$	–23.2 kcal/mol
S°	25.6 cal/deg mol
C_ρ	12.5 cal/deg mol
ΔH_{fus}	2.18 kcal/mol
ΔH_{vap}	47.3 kcal/mol

Preparation

Silver bromide is prepared by double decomposition reaction. An aqueous solution of alkali bromide, such as sodium or potassium bromide, is slowly added to an aqueous solution of silver nitrate:

$$Ag^+ (aq) + Br^- (aq) \rightarrow AgBr(s)$$

The precipitate is washed repeatedly with hot water. Preparation should be in a dark room under a ruby red light.

Analysis

Elemental composition: Ag 57.45%, Br 42.55%. Silver bromide is digested with aqua regia, diluted and analyzed for silver by flame- or furnace-AA, or ICP-AES. The aqueous solution is appropriately diluted and analyzed for bromide by ion chromatography.

SILVER CHLORIDE

[7783-90-6]
Formula AgCl; MW 143.32

Uses

Silver chloride is used in silver plating and to obtain pure silver. The salt also finds applications in photography and optics; in photochromic glass; and in electrodes and batteries. It is used to make antiseptic silver solution. It occurs as the mineral cerargyrite.

Physical Properties

White granular powder or cubic crystals; refractive index 2.071; darkens on exposure to light; density 5.56 g/cm^3; Moh's hardness 2.5; melts at 455°C; vaporizes at 1,547°C; vapor pressure 1 and 5 torr at 912 and 1,019°C; insoluble in water, alcohol and dilute acids; soluble in ammonia solution and concentrated sulfuric acid, alkali cyanide, ammonium carbonate; also soluble in potassium bromide and sodium thiosulfate solutions.

Thermochemical Properties

$\Delta H_f°$	–30.4 kcal/mol

$\Delta G_f°$	–26.2 kcal/mol
S°	23.0 cal/deg mol
C_ρ	12.1 cal/deg mol
ΔH_{fus}	3.15 kcal/mol
ΔH_{vap}	47.6 kcal/mol

Preparation

Silver chloride is prepared by slowly adding an alkali metal chloride solution to a hot solution of silver nitrate. The solution mixture is boiled:

$$Ag^+ (aq) + Cl^- (aq) \rightarrow AgCl (s)$$

The precipitate is washed with hot water. The product is purified by dissolving in ammonia solution, filtering out any insoluble residues, and then adding hydrochloric acid to reprecipitate silver chloride. Preparation should be carried out in the dark in ruby red light.

Analysis

Elemental composition: Ag 75.26%, Cl 24.74%. The salt is dissolved in concentrated sulfuric acid, diluted, and analyzed for silver (see Silver). Solid powder may be characterized by its physical properties and its reaction with cyanide ion, forming the complex ion $[Ag(CN)_2]^-$.

SILVER CHROMATE

[7784-01-2]
Formula Ag_2CrO_4; MW 331.73

Uses

Silver chromate is a catalyst in conversion of alcohol to aldol. It's formation signals the end point in argentometric titration in measuring halides.

Physical Properties

Red monoclinic crystals or brownish-red powder; density 5.625 g/cm^3; insoluble in water; soluble in nitric acid, ammonia and solutions of alkali cyanides and chromates.

Thermochemical Properties

$\Delta H_f°$	–174.9 kcal/mol
$\Delta G_f°$	–153.4 kcal/mol
S°	52.0 cal/deg mol
C_ρ	34.0 cal/deg mol

Preparation

Silver chromate is prepared by slowly adding a solution of potassium chromate to a solution of silver nitrate:

$$2Ag^+ (aq) + CrO_4^{2-} (aq) \rightarrow Ag_2CrO_4 (s)$$

The precipitate is washed with hot water.

Analysis

Elemental composition: Ag 65.03%, Cr 15.68%, O 19.29%. The salt is dissolved in nitric acid, diluted, and analyzed for silver and chromium by flame- and furnace-AA, ICP-AES or other instrumental method to measure the contents of these metals.

SILVER CYANIDE

[506-64-9]
Formula AgCN; MW 133.89

Uses

Silver cyanide is used for silver plating.

Physical Properties

Grayish-white hexagonal crystals; density 3.95 g/cm^3; decomposes at 320°C; insoluble in water, alcohol or dilute acids; moderately soluble in concentrated ammonia; soluble in concentrated boiling nitric acid; also soluble in alkali cyanide solutions.

Thermochemical Properties

$\Delta H_f°$	34.9 kcal/mol
$\Delta G_f°$	37.5 kcal/mol
S°	25.6 cal/deg mol
C_ρ	15.9 cal/deg mol

Preparation

Silver cyanide is prepared by adding a solution of an alkali cyanide to a solution of silver nitrate:

$$Ag^+ (aq) + CN^- (aq) \rightarrow AgCN (s)$$

Analysis

Elemental composition: Ag 80.57%, C 8.97%, N 10.46%. The salt is digested with concentrated nitric acid, diluted, and analyzed for silver.

Toxicity

Silver cyanide is highly toxic by ingestion. Contact with skin and eyes can cause severe irritation.

LD_{50} oral (rat): 123mg/kg

SILVER IODIDE

[7783-96-2]
Formula AgI; MW 234.77

Uses

Silver iodide is used in cloud seeding for artificial rain making and in photography. Its colloidal suspension is used as a local antiseptic.

Physical Properties

Light yellow hexagonal crystals or powder; darkens on exposure to light; density 5.68 g/cm^3; melts at 558°C; vaporizes at 1,506°C; insoluble in water, most acids and ammonium carbonate solution; moderately soluble in concentrated solutions of alkali chloride, bromide, and thiosulfate; readily soluble in solutions of alkali cyanides, iodides and in hot concentrated hydriodic acid.

Thermochemical Properties

$\Delta H_f°$	–14.8 kcal/mol
$\Delta G_f°$	–15.8 kcal/mol
S°	27.6 cal/deg mol
C_ρ	13.6 cal/deg mol
ΔH_{fus}	2.25 kcal/mol
ΔH_{vap}	34.4 kcal/mol

Preparation

Silver iodide is prepared by adding a solution of sodium or potassium iodide to a hot solution of silver nitrate:

$$Ag^+ (aq) + I^- (aq) \rightarrow Ag\,I\,(s)$$

The precipitate is washed with boiling water. The preparation is done in the dark under ruby red light.

Analysis

Elemental composition: Ag 45.95%, I 54.05%. The salt is dissolved in hot concentrated nitric acid, diluted appropriately with water and analyzed for silver.

SILVER NITRATE

{7761-88-8]
Formula $AgNO_3$; MW 169.87; Synonym: lunar caustic

Uses

Silver nitrate is probably the most important silver salt. It is used to make most silver salts. It is used in photographic film, indelible ink, and hair dyeing. Other uses are in making silver mirrors, etching ivory, and as a catalyst in preparing ethylene oxide. Silver nitrate is a titrant in all argentometric titration (Mohr titrations). In medicine, it is a topical anti-infective, an antiseptic, and its dilute solution is an eye lotion.

Physical Properties

Colorless, transparent, large rhombohedral crystals, or white small crystals; bitter, caustic metallic taste; odorless; pure compound is not sensitive to light but trace organics promote photo reduction, turning the salt to grayish black on exposure to light; density 4.35 g/cm^3; melts at 212°C; decomposes at 440°C; very soluble in water, soluble in ethanol and acetone.

Thermochemical Properties

$\Delta H_f°$	–29.7 kcal/mol
$\Delta G_f°$	–7.98 kcal/mol
S°	33.7 cal/deg mol
C_ρ	22.3 cal/deg mol
ΔH_{fus}	2.75 kcal/mol

Preparation

Silver nitrate is prepared by dissolving silver metal in dilute nitric acid. The solution is evaporated and residue is heated to dull red heat with concentrated nitric acid to decompose impurities such as copper nitrate. Residue then is dissolved in water, filtered, and recrystallized to obtain pure silver nitrate.

Analysis

Elemental composition: Ag 63.50%, N 8.25%, O 28.25%. The salt is dissolved in water, diluted, and analyzed for silver. The nitrate ion, NO_3^- , can be analyzed in aqueous solution by nitrate ion-selective electrode, ion chromatography, or colorimetry after reduction to NO_2^- ion with cadmium. The nitrate content of the salt is 36.50%.

Toxicity

Silver nitrate is toxic by all routes of exposure. Ingestion can cause severe gastroenteritis. Also, it is a severe irritant to eyes and skin.

LD_{LO} oral (rabbit): 800 mg/kg

SILVER(I) OXIDE

[20667-12-3]
Formula Ag_2O; MW 231.74
Synonyms: silver oxide; argentous oxide

Uses

Silver(I) oxide is used for polishing and coloring glass yellow. Also, it is used in purifying drinking water; as a catalyst; and as a germicide and parasiticide.

Physical Properties

Brownish-black cubic crystals; density 7.14 g/cm^3 at 16°C; begins to decompose around 200°C, decomposition becoming rapid at 250 to 300°C; insoluble in water and ethanol; soluble in acids and alkalis; sparingly soluble in solutions of caustic alkalis; insoluble in alcohol.

Thermochemical Properties

ΔH_f°	–7.43 kcal/mol
ΔG_f°	–2.68 kcal/mol
S°	29.0 cal/deg mol
C_ρ	15.75 cal/deg mol

Preparation

Silver(I) oxide is precipitated by mixing solutions of silver nitrate and caustic soda:

$$2AgNO_3 + 2NaOH \rightarrow Ag_2O + 2NaNO_3 + H_2O$$

Reactions

When heated with hydrogen, carbon, carbon monoxide, or most metals silver(I) oxide is reduced to metallic silver:

$$Ag_2O + H_2 \rightarrow 2Ag + H_2O$$

$$Ag_2O + CO \rightarrow 2Ag + CO_2$$

Silver(I) oxide absorbs carbon dioxide in the presence of moisture producing silver carbonate:

$$Ag_2O + CO_2 \rightarrow Ag_2CO_3$$

The oxide dissolves in acids. Evaporation forms the silver salt.

Analysis

Elemental composition: Ag 93.10%, O 6.90%. The oxide is dissolved in nitric acid, diluted, and analyzed for silver. Its oxygen content may be measured by gravimetry following its reduction with hydrogen.

SILVER(II) OXIDE

[1301-96-8]
Formula AgO; MW 123.87
Synonyms: silver peroxide; argentic oxide; silver suboxide; Divasil

Uses

Silver(II) oxide is used to make silver oxide-zinc alkali batteries. Also, it is an oxidizing agent.

Physical Properties

Gray monoclinic or cubic crystals or powder; diamagnetic; semiconductor; density 7.48 g/cm^3; decomposes to its elements above 100°C; insoluble in water (solubility 27 mg/L at 25°C); soluble in alkalis; decomposes in ammonia solution evolving nitrogen; dissolves in dilute acids with decomposition evolving oxygen; forms a brown solution in concentrated nitric acid, and forms intense green coloration in concentrated sulfuric acid.

Preparation

Silver(II) oxide is prepared by reacting silver nitrate with potassium persulfate in the presence of a base.

Analysis

Elemental composition: Ag 87.08%, O 12.92%. When dissolved in dilute nitric acid, oxygen is liberated immediately, which can be measured by GC or GC/ MS (m/z 32). Acid solution may be analyzed for silver by AA, ICP, or other methods. When treated with ammonia solution, nitrogen is evolved which can be measured by GC or GC/MS (m/z 28).

SILVER SULFATE

[10294-26-5]
Formula Ag_2SO_4; MW 311.80

Uses

Silver sulfate is used as a catalyst to oxidize long chain aliphatic hydrocarbons in the determination of chemical oxygen demand (COD).

Physical Properties

Colorless crystals or powder; slowly darkens when exposed to light; density 5.45 g/cm^3; melts at 652°C; decomposes at 1,085°C; slightly soluble in water; dissolves in nitric acid, concentrated sulfuric acid and ammonia solution.

Thermochemical Properties

$\Delta H_f°$	–171.1 kcal/mol
$\Delta G_f°$	–147.8 kcal/mol
S°	47.9 cal/deg mol

Preparation

Silver sulfate is precipitated by adding sulfuric acid to a solution of silver nitrate:

$$2Ag^+(aq) + SO_4^{2-}(aq) \rightarrow Ag_2SO_4(s)$$

The precipitate is washed with hot water and preparation is under ruby red illumination.

Analysis

Elemental composition: Ag 69.19%, S 10.28%, O 20.52%. The salt is dissolved in nitric acid, the solution diluted, and analyzed for silver. It is very slightly soluble in water. The supernatant solution containing trace sulfate anion may be measured by ion chromatography or by treating with barium chloride followed by colorimetric measurement at 420 nm.

SILVER SULFIDE

[21548-73-2]
Formula Ag_2S; MW 247.80
Synonym: argentous sulfide

Occurrence and Uses

Silver sulfide occurs in nature as mineral argentite. It is used in ceramics.

Physical Properties

Grayish-black orthogonal crystals or powder; density 7.23 g/cm^3; Moh's hardness 2.3; melts at 825°C; insoluble in water; soluble in nitric and sulfuric acids.

Thermochemical Properties

$\Delta H_f°$	–7.79 kcal/mol
$\Delta G_f°$	–9.73 kcal/mol
$S°$	34.4 cal/deg mol
C_ρ	18.3 cal/deg mol
ΔH_{fus}	3.37 kcal/mol

Preparation

Mineral argentite is mined from mineral deposits, crushed, ground, and washed for use. In the laboratory, silver sulfide is obtained by passing hydrogen sulfide gas through a solution of silver nitrate. The precipitate is washed with hot water.

Analysis

Elemental composition: Ag 87.06% and S 12.94%. Silver sulfide is dissolved in nitric acid, the solution diluted and analyzed for silver. Also, it may be characterized nondestructively by x-ray diffraction.

SODIUM

[7440-23-5]
Symbol Na; atomic number 11; atomic weight 22.9898; a Group 1A (Group 1) alkali metal element; electron configuration [Ne]$3s^1$; valence +1; atomic radius 1.85Å; ionic radius, Na^+ in crystals 1.02Å (for a coordination number 6); ionization potential 5.139 eV; standard electrode potential, $E°(Na^+ + e^- \leftrightarrow Na)$ –2.71 V; one naturally-occurring stable isotope, Na-23 (100%); sixteen artificial radioactive isotopes in the mass range 19–22, 24–35; longest–lived radioisotope, Na-22, $t_{1/2}$ 2.605 year; shortest-lived isotope Na-35, $t_{1/2}$ 1.5 ms.

History, Occurrence, and Uses

Sodium was first isolated by Sir Humphry Davy in 1807 by electrolysis of caustic soda. In the following year, Gay Lussac and Thenard obtained metallic sodium by chemical reduction of caustic soda with iron at elevated temperatures. Deville, in 1854, prepared the metal by reduction of sodium carbonate and lime with charcoal at a temperature above the boiling point of sodium. Castner, in 1886, improved the chemical reduction process preparing the metal by heating sodium hydroxide with iron carbide at high temperature. Five years later he patented a process based on electrolytic reduction of sodium hydroxide. The first major commercial plant was set up in 1921 with the introduction of Downs cell.

The element derived its name from the Latin word *sodanum* meaning "headache remedy." Its symbol Na was derived from the Latin word, *natrium*.

Sodium is the sixth most abundant element on earth. It comprises about 2.6% weight of the earth's crust. Its salt, sodium chloride, is the major component of seawater. The concentration of sodium in seawater is 1.08%. As a very reactive element, sodium is never found in free elemental form. It occurs in nature in many minerals such as cryolite, amphibole, zeolite, sodalite, and soda niter. Sodium chloride (NaCl) is the most common salt of sodium. Some other important salts are caustic soda (NaOH), soda ash (Na_2CO_3), baking soda ($NaHCO_3$), Chile saltpeter ($NaNO_3$), borax ($Na_2B_4O_7 \cdot 10H_2O$), sodium thiosulfate ($Na_2S_2O_3$), sodium sulfate (Na_2SO_4), and sodium phosphates.

Metallic sodium is a strong reducing agent, used in many organic syntheses. It is used in the manufacture of sodamide, sodium peroxide, and esters. Other uses are in purifying molten metals, to descale metal, to improve structure of certain alloys, and as a heat transfer agent, for example, in nuclear reactors. Sodium is useful in producing other metals, such as titanium. It is used in sodium vapor lamps in small amounts. Sodium wire is used to remove traces of water from organic solvents.

Physical Properties

Soft, bright, silvery metal; malleable, can be readily cut with a knife or extruded as wire; liquid sodium in inert atmosphere appears like mercury; blue vapor, appears brilliant green at high temperatures; imparts golden-yellow color to flame; body-centered cubic structure; paramagnetic; density 0.97

g/cm^3; melts at 97.72°C; vaporizes at 883°C; vapor pressure 1torr at 439°C and 5 torr at 511°C; electrical resistivity 4.69 microhm-cm at 20°C and 6.60 microhm-cm at its melting point; viscosity 0.680 centipoise at 100°C; surface tension 192dyne/cm at its melting point; neutron absorption cross section 0.505 barns; reacts violently with water; soluble in liquid ammonia forming a deep blue solution; soluble in ethylenediamine.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0 kcal/mol
$\Delta H_f°$ (gas)	25.7 kcal/mol
$\Delta G_f°$ (gas)	18.4 kcal/mol
S° (cry)	12.3 cal/deg mol
S° (gas)	36.7 cal/deg mol
C_r (cry)	6.74 cal/deg mol
C_r (gas)	4.97 cal/deg mol
ΔH_{fus}	0.62 kcal/mol
Thermal conductivity (at 27°C)	1.41 W/cm K
Coefficient of linear expansion (at 25°C)	$71\text{x}10^{-6}$/°C

Production

Sodium metal is produced by both electrolytic and chemical reduction processes. All commercial processes employed today are based on electrolytic methods. Such processes are in wide use since Davy prepared the metal the first time in 1807.

There are two electrolytic methods that are of major importance. One involves the electrolysis of fused sodium chloride using the Downs cell. This method currently is most prevalent. The Downs cell consists of a steel cell with brick lining containing the fused bath. The multiple electrode arrangement consists of four cylindrical graphite anodes that project upward from the base of the cell. Each anode is surrounded by a diaphragm of iron gauge and a steel cathode.

Fused sodium chloride is electrolyzed at bath temperature varying between 565 to 600°C at a cell voltage of 5.7 to 7 V and the cell current varying from 25 to 35 kA. The cathode current density is mostly about 9.8 kA/m^2. Often calcium chloride is added to sodium chloride in the cell bath to lower its melting point. Calcium is largely removed from sodium by filtration at about 110°C. Other electrolyte compositions have been used in which calcium is partially or fully replaced. The cell feed must be free of sulfate and other impurities.

Electrolysis of fused sodium hydroxide has been achieved successfully with a Castner cell. The Castner cell was used in commercial production prior to introduction of Downs cell. The cell is operated at a bath temperature 320 ± 10°C, at 9.0 ± 0.5 amp current and a voltage of 4.3 to 5.0 V. The cathode current density is about 10.9 kA/m^2. The cell consists of a copper cathode and a nickel anode and a cylindrical iron-gauge diaphragm placed between the electrodes. The cell reactions are as follows:

cathode: $4Na^+ + 4e^- \rightarrow 4Na$

anode: $4OH^- - 4e^- \rightarrow 2H_2O + O_2$

Water generated at the anode diffuses through the diaphragm and goes to the cathode, reacting with sodium to form sodium hydroxide.

$$2H_2O + 2Na \rightarrow 2NaOH + H_2$$

The overall change may be represented as:

$$2NaOH \rightarrow 2Na + H_2 + O_2$$

Because water is reacting with sodium produced at the cathode, the yield of sodium is reduced almost by 50%. Lesser yield is the major disadvantage of the Castner process. At present, this process is not used commercially.

Thermal reduction processes are not being practiced anywhere in the world at present for large-scale production of sodium. Such methods, however, can be conveniently adapted for laboratory preparation of metallic sodium. Sodium can be prepared by thermal reduction of its hydroxide, carbonate, or chloride at elevated temperatures. These salts are heated with carbon, calcium carbide, iron carbide, ferrosilicon, or other reducing agents at temperatures above 800°C under vacuum:

$$6NaOH + 2C \rightarrow 2Na + 2Na_2CO_3 + 3H_2$$

$$Na_2CO_3 + 2C \rightarrow 2Na + 3CO$$

$$2NaCl + CaC_2 \rightarrow 2Na + CaCl_2 + 2C$$

Reactions

Sodium is a highly reactive metal. Most reactions are violent. Sodium ignites in air when heated at 120°C, burning with a yellow flame, forming a dense white smoke with an acrid odor. It forms three oxides, the monoxide, Na_2O; the peroxide, Na_2O_2; and the superoxide, NaO_2. When heated below 160°C under a limited supply of oxygen, sodium monoxide, Na_2O, is the major product. At 250 to 300°C in adequate oxygen, sodium forms its peroxide, Na_2O_2, along with trace amounts of superoxide, NaO_2. When heated above 300°C under oxygen pressure, the metal forms the superoxide, NaO_2. Sodium dissolved in liquid ammonia reacts with oxygen to produce the superoxide. The reaction is rapid, but the product is impure. Sodium also reacts with ozone forming an unstable ozonide, NaO_3.

Sodium combines with hydrogen forming sodium hydride, NaH. The reaction is slow at ambient temperature but proceeds rapidly above 200°C when the metal is dispersed or spread over the surface of an inert solid (such as a hydrocarbon). Sodium and hydrogen react with aluminum powder to form sodium aluminum hydrides. Two such complex hydrides, the tetrahydride, $NaAlH_4$, and the hexahydride, Na_3AlH_6, are produced. The nature of the product depends on reaction conditions. Under high hydrogen pressure and higher aluminum to sodium ratio, formation of the tetrahydride is favored. Such reactions are catalyzed by trialkyl aluminum.

Sodium reacts violently with water liberating hydrogen:

$$2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow$$

The reaction is highly exothermic; the heat of reaction is about 99 kcal/mol. In a closed system excessive pressure generated can cause an explosion. The reaction can be well controlled in inert atmosphere if the heat of reaction is dissipated. The reaction occurs vigorously even at –80°C.

Sodium is stable in nitrogen at most temperatures. Reaction, however, occurs at very high temperatures or when nitrogen is activated by electric discharge. The products are sodium azide, NaN_3, and sodium nitride, Na_3N:

$$2Na + 3N_2 \rightarrow 2NaN_3$$

$$6Na + N_2 \rightarrow 2Na_3N$$

Reactions with dilute mineral acids can be vigorous to violent with liberation of hydrogen:

$$2Na + 2HCl \rightarrow 2NaCl + H_2\uparrow$$

Sodium is a powerful reducing agent. It reduces a number of metal oxides to metals at high temperatures. Examples are oxides of iron, copper, zinc, cadmium, mercury, chromium, titanium, and many other metals. It does not reduce oxides of lithium, magnesium, or calcium.

Sodium reduces most metal chlorides to metals. Thus, when heated with titanium or zirconium tetrachloride, sodium converts the halides to free metals. Chlorides of calcium, magnesium, and potassium are only partially reduced.

Sodium dissolves in liquid ammonia forming an unstable blue solution. The reaction is slow. Sodium amide and hydrogen are generated:

$$Na + NH_3 \rightarrow NaNH_2 + \tfrac{1}{2}H_2$$

This reaction is catalyzed by iron, cobalt, and nickel. Rate of reaction depends on temperature and concentration of sodium in liquid ammonia. At a temperature of –41.6°C and high concentration, the solution separates into two liquid phases that consist of a deep blue dilute solution at the bottom that is low in sodium, and a lighter solution of metallic bronze color on the top with a high sodium. Molten sodium reacts with ammonia gas at 300 to 400°C to form sodium amide.

Sodium reacts with carbon monoxide at 250 to 340°C forming sodium carbonyl, $(NaCO)_6$. At higher temperatures, sodium carbide Na_2C_2 is formed. With acetylene the products are sodium acetylide, $NaC{\equiv}CH$ and disodium acetylide NaC≡CNa (also known as sodium carbide). The latter compound also is obtained by heating sodium metal with sodium carbonate at 500 to 700°C.

Sodium reacts with phosphorus on heating to form sodium phosphide, Na_3P. When ignited with phosphorus in the presence of air, sodium phosphate, Na_3PO_4, is obtained. When heated with phosphorus trichloride, sodium reduces the latter compound to elemental phosphorus:

$$3Na + PCl_3 \rightarrow 3NaCl + P$$

On the other hand, heating the metal with phosphorus pentachloride yields sodium phosphide:

$$6Na + 2PCl_5 \rightarrow 2Na_3P + 5Cl_2$$

Sodium combines with sulfur, selenium, and tellerium at high temperatures forming binary compounds. With sulfur the product is sodium sulfide:

$$2Na + S \rightarrow Na_2S$$

Sodium sulfide also is produced when the metal is heated with carbon disulfide. The reaction is violent:

$$4Na + CS_2 \rightarrow 2Na_2S + C$$

Sodium combines with all halogens forming sodium halides. The metal ignites with fluorine, forming hydrogen fluoride. Thin metal film reacts readily with chlorine and bromine at ordinary temperatures. Molten sodium burns in chlorine producing sodium chloride. The metal reacts with iodine, only in vapor phase, forming sodium iodide.

Sodium reacts with caustic soda at temperatures between 300 to 385°C:

$$2Na + NaOH \rightarrow Na_2O + NaH$$

Reaction with caustic potash is complicated, involving several intermediates that finally yield potassium metal and sodium hydroxide:

$$Na + KOH \rightarrow K + NaOH$$

Reaction with nitrous oxide yields sodium oxide:

$$2Na + N_2O \rightarrow Na_2O + N_2$$

Reaction with liquid nitrogen pentoxide at low temperatures forms sodium nitrate and nitrogen dioxide:

$$2Na + N_2O_5 \rightarrow NaNO_3 + NO_2$$

Sodium reacts rapidly with hydrogen sulfide in the presence of moisture to form sodium sulfide. With dry hydrogen sulfide the reaction is slow.

The molten metal reacts violently with sulfur dioxide to form sodium hydrosulfite, $Na_2S_2O_4$:

$$2Na + 2SO_2 \rightarrow Na_2S_2O_4$$

Sodium forms alloys with a number of metals including lead, chromium, mercury, aluminum, silicon, and iron. With mercury, it forms sodium amalgam. Sodium-lead alloy is commercially used to produce tetraethyllead, which was used historically as an additive to gasoline:

$$4C_2H_5Cl + 4NaPb \rightarrow (C_2H_5)_4Pb + 3Pb + 4NaCl$$

Sodium reacts with lower primary alcohols forming its alkoxide:

$$2Na + 2C_2H_5OH \rightarrow 2C_2H_5ONa + H_2$$

Reaction is slow with secondary and tertiary alcohol.

Sodium displaces halogens from alkyl halides forming alkanes (Wurtz reaction):

$$2RX + 2Na \rightarrow R—R + 2NaX$$

Carboxylic acids may react with sodium forming sodium salts, liberating hydrogen or they may decompose:

$$2CH_3COOH + 2Na \rightarrow 2CH_3COONa + H_2$$

Sodium reacts with naphthalene in dimethyl ether to form a dark green reactive complex. This addition product, naphtalenesodium, $C_{10}H_8Na$, is stabilized by solvation with ether. Anthracene, phenanthrene, biphenyl, and many other aromatics form similar complexes with sodium in the presence of methylethyl ether, tetrahyrofuran, dioxane, and other ethers.

Analysis

All sodium compounds impart a golden yellow color to flame. Sodium can be identified spectroscopically by characteristic line spectra. Trace sodium may be measured quantitatively by flame atomic absorption or flame emission photometric method. The element may be measured at 589 nm using an air–acetylene flame. If using an ICP-atomic emission spectrophotometer, sodium may be measured at 589.00 or 589.59nm. Metallic sodium may be analyzed quantitatively by treating with ethanol and measuring the volume of hydrogen liberated.

Hazard

Sodium is a highly reactive metal. It ignites in air and reacts violently with water. Many of its reactions are explosive (see Reactions). It should be stored under kerosene or hydrocarbon solvents. Contact with skin can cause serious burns. Contact with the eyes can cause blindness.

SODIUM ACETATE

[127-09-3]
Formula: CH_3COONa; MW 82.035; also forms a stable trihydrate, $CH_3COONa \cdot 3H_2O$ [6131-90-4], MW 136.08

Uses

Sodium acetate is a mordant in dyeing. Other applications are in photography, as an additive to food, in purification of glucose, in preservation of meat, in tanning, and as a dehydrating agent. In analytical chemistry it is used to prepare buffer solution.

Physical Properties

Anhydrous salt is a colorless crystalline solid; density 1.528 g/cm³; melts at 324°C; very soluble in water; moderately soluble in ethanol.

The colorless crystalline trihydrate has a density 1.45 g/cm³; decomposes at 58°C; is very soluble in water; pH of 0.1M aqueous solution is 8.9; moderately soluble in ethanol, 5.3 g/100mL.

Thermochemical Properties

$\Delta H_f°$	–169.4 kcal/mol
$\Delta G_f°$	–145.2 kcal/mol
S°	23.4 cal/deg mol
C_ρ	19.1 cal/deg mol

Preparation

Sodium acetate is prepared by reacting sodium hydroxide or sodium carbonate with acetic acid in aqueous solution. The solution is evaporated to obtain hydrated crystals of sodium acetate.

$$NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$$

$$Na_2CO_3 + CH_3COOH \rightarrow 2CH_3COONa + CO_2 + H_2O$$

SODIUM AMIDE

[7782-92-5]
Formula $NaNH_2$; MW 39.013

Synonym: sodamide

Uses

Sodium amide is a dehydrating agent. It is used in preparing sodium cyanide and hydrazine, and in many organic synthetic reactions such as Claisen condensations, alkylations of ketones and nitriles, and in ammonolysis reactions.

Physical Properties

White crystalline powder with odor of ammonia; orthogonal crystals; density 1.39 g/cm^3; melts at 210°C; begins to volatilize at 400°C; decomposes at 500°C; decomposed by water and hot alcohol; in fused state it dissolves zinc, magnesium and other metals, as well as, quartz, glass, and silicates.

Thermochemical Properties

$\Delta H_f°$	–29.6 kcal/mol
$\Delta G_f°$	–15.3 kcal/mol
S°	18.4 cal/deg mol
C_ρ	15.8 cal/deg mol

Preparation

Sodium amide is prepared by passing dry ammonia gas over sodium metal at 350°C:

$$2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$$

Also, it may be prepared by reacting sodium metal with liquid ammonia in the presence of a catalyst such as iron(III) nitrate. The compound must be stored in well-sealed containers free from air or moisture.

Reactions

Sodium amide dissociates to its elements, sodium, nitrogen, and hydrogen at temperatures between 500 and 600°C.

Its reaction with water is violent, forming sodium hydroxide and ammonia:

$$NaNH_2 + H_2O \rightarrow NaOH + NH_3$$

With alcohol the reaction is moderate forming sodium alkoxide and ammonia:

$$NaNH_2 + CH_3OH \rightarrow NaOCH_3 + NH_3$$

When heated with nitrous oxide at 200°C the products are sodium azide, caustic soda, and ammonia:

$$2NaNH_2 + N_2O \rightarrow NaN_3 + NaOH + NH_3$$

Sodium amide reacts with carbon at 800°C to form sodium cyanamide and hydrogen:

$$2NaNH_2 + C \rightarrow Na_2CN_2 + 2H_2$$

Analysis

Elemental composition: Na 58.93%, N 35.90%, H 5.17%. The compound may be decomposed cautiously with water (reaction is violent) under cooling to yield sodium hydroxide and ammonia. (Or it may be decomposed with anhyrous alcohol to form ammonia and sodium alcoholate. The alcoholate then may be treated with water to form sodium hydroxide). Ammonia liberated is dissolved in water and the solution is measured using an ammonia-selective electrode. Alternatively, ammonia is collected over boric acid solution containing a small quantity of methyl red indicator. The solution is titrated with a standard solution of sulfuric acid. Sodium hydroxide is measured by titration with a standard solution of hydrochloric or sulfuric acid.

Hazard

Sodium amide is a flammable solid. It undergoes violent reactions with oxygen (air), water, and oxidants. Also, it explodes when heated, crushed or grinded. If not properly sealed, it can become explosive on storage, the warning sign for which is development of yellow or brownish color. Such material may be destroyed safely by covering with benzene or toluene and slowly adding ethanol while stirring.

The compound is a strong irritant to skin and eye.

SODIUM AZIDE

[26628-22-8]
Formula NaN_3; MW 65.01

Uses

Sodium azide is used to make lead azide and hydrazoic acid, and as a propellant for automotive safety bags. It also is used as an antihypertensive agent to control blood pressure.

Physical Properties

Colorless hexagonal crystals; density 1.846 g/cm^3 at 20°C; decomposes on heating to produce sodium and nitrogen; also decomposes in vacuum; soluble in water partially converting to hydrazoic acid, solubility in water, 41.7 g/100mL; slightly soluble in alcohol, 0.316g/100mL at 16°C; soluble in liquid ammonia.

Thermochemical Properties

$\Delta H_f°$ (cry)	5.19 kcal/mol
$\Delta G_f°$ (cry)	22.41 kcal/mol
S° (cry)	23.15 cal/deg mol

C_ρ (cry) 18.31 cal/deg mol

Preparation

Sodium azide is prepared by reacting sodium amide with nitrous oxide. The amide is heated with nitrous oxide at 200°C or its solution in liquid ammonia is treated with nitrous oxide at ambient temperature:

$$2NaNH_2 + N_2O \rightarrow NaN_3 + NaOH + NH_3$$

Analysis

Elemental composition: Na 35.36%, N 64.64%. The salt is dissolved in water, sufficiently diluted, and analyzed for sodium (see Sodium). The solid powder is decomposed cautiously and liberated nitrogen is measured by GC-TCD or GC/MS. The characteristic mass for N_2 is 28.

Hazard

Sodium azide is a toxic as well as an explosive substance (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2^{nd} ed. New York: John Wiley & Sons). Although inert to shock, violent decomposition can occur when heated at 275°C. Contact of solid or solution with lead and copper must be avoided. Reactions with halogens, carbon disulfide, or chromyl chloride can be explosive. Dissolution in water produces toxic vapors of hydrazoic acid. The salt is an acute poison causing headache, hypotension, hypothermia, and convulsion.

LD_{50} oral (rats): 27 mg/kg

SODIUM BICARBONATE

[144-55-8]
Formula $NaHCO_3$; MW 84.007
Synonyms: baking soda; sodium hydrogen carbonate; sodium acid carbonate

Uses

Sodium bicarbonate is an ingredient of baking powder. It also is used in making effervescent salts and beverages, artificial mineral waters, and several other sodium salts. It is used in fire extinguishers, in gold plating, in cleaning formulations, in preventing mold growth on timber, in mouthwash, and as a laboratory reagent. In medicine it is used in antacids and alkalizers.

Physical Properties

White crystalline powder or granules; monoclinic crystals; density 2.20 g/cm^3; decomposes around 50°C, begins to lose carbon dioxide; converts to sodium carbonate at 100°C; soluble in water, 10g/100 mL at 20°C; slowly decomposes to CO_2 and Na_2CO_3 in aqueous solution at ambient temperature; decomposes to Na_2CO_3 in boiling water; aqueous solution slightly alkaline; pH of 0.1M solution at 25°C is about 8.3; insoluble in alcohol; decomposes in acids.

Thermochemical Properties

$\Delta H_f°$	–227.2 kcal/mol
$\Delta G_f°$	–203.4 kcal/mol
S°	24.3 cal/deg mol
C_ρ	20.9 cal/deg mol

Preparation

Sodium bicarbonate is prepared by passing carbon dioxide into a saturated solution of sodium carbonate. The bicarbonate, being less soluble than carbonate, precipitates:

$$Na_2CO_3\ (aq) + CO_2(g) + H_2O\ (l) \rightarrow 2NaHCO_3\ (s)$$

Also, sodium bicarbonate is obtained as a by-product of sodium carbonate manufacture using the Solvay process (see Sodium Carbonate).

SODIUM CHLORIDE

[7647-14-5]
Formula NaCl; MW 58.443
Synonyms: common salt; salt; rock salt; halite; table salt.

Occurrence and Uses

Sodium chloride is widely distributed in nature. Oceans are the vast source of sodium chloride. It occurs in seawater at an average concentration of 2.68 wt%. It also occurs in many inland saline waters and in salt deposits in sedimentary rocks, as the mineral halite.

Sodium chloride is probably the most important salt of both sodium and chlorine. Sodium chloride, common table salt, is an essential component of most food preparation, imparting flavor to food and providing the sodium nutritional requirement. Also, it is used for preserving food. Therapeutically, NaCl solution is used to combat dehydration as an electrolyte replenisher, and it is an emetic.

The most important applications of sodium chloride in the chemical industry are in making a number of important industrial chemicals such as hydrochloric acid, sodium hydroxide, sodium carbonate, and metallic sodium. It is the starting material in manufacturing these substances. Other uses are in dyeing and printing fabrics, glazing pottery, in making soap, and for curing hides. Sodium chloride is a component of many freezing mixtures.

Physical Properties

White granular crystals or powder; large crystals are colorless, transparent, or translucent; saline taste; cubic structure; refractive index 1.5442; density 2.165 g/cm^3; melts at 801°C; vaporizes at 1,413°C; soluble in water, 35.7g/100mL at 0°C and 39.1 g/100mL at 100°C; aqueous solution neutral; soluble in glycerol, ethylene glycol, and formic acid; sparingly soluble in methanol (1.49 g/100 mL) and liquid ammonia (2.15 g/100mL); insoluble in hydrochloric acid.

Thermochemical Properties

$\Delta H_f°$ (cry)	–98.27 kcal/mol
$\Delta H_f°$ (gas)	–42.22 kcal/mol
$\Delta G_f°$ (cry)	–91.82 kcal/mol
$\Delta G_f°$ (gas)	–47.00 kcal/mol
S° (cry)	17.24 cal/deg mol
S° (gas)	54.90 cal/deg mol
C_ρ (cry)	12.07 cal/deg mol
C_ρ (gas)	8.55 cal/deg mol

Production

Sodium chloride is produced by solar evaporation of seawater or brine from underground salt deposits. It also is produced by mining rock salt. The commercial product contains small amounts of calcium and magnesium chlorides.

Analysis

Elemental composition: Na 39.34%, Cl 60.66%. Aqueous solution may be analyzed for sodium by various instrumental methods (see Sodium) and for chloride ion by ion chromatography or chloride-ion selective electrode. Alternatively, the chloride ion may be measured by titration with a standard solution of silver nitrate using potassium chromate as indicator. Also, the salt can be identified by its physical properties.

SODIUM BISULFATE

[7681-38-1]
Formula $NaHSO_4$; MW 120.06; forms a monohydrate, $NaHSO_4 \cdot H_2O$
Synonyms: sodium hydrogen sulfate; sodium acid sulfate; niter cake

Uses

Sodium bisulfate is used for pickling metals; bleaching leather; carbonizing wool; in carbonic acid baths, and manufacturing magnesia cements

Physical Properties

Colorless crystals; triclinic structure; density 2.435g/cm^3 at 13°C; melts above 315°C; decomposes on further heating; soluble in water, 28.6 g/100mL at 25°C; highly soluble in boiling water, 100g/100 mL at 100°C; aqueous solution strongly acidic, pH of 0.1 M solution 1.4; insoluble in liquid ammonia; decomposed by alcohol into sodium sulfate and sulfuric acid

Thermochemical Properties

$\Delta H_f°$	–269.0 kcal/mol
$\Delta G_f°$	–237.3 kcal/mol

S°	27.0 cal/deg mol

Production

Sodium bisulfate is a by-product of sodium sulfate manufacture. One process involves reacting sulfuric acid with sodium nitrate at high temperature to form nitric acid and sodium bisulfate:

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3\,(g)$$

In the above reaction, nitric acid is obtained as vapor. It is purged from the system and collected in water to obtain nitric acid solution of desired concentration. Sodium bisulfate is separated by fractional crystallization.

Analysis

Elemental composition: Na 19.15%, S 26.71%, H 0.84%, O 53.30% An aqueous solution is analyzed to determine sodium content. Bisulfate anion can be measured by ion chromatography. The HSO_4^- can be measured quantitatively by titrating its aqueous solution (strongly acidic) with a standard solution of base.

SODIUM BOROHYDRIDE

[16940-66-2]
Formula $NaBH_4$; MW 37.833
Synonym: sodium tetrahydroborate

Uses

Sodium borohydride is used mostly as a reducing agent in a number of organic synthetic reactions. It reduces aldehydes, ketones and acid chlorides. The salt also is a source of hydrogen and is used to prepare other borohydrides. Other uses are bleaching wood pulp, removal of mercury from effluent wastes, decolorizing plasticizers, and as a blowing agent for plastics.

Physical Properties

White cubic crystals; hygroscopic; density 1.07 g/cm^3; decomposes slowly at about 400°C in vacuum or in moist air; soluble in water, decomposing and evolving hydrogen; also soluble in alcohols, liquid ammonia, amines and pyridine.

Thermochemical Properties

$\Delta H_f°$	–45.1 kcal/mol
$\Delta G_f°$	–29.6 kcal/mol
S°	24.2 cal/deg mol
C_ρ	20.7 cal/deg mol

Preparation

Sodium borohydride is prepared by reacting sodium hydride with trimethyl borate at about 250°C:

$$4\ NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3$$

Also, sodium borohydride can be made by passing diborane, B_2H_6, through a solution of sodium methylate, $NaOCH_3$, in methanol:

$$2B_2H_6 + 3NaOCH_3 \rightarrow 3NaBH_4 + B(OCH_3)_3$$

Alternatively, diborane may be be passed through a solution of sodium tetramethoxyborohydride at low temperatures:

$$3\ NaB(OCH_3)_4 + 2B_2H_6 \rightarrow 3NaBH_4 + 4B(OCH_3)_3$$

Reactions

Sodium borohydride liberates hydrogen in contact with water, alcohol, and several other compounds. Because of its ability to release hydrogen readily, this salt is a very effective reducing agent.

Analysis

Elemental composition: Na 60.77%, B 28.58%, H 10.65%. Sodium and boron content can be measured by AA or ICP measuremeant. The borohydride should be dissolved cautiously in water for the metal analysis. The compound is treated with ethanol and volume of liberated hydrogen is measured to determine hydrogen content.

Hazard

Contact with oxidizers can produce violent reactions. The compound is a fire hazard because of its easy hydrogen release.

SODIUM BROMIDE

[7647-15-6]
Formula: NaBr: MW 102.89; forms a dihydrate, $NaBr \cdot 2H_2O$ [13466-08-5], MW 138.92

Occurrence and Uses

Sodium bromide occurs in seawater at an average concentration of 0.008%. It also is found naturally in some salt deposits. It is used in photography for preparing light-sensitive silver bromide emulsions. The salt also is used as a bleaching and disinfecting agent for water treatement in swimming pools, health spas, and hot tubs. Other uses are as a catalyst for partial oxidation of hydrocarbons, for increasing density of aqueous drillng fluids for oil wells, as an electrolyte component in sodium-halogen batteries, as a brominating agent in organic synthesis, in preparing bromide salts, and as a laboratory reagent. Sodium bromide is used in medicine as a sedative and hypnotic.

Physical Properties

White crystalline powder or granules; saline and slight bitter taste; cubic structure; density 3.20 g/cm^3; melts at 747° C; vaporizes at 1,390°C; vapor pressure 1 torr at 806°C and 5 torr at 903°; highly soluble in methanol, 16.7 g/100mL.

The dihydrate is a white crystalline solid; density 2.18 g/cm^3; decomposes at 36°C; soluble in water; sparingly soluble in methanol.

Thermochemical Properties

$\Delta H_f°$(cry)	–86.30 kcal/mol
$\Delta H_f°$(gas)	–34.20 kcal/mol
$\Delta G_f°$(cry)	–83.41 kcal/mol
$\Delta G_f°$(gas)	–42.33 kcal/mol
S°(cry)	20.75 cal/deg mol
S°(gas)	57.65 cal/deg mol
C_ρ(cry)	12.28 cal/deg mol
C_ρ(gas)	8.68 cal/deg mol
ΔH_{fus}	6.24 kcal/mol

Preparation

Sodium bromide can be prepared by several methods. Pure salt can be made by neutralizing sodium hydroxide or sodium carbonate with hydrobromic acid. The solution is evaporated for crystallization:

$$NaOH + HBr \rightarrow NaBr + H_2O$$

$$NaCO_3 + HBr \rightarrow NaBr + CO_2 + H_2O$$

Sodium bromide can be made by passing bromine through an aqueous solution of sodium hydroxide or carbonate in the presence of a reducing agent, such as ammonia, hydrazine, activated charcoal, or Fe^{2+} ion. A typical method involves adding iron to bromine water to form ferrosoferric bromide, $Fe[FeBr_5]$. This double salt is dissolved in excess water followed by addition of sodium carbonate. The product mixture is filtered and the filtrate is evaporated to crystallize sodium bromide. The overall reaction may be written as follows:

$$3Fe + 4Br_2 + 4Na_2CO_3 \rightarrow 8NaBr + FeCO_3 + Fe_2(CO_3)_3$$

Another method involves adding excess bromine to a solution of sodium hydroxide. This forms sodium bromide and bromate. The product solution is evapoated to dryness. The bromate is reduced to bromide by heating with carbon:

$$3Br_2 + 2NaOH + H_2O \rightarrow NaBr + NaBrO_3 + 4HBr$$

Analysis

Elemental composition: Na 22.35%, Br 77.65%. The salt is dissolved in water. The aqueous solutions are analyzed for sodium by AA or ICP and for bromide by ion chromatography. The titrimetric, colorimetric, and electrode tests for bromide ion are susceptible to interference from chloride ion. Ion chromatography should be the most reliable confirmatory test.

SODIUM CARBONATE

[497-19-8]
Formula: Na_2CO_3; MW 105.99; forms a monohydrate $Na_2CO_3 \cdot H_2O$ [5968-11-6], MW 124.00 and a decahydrate, $Na_2CO_3 \cdot 10H_2O$ [6132-02-1] having a molecular weight 286.14
Synonyms: The anhydrous salt Na_2CO_3 also is called “Solvay soda” and “soda ash” (technical grade is about 99% purity). The decahydrate $Na_2CO_3 \cdot 10H_2O$ also is known as “washing soda” or “sal soda.” These two names usually refer to the technical product. Other synonyms for the decahydrate are “soda” and “Nevite.”

Occurrence and Uses

Sodium carbonate occurs in nature as monohydrate in the mineral thermonatrite. It also occurs naturally as the mineral natron or natrite in its decahydrate form.

Sodium carbonate is one of the most important salts of sodium, used in manufacturing several other sodium salts. Other major uses are in manufacturing glass, soaps and detergents, pulp, and paper. Also, it is used for washing textiles and wool, in cleaning preparations, for bleaching linen and cotton, in water treatment, and in photography. Sodium carbonate is used as an emetic. Sodium carbonate solution cleanses skin and softens skin rashes. The salt is a common laboratory reagent with wide applications in analytical chemistry.

Physical Properties

The anhydrous salt is an odorless white powder; alkaline taste; hygroscopic; density 2.54 g/cm^3; melts at 851°C; begins to loose CO_2 well before melting; soluble in water; insoluble in alcohol; dissolves in acids liberating CO_2.

The monohydrate consists of colorless and odorless small crystals or cystalline powder; orthorhombic structure; refractive index 1.420; hardness 1.3 Mohs; density 2.25 g/cm^3; loses water at 100°C becoming anhydrous; very soluble in water; insoluble in ethanol.

The decahydrate consists of transparent crystals; effloresces on exposure to air; density 1.46 g/cm^3; decomposes at 34°C; very soluble in water; insoluble in ethanol.

Aqueous solutions are strongly alkaline.

Thermochemical Properties

$\Delta H_f°$	–270.2 kcal/mol
$\Delta G_f°$	–249.6 kcal/mol

S°	32.27cal/deg mol
C_ρ	26.84 cal/deg mol
ΔH_{fus}	7.10 kcal/mol

Production

Sodium carbonate at present is mostly mined from its natural deposits. It also is manufactured synthetically by Solvay (or ammonia-soda) process. The natural production of sodium carbonate currently has supassed its synthetic production.

The Solvay process involves a series of partial reactions. The first step is calcination of calcium carbonate to form lime and CO_2. Lime is converted to calcium hydroxide. The most crucial step of the process involves reacting brine solution with carbon dioxide and ammonia to produce sodium bicarbonate and ammonium chloride. Sodium bicarbonate converts to sodium carbonate. The calcium hydroxide and ammonium chloride react to form calcium chloride as the by-product. The partial reactions are shown below:

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$2NaCl + 2CO_2 + 2NH_3 + 2H_2O \rightarrow 2NaHCO_3 + 2NH_4Cl$$

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + 2H_2O$$

The overall reaction:

$$CaCO_3 + 2NaCl \rightarrow Na_2CO_3 + CaCl_2$$

Sodium carbonate was made historically by the Leblanc process. The first commercial production was carried out by the Leblanc process. In this process, sodium chloride was treated with sulfuric acid to produce sodium sulfate and hydrochloric acid. Heating the sodium sulfate with coal and limestone produced a “black ash” that contained sodium carbonate, calcium sulfide, unreacted coal, and calcium carbonate. Sodium carbonate was separated from the black ash by leaching with water. The overall reaction is as follows:

$$Na_2SO_4 + 2C + CaCO_3 \rightarrow Na_2CO_3 + CaS + 2CO_2$$

Analysis

Elemental composition: Na 43.39%, C 11.33%, O 45.29%. Aqueous solution of sodium carbonate is strongly alkaline and its normality can be measured by acid-base titration. Sodium content can be measured by AA, ICP, and other instrumental analyses. Carbonate anion can be measured by ion chromatography or from carbon dioxide liberated when the salt is treated with dilute acid. Liberated CO_2 can be identified by the limewater test or by GC-TCD or GC/MS (m/z 44).

SODIUM CYANIDE

[143-33-9]
Formula: NaCN; MW 49.008

Uses

Sodium cyanide is used in extracting gold and silver from their ores. It forms soluble complexes with these metals. Other uses are in electroplating baths, heat treatment of metals, fumigation, and preparing other cyanide salts and complexes.

Physical Properties

White cubic crystals; hygroscopic; density 1.6 g/cm^3; melts at 563°C; very soluble in water; aqueous solution strongly alkaline and decomposes rapidly.

Thermochemical Properties

$\Delta H_f°$	–20.9 kcal/mol
$\Delta G_f°$	–18.3 kcal/mol
S°	27.6 cal/deg mol
C_ρ	16.8 cal/deg mol

Preparation

Sodium cyanide can be prepared by several methods (See Potassium Cyanide).

It is prepared by passing hydrogen cyanide through a 50% aqueous solution of sodium hydroxide followed by evaporation of the solution in vacuum:

$$NaOH + HCN \rightarrow NaCN + H_2O$$

Another method is to reduce sodamide with carbon at red heat:

$$NaNH_2 + C \rightarrow NaCN + H_2\uparrow$$

Also, sodium cyanide can be made by heating a mixture of sodium carbonate and carbon with ammonia at high temperatures:

$$Na_2CO_3 + 4C + 2NH_3 \rightarrow 2NaCN + 3CO\uparrow + 3H_2\uparrow$$

Reactions

Reactions of sodium cyanide are similar to those of potassium cyanide (See Potassium Cyanide).

Analysis

Elemental composition: Na 46.92%, C 24.50%, N 28.58%. An aqueous solution is analyzed for sodium. Cyanide is measured by an electrode specific to cyanide ion. Alternatively, cyanide may be measured by pyridine-barbituric acid colorimetric test (See Hydrogen Cyanide).

Toxicity

Sodium cyanide is extremely toxic. Ingestion of a small quantity can be fatal. The toxic properties are similar to Potassium Cyanide (See Potassium Cyanide).

SODIUM ETHOXIDE

[141-52-6]
Formula: C_2H_5ONa; MW 68.06
Synonyms: sodium ethylate; caustic alcohol

Uses

Sodium ethoxide is used in organic synthesis for condensation reactions. It also is a catalyst in many organic reactions.

Physical Properties

White or yellowish powder; hygroscopic; darkens and decomposes on exposure to air; decomposes in water forming sodium hydroxide and ethanol; dissolves in absolute ethanol.

Preparation

Sodium ethoxide is prepared by reacting sodium with absolute ethanol:

$$2Na + 2C_2H_5OH \rightarrow 2C_2H_5ONa + H_2$$

Sodium in small quantities is added to absolute alcohol at 10°C. The temperature is raised to warming (to about 38°C). The mixture is cooled again and sodium and absolute alcohol are added gradually followed by careful warming. The process is repeated to obtain a sufficient yield of the product.

Analysis

Elemental composition: Na 33.79%, C 35.29%, H 7.41%, O 23.51%. The compound is decomposed in water cautiously. A portion of the aqueous solution is measured for sodium hydroxide by acid-base titration, while another portion is analyzed for sodium by AA or ICP.

SODIUM FLUORIDE

[7681-49-4]
Formula: NaF; MW 41.988

Uses

Sodium fluoride is used in electroplating, as a steel degassing agent, in vitreous glasses and enamels, in heat-treating salt compositions, and preserving wood. The salt also is used in pesticide formulations and as an insecticide for ant and roach control. Sodium fluoride is used for fluoridating drinking water and for disinfecting apparatus in distilleries. An important application of this salt is preparing other fluoride salts. Sodium fluoride occurs in nature as the mineral villiaumite.

Physical Properties

Colorless cubic or tetragonal crystals; density 2.78 g/cm^3; melts at 993°C; vaporizes at 1,695°C; moderately soluble in water 4.22 g/100mL at 18°C; soluble in hydrofluoric acid; insoluble in ethanol.

Thermochemical Properties

$\Delta H_f°$	–137.1 kcal/mol
$\Delta G_f°$	–129.9 kcal/mol
S°	12.3 cal/deg mol
C_ρ	11.2 cal/deg mol

Preparation

Sodium fluoride is prepared by adding sodium hydroxide or sodium carbonate to a 40% solution of hydrofluoric acid. In excess hydrofluoric acid, sodium bifluoride, $NaHF_2$, is formed. NaF also is made by fusion of cryolite with caustic soda. Technical grade products are usually sold at 90 to 95% purity.

Analysis

Elemental composition Na 54.75%, F 45.25%. The salt is dissolved in water and analyzed for sodium and fluoride anion. The anion can be measured effectively with a fluoride ion-selective electrode or by ion chromatography.

Toxicity

Sodium fluoride is an acute toxicant. Ingestion of large quantites (5 to 10g) can cause death in humans. Smaller quantities can produce nausea, vomiting, diarrhea, stupor, and weakness. Other symptoms are tremor, muscular weakness, and dyspnea. Mottling of teeth can occur from chronic exposure.

SODIUM FORMATE

[141-53-7]
Formula HCOOH; MW 68.008

Uses

Sodium formate is used as a reducing agent, in dyeing and printing fabrics, in manufacturing formic and oxalic acids and sodium dithionite, as an analytical reagent for precipitating noble metals, and as a complexing agent. Sodium formate also is used as a buffering agent to adjust the pH of strong acids to higher values.

Physical Properties

White crystals; slightly hygroscopic; faint odor of formic acid; density 1.92 g/cm^3; melts at 253°C; decomposes on further heating, first forming sodium oxalate and hydrogen and then sodium carbonate; very soluble in water; the aqueous solution neutral, pH about 7; soluble in glycerol; slightly soluble in alcohol; insoluble in ether.

Preparation

Sodium formate is prepared by heating sodium hydroxide with carbon monoxide under pressure:

$$NaOH + CO \rightarrow HCOONa$$

Also, it is obtained as a byproduct from manufacturing pentaerythritol, $C(CH_2OH)_4$.

Analysis

Elemental composition: Na 33.81%, C 17.66%, H 1.48, O 47.05%. An aqueous solution may be analyzed to measure the sodium content of the salt. Reaction with noble metal in solution precipitates metal formate which can be filtered, dried and weighed to determine formate concentration. Also, an aqueous solution may be titrated against a standard solution of any suitable oxidizing agent. Another method is to decompose sodium formate to sodium oxalate above 253°C, cooling the mixture, dissolving with water and analyzing the aqueous solution for the oxalate ion by redox titration or ion chromatography, and analyzing sodium by AA or ICP method.

$$2HCOONa \rightarrow Na_2C_2O_4 + H_2$$

SODIUM HYDRIDE

[7646-69-7]
Formula NaH; MW 24.00

Uses

Sodium hydride is used as a reducing agent and reduction catalyst. It also reduces oxide scale on metals.

Physical Properties

Silvery needles; refractive index 1.470; density 0.92 g/cm^3; decomposes at 800°C; decomposes explosively in water; reacts violently with lower alcohols;dissolves in molten sodium and molten sodium hydroxide; insoluble in liquid ammonia, benzene, carbon tetrachloride and carbon disulfide.

Preparation

Sodium hydride is prepared by passing hydrogen gas into molten sodium metal dispersed in oil. Alternatively, the hydride can be made by passing hydrogen into sodium dispersed over the surface of an inert solid, such as, hydrocarbon above 200°C

$$2Na + H_2 \rightarrow 2NaH$$

Reactions

Sodium hydride is a powerful reducing agent. It reduces metal oxides, metal chlorides, and a number of oxidizible substances. Its reactions with water can proceed with explosive violence:

$$NaH + H_2O \rightarrow NaOH + H_2$$

Also, its reactions with alcohols can be vigorous to violent. With lower alcohols the reaction is usually violent:

$$NaH + CH_3OH \rightarrow NaOCH_3 + H_2$$

Analysis

Elemental composition: Na 95.79%, H 4.21%. The hydride is dissolved in water in small amounts (violent reaction occurs with water) very cautiously and the solution is analyzed for sodium. Another aliquot of solution is measured to determine concentration of OH$^-$ (of the product NaOH) formed by acid-base titration.

SODIUM HYDROXIDE

[1310-73-2]
Formula: NaOH; MW 39.997
Synonyms: caustic soda; white caustic; sodium hydrate

Uses

Sodium hydroxide is one of the most important industrial chemicals. In volume, it is in the top ten chemicals produced in the United States. It is used in manufacturing a large number of compounds including several sodium salts, in treating cellulose for producing rayon and cellophane, and in manufacturing soaps, detergents, pulp, and paper. Sodium hydroxide is a common neutralizing agent for acids in acid-base titrations and petroleum refining. Another major application is extracting metals from their ores where alkali fusion, such as fusion with caustic soda, often is applied to open the ores. Additionally, sodium hydroxide is used to precipitate metals as hydroxides. Other uses are in reclaiming rubber, dissolving casein in plastics production, refining vegetable oils, processing textiles, as an eluant in ion chromatography, etching and electroplating, and as a laboratory reagent. Sodium hydroxide also is used as a strong base in many organic synthesis and base-catalyzed reactions.

Physical Properties

White orthorhombic crystals, produced in the form of pellets, lumps, sticks, beads, chips, flakes or solutions; hygroscopic; very corrosive; rapidly absorbs CO_2 and water from the air; density 2.13 g/cm^3; melts at 323°C; vaporizes at 1388°C; vapor pressure 1 torr at 739°C and 5 torr at 843°C; very soluble in water (110 g/100mL at room temperature), generating heat on dissolution; aqueous solutions highly alkaline, pH of 0.5% solution about 13 and 0.05% solution about 12; soluble in methanol, ethanol and glycerol (23.8 g/100 mL methanol and 13.9 g/100 mL ethanol at ambient temperatures.)

Thermochemical Properties

$\Delta H_f°$	–101.7 kcal/mol
$\Delta G_f°$	–90.7kcal/mol
$S°$	15.4cal/deg mol
C_ρ	14.2cal/deg mol
ΔH_{fus}	1.58 kcal/mol
ΔH_{vap}	41.8 kcal/mol
ΔH_{soln}	–10.64 kcal/mol

Production

Sodium hydroxide is manufactured together with chlorine by electrolysis of sodium chloride solution. Various types of electrolytic cells are used commercially. They include the mercury cell, the diaphragm cell, and the membrane cell.

A saturated solution of brine is electrolyzed. Chlorine gas is liberated at the anode and sodium ion at the cathode. Decomposition of water produces hydrogen and hydroxide ions. The hydroxide ion combines with sodium ion forming NaOH. The overall electrolytic reactions may be represented as:

$$2Na^+ + 2Cl^- + 2H_2O \xrightarrow{energy} Cl_2\,(g) + H_2\,(g) + 2NaOH\,(aq)$$

The mercury cell proceeds in two stages that occur separately in two cells. The first is known as the brine cell or the primary electrolyzer in which sodium ion deposits on the mercury cathode forming amalgam, while chlorine gas is liberated at the anode:

$$Na^+ + Cl^- \rightarrow Na\text{-}Hg \text{ (cathode)} + \tfrac{1}{2}Cl_2(g) \text{ (anode)}$$

In the second cell, known as the decomposer cell, a graphite cathode is used while sodium amalgam serves as the anode. Water reacts with the sodium metal of the amalgam in the decomposer:

$$Na\text{-}Hg + H_2O \rightarrow Na^+ + OH^- + \tfrac{1}{2}H_2\uparrow + Hg$$

In chlor-alkali diaphragm cells, a diaphragm is employed to separate chlorine liberated at the anode from the sodium hydroxide and hydrogen generated at the cathode. Without a diaphragm, the sodium hydroxide formed will combine with chlorine to form sodium hypochlorite and chlorate. In many cells, asbestos diaphragms are used for such separation. Many types of diaphragm cells are available.

Sodium hydroxide is produced either as an anhydrous solid or as a 50% aqueous solution.

Reactions

Sodium hydroxide is a strong base. The most important reactions are the neutraliztion reactions with acids that form salts and water. Thus with sulfuric, hydrochloric, and nitric acids, the corresponding sodium salts are obtained when solutions are evaporated for crystallization. Neutralization with weak acids forms basic salts. Reactions with organic acids produce their soluble sodium salts.

Another type of reaction is double decomposition producing metal hydroxides. Thus, insoluble heavy metal hydroxides may be precipitated by treating caustic soda with a soluble metal salt:

$$PbCl_2 + 2NaOH \rightarrow Pb(OH)_2 + 2NaCl$$

Reactions with the oxides and hydroxides of amphoteric metals form soluble sodium salts of metal oxides:

$$Ga_2O_3 + 2NaOH \rightarrow 2NaGaO_2 + H_2O$$

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$$

Sodium hydroxide reacts with weak acid gases to form salts:

$$SO_2 + NaOH \rightarrow Na_2SO_3 + H_2O$$

$$H_2S + NaOH \rightarrow Na_2S + H_2O$$

$$HCN + NaOH \rightarrow NaCN + H_2O$$

A similar reaction occurs with carbon dioxide forming sodium carbonate:

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$$

Saponification of esters with sodium hydroxide is an important commerical reaction. In general, the reaction involves an ester reacting with sodium hydroxide to form an alcohol and sodium salt of the organic acid; for example, ethyl acetate forming ethanol and sodium acetate:

$$CH_3COOC_2H_5 + NaOH \rightarrow C_2H_5OH + CH_3COONa$$

or the formation of glyerol from fatty acid triglycerides:

$$C_3H_5\ (OOCR)_3 + 3NaOH \rightarrow C_3H_5(OH)_3 + 3RCOONa$$

Analysis

As a strong base, the strength of caustic soda solution can be determined by titration with a standard solution of strong acid using a color indicator or by potentiometric titration using a pH meter. Also, concentration of sodium in an aqueous solution can be measured by AA or ICP spectrophotometry.

Toxicity

Sodium hydroxide is highly corrosive to skin. Contact with eyes can damage vision.

SODIUM HYPOCHLORITE

[7681-52-9]
Formula $NaClO$; MW 74.442; exists as a stable pentahydrate, $NaClO \cdot 5H_2O$
Synonym: sodium oxychloride

Uses

Sodium hypochlorite is marketed only as an aqueous solution because the anhydrous solid is highly unstable and can explode. The solid pentahydrate also is unstable in air, decomposed by reaction with carbon dioxide from air. Aqueous solutions are very stable. They are used for bleaching textiles and paper pulp; in cleaning solutions; in water purification; as a disinfectant for swimming pools; and as a germicide and topical antiinfective. The hypochlorite also is used as an oxidizing agent in many preparative reactions. It is an ingredient of commercial bleaching products such as Clorox and Dazzle.

Physical Properties

Anhydrous sodium hypochlorite explodes; the pentahydrate is a pale-green crystalline solid; orthorhombic structure; density 1.6 g/cm^3; melts at 18°C; decomposed by CO_2 in the air; soluble in water, 29.3 g/100 mL at 0°C; the aqueous solution is highly stable.

Preparation

Sodium hypochlorite solution is obtained by passing chlorine into sodium hydroxide solution. The pentahydrate is obtained by crystallization.

Analysis

The hypochlorite ion may be identified most distinctly by ion chromatography. Its concentration in the aqueous solution combined as ClO^- and molecular Cl_2 (which is partly formed when hypochlorite is dissolved in water) can be measured by iodometric titration. A measured volume of sodium hypochlorite solution is added to a small volume of an acidified solution of potassium iodide (in excess). Iodine liberated is titrated with a standard solution of sodium thiosulfate or phenyl arsine oxide using starch as indicator. Blue color of starch solution decolorizes at the end point.

Toxicity

Skin contact with the solid hypochlorite pentahydrate or its concentrated solution can cause irritation. Ingestion may cause corrosion of mucous membranes and gastric perforation.

SODIUM IODIDE

7681-82-5]
Formula: NaI; MW 149.89

Uses

Sodium iodide is an iodine supplement in food, an expectorant, cloud seed to cause rain, and solubilizes iodine in aqueous solution for analytical work. The radioactive iodide salt of sodium, Na(I–131) is used to diagnose thyroid function.

Physical Properties

White crystalline deliquescent powder or granules; saline and slight bitter taste; absorbs moisture from air; slowly turns brown on exposure to air due to iodine evolved; density 3.67g/cm^3; melts at 660°C; vaporizes at 1,304°C; vapor pressure 1 torr at 767°C and 5 torr at 857°C; very soluble in water, 178.7 g/100 mL at 20°C and 294 g/100 mL at 70°C; soluble in ethanol and acetone.

Thermochemical Properties

$\Delta H_f°$	–68.79 kcal/mol
$\Delta G_f°$	–68.38 kcal/mol

S°	23.54 cal/deg mol
C_ρ	12.45 cal/deg mol

Preparation

Sodium iodide is prepared by adding hydriodic acid or an acidic iodide solution to a solution of sodium hydroxide or sodium carbonate, followed by evaporation and crystallization:

$$NaOH + HI \rightarrow NaI + H_2O$$

The solution is filtered to remove any impurities prior to its evaporation and crystallization.

Analysis

Elemental composition: Na 15.34%, I 84.66%. Aqueous solution is analyzed for sodium by AA or ICP and for iodide ion by ion chromatography or leukocrystal violent colorimetry (See Iodine). Alternatively, in an acidified solution of sodium hypochlorite, a measured amount of sodium iodide is titrated against a standard solution of sodium thiosulfate or phenyl arsine oxide using starch indicator to detect the end point.

SODIUM NITRATE

[7631-99-4]
Formula: $NaNO_3$; MW 84.99
Synonyms: Chile saltpeter; Chilean nitrate; soda niter

Occurrence and Uses

There are several natural deposits of sodium nitrate in various parts of the world, including Chile, Mexico, Egypt, and the United States. The most important application of sodium nitrate is its use as a fertilizer in agriculture. It is an effective fertilizer for cotton, tobacco, and vegetable crops. Its agricultural applications, however, have dwindled considerably in recent years because of the growth of ammonium nitrate and other fertilizers.

Another major use of sodium nitrate is in manufacturing explosives. It is a component of many types of dynamites and water-based slurry type blasting explosives. Sodium nitrate also is used in making charcoal briquettes. Sodium nitrate is used as an oxidizing and fluxing agent in manufacturing vitreous glass, fiberglass, porcelain, and enamels. Other uses are in the heat-treatment baths for alloys and metals, as a food preservative, in curing meats, and in preparing various salts.

Physical Properties

Colorless crystalline solid; saline taste; trigonal, and rhombohedrals structure; density 2.257g/cm^3; refractive index 1.587 (trigonal) and 1.336 (rhombohedral); melts at 308°C; decomposes at 380°C; specific conductance 95 μmhos/cm at 300°C; viscosity 2.85 centipoise at 317°C; very soluble in water 92.1 g/100 mL at 25°C and 180 g/100 mL at 100°C; very soluble in liquid ammonia; soluble in alcohol.

Thermochemical Properties

$\Delta H_f°$	–111.82 kcal/mol
$\Delta G_f°$	–87.73 kcal/mol
S°	27.85 cal/deg mol
C_ρ	22.20 cal/deg mol
ΔH_{fus}	3.585 kcal/mol

Production

Sodium nitrate is recovered from natural deposits. One such process, known as the Guggenheim nitrate process, is briefly outlined below: The ore is crushed. Sodium nitrate is leached from the ore by extraction with a brine solution at 40°C. The brine for leaching is made up of an aqueous solution of magnesium sulfate, $MgSO_4$, and calcium sulfate, $CaSO_4$. The caliche variety of Chilean ore contains mostly sodium nitrate and sodium chloride as the main saline components, along with limestone, clays, sand, lime, and inert volcanic rocks. Sodium nitrate usually occurs in this ore as a double salt with sodium sulfate $NaNO_3 \cdot Na_2SO_4 \cdot H_2O$. This double salt, which is sparingly soluble in water, is broken down by magnesium in leaching brine solution, thus releasing more sodium nitrate into the extract. Sodium nitrate finally is recovered from the leachate brine by fractional crystallization.

Brines of other compositions have been used to extract sodium nitrate from its ores. Many such processes, including the Shanks process practiced in the past to produce sodium nitrate, are now obsolete.

Analysis

Elemental composition: Na 27.08%, N 16.48%, O 56.47%. An aqueous solution of the salt is analyzed for sodium by various instrumental techniques (See Sodium). Nitrate ion in solution can readily be measured by ion chromatography, nitrate-ion selective electrode, or various colorimetric methods, such as its reduction with cadmium to nitrite followed by diazotization.

SODIUM OXALATE

[62-76-0]
Formula $Na_2C_2O_4$; MW 134.00
Synonym: ethanedioic acid disodium salt

Uses

Sodium oxalate is used as an analytical standard for standardization of potassium permanganate and other strong oxidizing agents. It also is used in finishing textiles, tanning leather, and blue printing.

Physical Properties

White crystalline powder; density 2.34 g/cm^3; decomposes around 250° C; sparingly soluble in water, 3.7 g/100 mL at room temperature; moderately soluble in boiling water, about 6.25 g/100 mL; the aqueous solution is practically neutral; insoluble in alcohol

Thermochemical Properties

$\Delta H_f°$ (gas)	–315.0 kcal/mol

Preparation

Sodium oxalate can be made by heating sodium formate at about 250°C:

$$2HCOONa \rightarrow Na_2C_2O_4 + H_2$$

It also can be prepared by reacting oxalic acid with a dilute aqueous solution of sodium hydroxide followed by evaporation and crystallization.

Analysis

Elemental composition: Na 34.32%, C 17.92%, O 47.76%. The aqueous solution is analyzed for sodium by AA or ICP method. The oxalate ion is quantitatively determined by titration against a standard solution of potassium permanganate.

SODIUM PHOSPHATE, DIBASIC

[7558-79-4]
Formula: Na_2HPO_4; MW 141.96; forms a dihydrate, $Na_2HPO_4 \cdot 2H_2O$, heptahydrate, $Na_2HPO_4 \cdot 7H_2O$ and a dodecahydrate, $Na_2HPO_4 \cdot 12H_2O$.
Synonyms: sodium hydrogen phosphate; disodium hydrogen phosphate; dibasic sodium phosphate; disodium phosphate; disodium orthophosphate; and sodium orthophosphate, secondary. The dihydrate is known as Sorensen's phosphate.

Uses

The dibasic salt is used as a laboratory reagent and a buffer in chemical analysis. Other uses are in manufacturing ceramics, detergents, and enamels; as a mordant in dyeing; for fireproofing paper and wood; for weighting and printing silk; in the treatment of boiler water; as a sequestrant in food; as a dietary supplement; in soldering enamels; and in fertilizers. It is used therapeutically as a cathartic.

Physical Properties

The anhydrous compound is white crystalline powder; hygroscopic; density 1.70 g/cm^3; converts to sodium pyrophosphate at 240°C; soluble in water;

insoluble in alcohol.

The dihydrate is a crystalline powder or granular solid; density 2.066 g/cm^3 at 15°C; loses water of crystallization at 92.5°C.

The heptahydrate is a powdered or granular crystalline solid; density 1.679 g/cm^3; loses five molecules of water at 48°C.

The dodecahydrate is made up of translucent crystals or granules; density 1.524 g/cm^3; readily loses five water molecules on exposure to air at ambient temperature; melts at 35°C when the salt contains all water of crystallization; loses all water at 100°C.

All the hydrates are soluble in water and insoluble in alcohol.

Thermochemical Properties

$\Delta H_f°$	–417.8 kcal/mol
$\Delta G_f°$	–384.4 kcal/mol
S°	36.97 cal/deg mol
C_ρ	32.34 cal/deg mol

Preparation

Dibasic sodium phosphate is prepared by treating phosphoric acid with a slight excess of sodium carbonate. The solution is boiled to expel carbon dioxide. Upon cooling dodecahydrate crystallizes out. Heating dodecahydrate at 100°C forms the anhydrous salt.

$$H_3PO_4 + Na_2CO_3 \rightarrow Na_2HPO_4 + CO_2 + H_2O$$

Dibasic sodium phosphate also is prepared by reacting dibasic calcium phosphate with sodium carbonate. The product calcium carbonate precipitates leaving dibasic sodium salt in the solution. The solution on cooling yields crystals of hydrated product.

$$CaHPO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2HPO_4$$

Analysis

Elemental composition (anhydrous salt): Na 32.39%, P 21.82%, H 0.71%, O 45.08%. An aqueous solution may be analyzed to determine the sodium content. Phosphorus may be analyzed by various colorimetric methods (See Phosphorus).

SODIUM PHOSPHATE, MONOBASIC

[7558-80-7]

Formula NaH_2PO_4; MW 119.98; forms a monohydrate, $NaH_2PO_4 \cdot H_2O$, [10049-21-5], MW 137.99; and a dihydrate, $NaH_2PO_4 \cdot 2H_2O$ [13472-35-0], MW 156.01.

Synonyms: sodium dihydrogen phosphate; sodium orthophsophate, primary; primary sodium phosphate; sodium biphosphate; monobasic sodium phosphate

Uses

Monobasic sodium phosphate is used in baking powders, acid cleansers, electroplating, as a dry acidulant, and in treating boiler water. It also is a nutrient supplement in food. It is a laboratory reagent used as a buffer.

Physical Properties

Anhydrous salt: white crystalline powder; slightly hygroscopic; forms sodium acid pyrophosphate, $Na_2H_2P_2O_7$ on heating above 225°C and sodium metaphosphate $(NaPO_3)_n$ at about 350 to 400°C; very soluble in water, aqueous solution acidic.

Monohydrate: white orthorhombic crystals or granules; density 2.04 g/cm^3; loses its water of crystallization at 100°C; very soluble in water, pH of 1% solution 4.5; insoluble in alcohol.

Dihydrate: large transparent crystals; orthorhombic bisphenoidal structure; density 1.915 g/cm^3; decomposes at 60°C; very soluble in water; insoluble in alcohol.

Preparation

Monobasic sodium phosphate can be prepared by partial neutralization of phosphoric acid with sodium hydroxide in equimolar amounts:

$$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$$

It also can be made by treating disodium hydrogen phosphate with phosphoric acid in proper stoichiometric amount:

$$Na_2HPO_4 + H_3PO_4 \rightarrow 2NaH_2PO_4$$

Analysis

Elemental composition: Na 19.16%, P 25.81%, H 1.68%, O 53.34%. The compound is dissolved in water and analyzed by AA or ICP to determine its sodium content. The phosphorus is analyzed as total P by acid digestion and colorimetric method (See Phosphorus and also Phosphoric Acid).

SODIUM PHOSPHATE, TRIBASIC

[7601-54-9]
Formula: Na_3PO_4; MW 163.94; forms a stable dodecahydrate, $Na_3PO_4 \cdot 12H_2O$ [7601-54-9], MW 380.12
Synonyms: trisodium phosphate; tertiary sodium phosphate; trisodium orthophosphate; tribasic sodium phosphate

Uses

Trisodium phosphate is used in detergents; in industrial cleaning solutions; in metal cleaner formulations; as a water softener; for the treatment of boiler water; as a paint remover; in photographic developers; for tanning leather; for manufacturing paper; in laundering; for clarifying sugar; as a dietary supplement; and a food additive. Also, it is a common laboratory reagent.

Physical Properties

The dodecahydrate is a white or colorless hexagonal crystal; density 1.62 g/cm^3; melts around 75°C on rapid heating; partially loses water of crystallization at 100°C; retains the last water molecule even at moderate ignition; soluble in water, about 28 g/100 mL at 20°C; the solution is strongly alkaline; the pH of a 0.1M solution 11.5; insoluble in alcohol.

Preparation

Trisodium phosphate may be prepared in two steps, first by adding a little excess of sodium carbonate to phosphoric acid and then boiling the solution to expel carbon dioxide. Sodium hydroxide is then added to the solution:

$$Na_2CO_3 + H_3PO_4 \rightarrow Na_2HPO_4 + CO_2 + H_2O$$

$$Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O$$

Alternatively, trisodium phosphate may be prepared by complete neutralization of phosphoric acid with sodium hydroxide, followed by evaporation and crystallization:

$$H_3PO_4 + 3NaOH \rightarrow Na_3PO_4 + 3H_2O$$

Analysis

Sodium is analyzed in aqueous solution by AA or ICP methods. Phosphate anion is measured by colorimetric methods (See Phosphoric Acid) or ion chromatography. The solution must be diluted appropriately. The compound is also identified from its physical properties.

SODIUM SULFATE

[7757-82-6]

Formula Na_2SO_4; MW 142.04; forms a decahydrate, $Na_2CO_3 \cdot 10H_2O$ (Glauber's salt) [7727-73-3]

Occurrence and Uses

Sodium sulfate occurs in nature as the minerals mirabilite and thenardite. While thenardite is the anhydrous form of Na_2SO_4, mirabilite is a naturally-occurring decahydrate, $Na_2SO_4 \cdot 10H_2O$.

Sodium sulfate is one of the most important sodium salts. The decahydrate, commonly known as the Glauber's salt, was first prepared by Johann Glauber in the seventeenth century as a by-product in making hydrochloric acid from sulfuric acid and sodium chloride.

Sodium sulfate is used in manufacturing paper pulp by the Kraft Process. Other uses are in manufacturing glass and ultramarine; in dyeing and printing textiles; as a filler in synthetic detergents; and for standardizing dyes. A major use of anhydrous sodium sulfate is as an agent to remove water from organic solvents and their extracts for organic synthesis and instrumental analysis. Sodium sulfate is a common laboratory reagent. Also, it is used to prepare other sodium salts.

Physical Properties

Anhydrous sodium sulfate is a white crystalline powder; orthorhombic or hexagonal structure; hygroscopic; refractive index 1.468; hardness 2.8 Mohs; density 2.664 g/cm^3; melts at 884°C; soluble in water, insoluble in ethanol.

The decahydrate consists of colorless monoclinic crystals; refractive index 1.394; hardness 1.8 Mohs; density 1.4 6g/cm^3; decomposes at 32°C; soluble in water; insoluble in ethanol.

Thermochemical Properties

$\Delta H_f°$	–331.5 kcal/mol
$\Delta G_f°$	–303.6 kcal/mol
$S°$	35.76 cal/deg mol
C_ρ	30.64 cal/deg mol
ΔH_{fus}	5.64 kcal/mol

Production

Sodium sulfate is mined from its natural mineral deposits and subjected to purification.

Sodium sulfate is synthesized by the Mannheim process or Hargreaves process. Manheim's process is based on Glauber's reaction between sulfuric acid and sodium chloride:

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl\uparrow$$

The process was devised by Johann Glauber to produce hydrochloric acid. Sodium sulfate is isolated from the solution by fractional crystallization.

Hargreaves' process also was developed to produce hydrochloric acid. It is a variation of Mannheim's method. In this method, sulfur dioxide is used instead of sulfuric acid. The reaction is as follows:

$$4NaCl + 2SO_2 + O_2 + 2H_2O \rightarrow 2Na_2SO_4 + 4HCl\uparrow$$

Sodium sulfate also is obtained as a byproduct of manufacturing phenol by caustic fusion.

Analysis

Elemental composition: Na 32.38%, S 22.57%, O 45.06%. An aqueous solution may be analyzed to measure sodium content (See Sodium). Sulfate may be analyzed by gravimetry following precipitation with barium chloride solution as barium sulfate. Sulfate may be directly measured in the aqueous solution by ion chromatography. Water of crystallization in Glauber's salt can be measured by gravimetric analysis. Solid crystalline sodium sulfate can be identified by physical properties (i.e. refractive index) and x-ray properties.

SODIUM SULFIDE

[1313-82-2]
Formula Na_2S; MW 78.046; forms a pentahydrate, $Na_2S \cdot 5H_2O$ [1313-83-3], MW 168.12 and a nonahydrate, $Na_2S \cdot 9H_2O$ [1313-84-4], MW 240.18
Synonym: sodium monosulfide

Uses

Sodium sulfide is used in making sulfur dyes; for dehairing of hides; removing sulfur from viscous rayon; engraving and lithography; cotton printing; manufacturing rubber; paper pulp; and as a photographic reagent. Other major applications are for treating paper and for extracting gold ores where oxidized metal ores are converted to sulfides prior to froth flotation. Sodium sulfide also is used in preparing many other sulfides and as an analytical reagent.

Physical Properties

White cubic crystal; hygroscopic; density 1.856 g/cm^3; melts at 1,172°C; soluble in water 18.6 g/100mL at 20°C and 39 g/100mL at 50°C; aqueous solutions strongly alkaline; slightly soluble in alcohol; insoluble in ether.

The pentahydrate consists of flat, shiny prismatic crystals; density 1.58 g/cm^3; loses three water molecules at 100°C; melts at 120°C losing all water molecules; soluble in water and alcohol; aqueous solutions strongly alkaline; insoluble in ether.

The nonahydrate is a yellowish-white crystalline solid; tetragonal crystals; odor of hydrogen sulfide; the color changes on exposure to light and air, first turning to yellow and then becoming brownish-black, deliquescent; density 1.43 g/cm^3; decomposes at about 50°C; very soluble in water; aqueous solution strongly alkaline; slightly soluble in alcohol; insoluble in ether.

Thermochemical Properties

$\Delta H_f°$	–87.19 kcal/mol
$\Delta G_f°$	–83.60 kcal/mol
S°	20.00 cal/deg mol
ΔH_{fus}	4.54 kcal/mol

Preparation

Sodium sulfide is prepared by heating sodium bisulfate with sodium chloride and coal above 950°C. The product mixture is extracted with water and the hydrated sulfide is obtained from the solution by crystallization:

$$NaHSO_4 + NaCl + 2C \rightarrow Na_2S + 2CO_2\uparrow + HCl\uparrow$$

Sodium sulfide also is produced from its elements in liquid ammonia:

$$Na + 2S \rightarrow Na_2S$$

Reactions

Sodium sulfide in solid form reacts with carbon dioxide in the presence of moisture to form hydrogen sulfide and sodium carbonate. Thus, the H_2S odor of sodium sulfide crystals is attributed to its exposure to moist air:

$$Na_2S + H_2O + CO_2 \rightarrow Na_2CO_3 + H_2S$$

In aqueous solution, sodium sulfide reacts with a number of metal salts forming insoluble sulfides.

When added to dilute mineral acids, hydrogen sulfide is generated.

Analysis

Elemental composition: Na 58.93%, S 41.07%. An aqueous solution is analyzed to determine sodium content. Also, an aqueous solution may be analyzed for sulfide by methylene blue colorimetric test or by iodometric titration (APHA, AWWA, and WEF. 1999. *Standard methods for the Examination of Water and Wastewater*, 20th ed. Washington, DC: American Public Health Association). The methylene blue test is based on reacting sulfide, ferric chloride and dimethyl–*p*–phenylenediamine to produce methylene blue. Also, sulfide can be measured by using a silver-silver sulfide electrode. Qualitatively, sulfide may be identified from the liberation of H_2S on treatment with acid. The H_2S turns the color of paper soaked with lead acetate black (See Hydrogen Sulfide).

SODIUM THIOCYANATE

[540-72-7]
Formula NaSCN; MW 81.074
Synonyms: sodium sulfocyanate; sodium sulfocyanide; sodium rhodanide; sodium rhodanate

Uses

Sodium thiocyanate is an analytical reagent for measuring iodide. Other uses are dyeing and printing textiles, preparing thiocyanate salts, and nickel plating.

Physical Properties

Colorless crystals or white powder; deliquescent; melts at 287°C; very soluble in water; soluble in alcohol.

Preparation

Sodium thiocyanate is prepared by boiling an aqueous solution of sodium cyanide with sulfur:

$$NaCN + S \rightarrow NaSCN$$

Analysis

Elemental composition: Na 28.36%, S 39.54%, C 14.81%, N 17.28%. The aqueous solution may be analyzed for sodium. Thiocyanate may be measured by gravimetry by reacting with ferric ion to form red ferric thiocyanate, $Fe(SCN)_3$, which may be filtered, washed, dried, and weighed.

SODIUM THIOSULFATE

[7772-98-7]
Formula $Na_2S_2O_3$; MW158.13; forms a stable pentahydrate, $Na_2S_2O_3 \cdot 5H_2O$ [10102-17-7], MW 248.19
Synonyms: sodium hyposulfite; hypo; antichlor

Uses

Sodium thiosulfate is a common analytical reagent used in iodometric titration to analyze chlorine, bromine, and sulfide. Other uses are in bleaching paper pulp, bleaching straw, ivory, and bones, for removing chlorine from solutions, silver extraction from its ores, a mordant in dyeing and printing textiles, and as an antidote to cyanide poisoning.

Another major application is in photography, where it is used as a fixer to dissolve unchanged silver salts from exposed negatives.

Physical Properties

Anhydrous thiosulfate is a white powder; soluble in water; insoluble in ethanol.

Sodium pentahydrate is a colorless, odorless, crystalline solid; density 1.69 g/cm³; decomposes around 50°C; effloresces in dry air above 33°C; very soluble in water and oil of turpentine; insoluble in ethanol.

Preparation

Sodium thiosulfate is a common reducing agent. It reduces iodine to iodide anion forming sodium tetrathionate. This reaction is utilized in the so–called iodometric titration:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Sodium thiosulfate reacts with chlorine to form sodium bisulfate and hydrochloric acid. This reaction removes chlorine from aqueous solutions:

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O \rightarrow 2NaHSO_4 + 8HCl$$

Sodium thiosulfate reacts with hydrochloric acid, decomposing to sulfur and sulfur dioxide:

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + S + SO_2 + H_2O$$

Analysis

Elemental composition: Concentration of sodium thiosulfate in aqueous solution can be measured by titration with a standard solution of potassium iodate, potassium biiodate, or potassium dichromate using starch indicator. The oxidant is added to an acidified solution of excess potassium iodide before titrating with the thiosulfate solution.

STRONTIUM

[7440-24-6]
Symbol Sr; atomic number 38; atomic weight 87.621; a Group II A (Group 2) alkaline earth metal positioned between calcium and barium in its group; electron configuration [Kr]$5s^2$; valence state +2; atomic radius 2.15Å; ionic radius, Sr^{2+} 1.26Å and 1.44Å for coordination numbers 8 and 12 in crystals; standard electrode potential, E° for $Sr^{2+} + 2e^- \leftrightarrow Sr$ is –2.899V; four stable natural isotopes: Sr-84(0.56%), Sr-86(9.86%), Sr-87(7.00%), Sr-88(82.58%); twenty-three artificial radioactive isotopes in the mass range 76-83, 85, 89-102; the longest-lived radioisotope is the beta emitter Sr-90, $t_{1/2}$ 29.1 year; the shortest-lived isotope is the beta-emitter Sr-102, $t_{1/2}$ 68ms.

History, Occurrence, and Uses

William Cruickshank in 1787 and Adair Crawford in 1790 independently detected strontium in the mineral strontianite, small quantities of which are associated with calcium and barium minerals. They determined that the strontianite was an entirely new mineral and was different from baryta and other barium minerals known at the time. In 1808, Sir Humphry Davy isolated strontium by electrolysis of a mixture of moist strontium hydroxide or chloride with mercuric oxide, using a mercury cathode. The element was named after the town Strontian in Scotland where the mineral strontianite was found.

Strontium is found in small quantities in many rocks and soils, mostly associated with calcium and barium. Its abundance in the earth's crust is about 370 mg/kg, about the same as barium. The average concentration of this metal in sea water is about 7.9 mg/L.

The two principal strontium minerals are its carbonate, strontianite, $SrCO_3$, and the more abundant sulfate mineral celestite, $SrSO_4$.

Elemental strontium has only minor uses, since most applications involve calcium and barium. Strontium alloys are used as “getters” for vacuum tubes. It is incorporated in glass for making picture tubes for color television. Strontium compounds are used in tracer bullets and in fireworks to produce red signal flares. Strontium titanate is a gemstone. The radioactive strontium-90 with a half-life of 29 years is a high-energy beta emitter. It is a product of nuclear fission. This isotope is a lightweight nuclear-electric power source in space vehicles and remote weather stations.

Physical Properties

Silvery-white metal when freshly cut; rapidly turns yellow on exposure to air forming a thin oxide coating; face-centered cubic structure; malleable, ductile, and somewhat softer than calcium; density 2.64 g/cm^3; melts at 777°C; vaporizes at 1,382°C; vapor pressure 5 torr at 847°C and 20 torr at 953°C; electrical resistivity 23 microhm-cm at 20°C; thermal neutron absorption cross section 1.21 barns; reacts with water; soluble in ethanol.

Thermochemical Properties

$\Delta H_f°$(cry)	0.0
$\Delta H_f°$(gas)	39.3 kcal/mol
$\Delta G_f°$(gas)	31.3 kcal/mol
S°(cry)	12.5 cal/deg mol
S°(gas)	39.3 cal/deg mol
C_ρ(cry)	6.31 cal/deg mol
C_ρ(gas)	4.97 cal/deg mol
ΔH_{fus}	1.78 kcal/mol
Thermal conductivity (at 27°C)	0.353 W/cm K
Coefficient of linear expansion (at 25°C)	22.5×10^{-6}/°C

Production

Strontium and its compounds are mostly derived from celestite, $SrSO_4$. The mineral is converted to its carbonate by heating with sodium carbonate. Alternatively, the mineral may be reduced to sulfide by heating with coke. The carbonate or the sulfide is then converted to other strontium salts.

Metallic strontium is produced by electrolysis of a mixed melt of strontium chloride and potassium chloride in a graphite crucible using an iron rod as cathode. The upper cathodic space is cooled and the strontium metal collects over the cooled cathode and forms a stick.

Strontium metal also can be prepared by thermal reduction of its oxide with aluminum. Strontium oxide-aluminum mixture is heated at high temperature in vacuum. Strontium is collected by distillation in vacuum. Strontium also is obtained by reduction of its amalgam, hydride, and other salts. The amalgam is heated and the mercury is separated by distillation. If hydride is used, it is heated at 1,000°C in vacuum for decomposition and removal of hydrogen. Such thermal reductions yield high–purity metal.

Reactions

Strontium is a reactive metal, similar to calcium. Exposure to air forms strontium oxide, SrO. In finely-divided form, the metal is pyrophoric. It ignites in air to form both the oxide, SrO, and the peroxide, SrO_2. Similarly, when heated with chlorine gas or bromine vapor, it burns brightly, forming its halides, $SrCl_2$ or $SrBr_2$. When heated with sulfur, strontium forms sulfide, SrS.

Strontium reacts vigorously with water forming the hydroxide, $Sr(OH)_2$, with liberation of hydrogen:

$$Sr + 2H_2O \rightarrow Sr(OH)_2 + H_2$$

Sr metal reacts with acids evolving hydrogen and forming corresponding salts:

$$Sr + 2HCl \rightarrow SrCl_2 + H_2$$

When heated under hydrogen it forms an ionic hydride, SrH_2, a stable crystalline salt. Heating Sr metal in a stream of nitrogen above 380°C forms nitride, Sr_3N_2.

Strontium also is a reducing agent. It reduces oxides and halides of metals at elevated temperatures to metallic form.

Analysis

Strontium and all its compounds impart crimson red color in the flame test. The metal in trace concentrations can be analyzed by various instrumental methods that include flame-and furnace-AA, ICP-AES, ICP/MS, x-ray fluorescence, and neutron activation analysis.

Hazard

The finely-powdered metal is pyrophoric. Its radioactive isotopes Sr-89 and Sr-90 emit high-energy beta radiation. They are extremely hazardous because they deposit in bones replacing calcium. Their radiation can damage bone marrow and blood-forming organs, inducing cancer.

STRONTIUM CARBONATE

[1633-05-2]
Formula: $SrCO_3$; MW 147.63

Occurrence and Uses

Strontium carbonate occurs in nature as mineral strontianite. The compound is used in pyrotechnics and ceramic ferrites. It also is used in making iridescent glass for color television tubes. Other uses are in refining sugar and preparing other strontium salts.

Physical Properties

White orthorhombic crystals; refractive index 1.518; hygroscopic; hardness 3.5 Mohs; density 3.5 g/cm^3; insoluble in water; soluble in dilute acids with liberation of carbon dioxide.

Thermochemical Properties

$\Delta H_f°$	–291.6 kcal/mol
$\Delta G_f°$	–272.5 kcal/mol
S°	23.2 cal/deg mol
C_ρ	19.5 cal/deg mol

Production

Strontium carbonate occurs in nature as strontianite and can be mined from its deposit. It is, however, usually made from the mineral celestite. Celestite is fused with sodium carbonate at elevated temperatures or boiled with a solution of ammonium carbonate:

$$SrSO_4 + Na_2CO_3 \rightarrow SrCO_3 + Na_2SO_4$$

$$SrSO_4 + (NH_4)_2CO_3 \rightarrow SrCO_3 + 2NH_3 + CO_2 + H_2O$$

Strontium carbonate is insoluble in water. It precipitates from the product mixture in the second reaction. If fused with sodium carbonate, the product mixture is leached with water. Insoluble carbonate separates from the water-soluble sodium sulfate.

Analysis

Elemental composition: Sr 59.35%, C 8.14%, O 32.51%. $SrCO_3$ is dissolved in dilute acid and carbon dioxide liberated is identified by the lime-water test (turns lime water milky). Strontium in solution is analyzed by various methods mentioned earlier (See Strontium).

STRONTIUM CHLORIDE

[10476-85-4]
Formula: $SrCl_2$; MW 158.53; forms a dihydrate, $SrCl_2 \cdot 2H_2O$ and a hexahydrate, $SrCl_2 \cdot 6H_2O$

Uses

Strontium chloride is used to produce strontium metal by electrolysis. It also is used to prepare other strontium salts, as a desensitizer in dentistry, and in pyrotechnics.

Physical Properties

Anhydrous salt is a colorless, cubic, crystalline solid; refractive index 1.650; density 3.052 g/cm^3; melts at 875°C; vaporizes at 1,250°C; very slightly soluble in absolute alcohol and acetone; insoluble in liquid ammonia.

The dihydrate exists as transparent leaflets; refractive index 1.594; density 2.672 g/cm^3 at 25°C. The hexahydrate is colorless trigonal crystals or white granules; refractive index 1.536; density 1.93 g/cm^3; effloresces in air; melts at

61°C on rapid heating; loses four molecules of water at 115°C; loses all its water at 150°C; highly soluble in water, 106 g/100 mL at 0°C, 206 g/100 mL at 40°C; moderately soluble in alcohol.

Thermochemical Properties

$\Delta H_f°$(cry)($SrCl_2$)	–198.1 kcal/mol
$\Delta H_f°$(gas)($SrCl_2$)	–116.1 kcal/mol
$\Delta H_f°$(cry)($SrCl_2 \cdot 2H_2O$)	–343.7 kcal/mol
$\Delta H_f°$(cry)($SrCl_2 \cdot 6H_2O$)	–627.1 kcal/mol
$\Delta G_f°$ (cry)($SrCl_2$)	–186.7 kcal/mol
$\Delta G_f°$ (gas)($SrCl_2$)	–118.6 kcal/mol
$\Delta G_f°$ (cry)($SrCl_2 \cdot 2H_2O$)	–306.4 kcal/mol
S°(cry)($SrCl_2$)	27.4 cal/deg mol
S°(gas)($SrCl_2$)	74.3 cal/deg mol
S°(cry)($SrCl_2 \cdot 2H_2O$)	52.0 cal/deg mol
S°(cry)($SrCl_2 \cdot 6H_2O$)	93.4 cal/deg mol
C_ρ(cry)	18.1 cal/deg mol
C_ρ (gas)	13.3 cal/deg mol
C_ρ (cry)	38.3 cal/deg mol

Preparation

Strontium chloride is prepared by reacting strontium oxide, hydroxide, or carbonate in hydrochloric acid:

$$SrO + 2HCl \rightarrow SrCl_2 + H_2O$$

$$SrCO_3 + 2HCl \rightarrow SrCl_2 + CO_2 + H_2O$$

On evaporation, the solution forms crystals of hydrated chloride which can be dehydrated to anhydrous salt.

Analysis

Elemental composition (for anhydrous $SrCl_2$): Sr 55.27%, Cl 44.73%. The salt is dissolved in water and analyzed for strontium by various instrumental techniques (see Strontium). Chloride ion is measured by ion chromatography or titration with a standard solution of silver nitrate, using potassium chromate indicator.

STRONTIUM HYDROXIDE

[18480-07-4]
Formula $Sr(OH)_2$; MW 121.63; forms an octahydrate, $Sr(OH)_2 \cdot 8H_2O$, MW 265.76

Uses

Strontium hydroxide is used in extracting sugar from beet sugar molasses and in making lubricant soaps and greases.

Physical Properties

White deliquescent crystal; density 3.625 g/cm^3; melts at 375°C in hydrogen atmosphere; converts to oxide at 710°C; slightly soluble in water at 0°C, 0.41 g/100 mL, soluble in boiling water at 100°C, 21.83 g/100 mL; soluble in acids and ammonium chloride solution.

The octahydrate consists of colorless, tetragonal, deliquescent crystals; density 1.90 g/cm^3; loses all its water molecules at 100°C; sparingly soluble in water at low temperatures, 0.90 g/100 mL at 0°C; soluble in boiling water, 47.7 g/100 mL at 100°C; aqueous solution highly alkaline; soluble in acids and in ammonium chloride solution; insoluble in acetone.

Thermochemical Properties

$\Delta H_f°$(cry)	–229.2 kcal/mol
$\Delta H_f°$(gas)	–135.0 kcal/mol

Preparation

Strontium hydroxide is prepared by treating strontium oxide with water:

$$SrO + H_2O \rightarrow Sr(OH)_2$$

Alternatively, $Sr(OH)_2$ is made by heating strontium carbonate or strontium sulfide with steam at temperatures around 500 to 600°C:

$$SrCO_3 + H_2O \rightarrow Sr(OH)_2 + CO_2$$

$$SrS + 2H_2O \rightarrow Sr(OH)_2 + H_2S$$

Analysis

Elemental composition: Sr 72.03%, O 26.31%, H 1.66%. The aqueous solution may be analyzed to measure strontium content. Basic strength (concentration of the OH^-) may be determined by acid-base titration.

Toxicity

Dry compound or aqueous solution is corrosive. Contact with skin or eyes can cause irritation.

STRONTIUM NITRATE

[10042-76-9]
Formula $Sr(NO_3)_2$; MW 211.63; also forms a tetrahydrate $Sr(NO_3)_2 \cdot 4H_2O$; MW 283.69

Uses

Strontium nitrate is used in pyrotechnics, for producing marine and railroad signals, and in matches.

Physical Properties

Colorless cubic crystals or white powder or granules; density 2.986 g/cm³; melts at 570°C; very soluble in water, 80 g/100 mL at 18°C; very slightly soluble in ethanol.

The tetrahydrate constitutes colorless monoclinic crystals; density 2.20 g/cm³; loses all water of crystallization at 100°C; converts to strontium oxide, SrO at 1,100°C; very soluble in water, 60.4g/100 mL at 0°C, 206 g/100 mL at 100°C; soluble in liquid ammonia; very slightly soluble in ethanol and acetone.

Thermochemical Properties

$\Delta H_f°$ (cry)	–233.8 kcal/mol
$\Delta H_f°$ (aq, 1M)	–229.6 kcal/mol
$\Delta G_f°$ (cry)	–186.5 kcal/mol
$\Delta G_f°$ (aq, 1M)	–186.9 kcal/mol
S° (cry)	46.5 cal/deg mol
S° (aq, 1M)	62.2 cal/deg mol
C_ρ (cry)	35.8 cal/deg mol

Preparation

Strontium nitrate is prepared by treating strontium carbonate with nitric acid. The solution is evaporated and crystallized:

$$SrCO_3 + HNO_3 \rightarrow Sr(NO_3)_2 + CO_2 + H_2O$$

Crystallization yields the tetrahydrate, $Sr(NO_3)_2 \cdot 4H_2O$, which on heating dehydrates to form the anhydrous nitrate.

Analysis

Elemental composition: Sr 41.40%, N 13.24%, O 45.36%. An aqueous solution of the salt may be analyzed for strontium by AA, ICP, or other methods. The nitrate anion may be measured by ion chromatography or by nitrate ion-specific electrode.

STRONTIUM OXIDE

[1314-11-0]
Formula SrO; MW 103.62
Synonyms: strontia; strontium monoxide

Uses

Strontium oxide is used for preparing other strontium compounds.

Physical Properties

Grayish-white porous mass; cubic crystalline structure; refractive index

1.810; density 4.70 g/cm^3; melts at 2430°C; vaporizes above 3,000°C; reacts with water forming strontium hydroxide, $Sr(OH)_2$ with evolution of heat; miscible with fused caustic potash; slightly soluble in alcohol; insoluble in acetone and ether.

Thermochemical Properties

$\Delta H_f°$	–141.5 kcal/mol
$\Delta G_f°$	–134.3 kcal/mol
S°	13.0 cal/deg mol
C_ρ	10.8 cal/deg mol

Preparation

Strontium oxide is prepared by thermal decomposition of strontium carbonate, hydroxide, or nitrate:

$$SrCO_3 \rightarrow SrO + CO_2$$

$$Sr(OH)_2 \rightarrow SrO + H_2O$$

$$Sr(NO_3)_2 \rightarrow SrO + N_2O_5$$

Analysis

Elemental composition: Sr 84.56%, O 15.44%. The oxide is digested cautiously in acid, diluted, and analyzed for strontium. The oxide is converted cautiously to hydroxide by treatment with water and the strength of the hydroxide is measured by acid-base titration.

STRONTIUM SULFATE

[7759-02-6]
Formula $SrSO_4$; MW 183.68

Occurrence and Uses

Strontium sulfate occurs in nature as mineral celestite, which is the principal ore of strontium. The sulfate is the starting material for producing strontium metal and practically all its salts. The sulfate also is used in pyrotechnics and in ceramics.

Physical Properties

White crystalline powder; orthorhombic crystals; refractive index 1.622; hardness 3.3 Mohs; density 3.96 g/cm^3; melts at 1,605°C; very slightly soluble in water 0.014 g/100mL at 30°C; soluble in alkali chloride solutions; slightly soluble in alcohol; insoluble in alkalis.

Thermochemical Properties

$\Delta H_f°$	–347.3 kcal/mol
$\Delta G_f°$	–320.05 kcal/mol

S°	28 cal/deg mol

Production

Strontium sulfate occurring in nature as celestite is mined from its natural deposits. Also, the sulfate can be made by reacting strontium oxide, hydroxide, or carbonate with dilute hydrochloric acid:

$$SrO + H_2SO_4 \rightarrow SrSO_4 + H_2O$$

$$SrCO_3 + H_2SO_4 \rightarrow SrSO_4 + CO_2 + H_2O$$

Analysis

Elemental composition: Sr 47.70%, S 17.46%, O 34.84%. Strontium sulfate can be characterized by x-ray crystallography. A nitric acid extract is analyzed for strontium. An aqueous solution (the salt is only slightly soluble) is filtered or decanted from insoluble material and measured by ion chromatography.

SULFUR

[7704-34-9]
Symbol S; atomic number 16; atomic weight 32.06; a Group VI A (Group 16) nonmetallic oxygen-group element; electron configuration [Ne]$3s^23p^4$; valence states 2, 4, 6; electronegativity 2.5; atomic radius 1.03Å; ionic radius 0.37Å for S^{4+} with coordination number 6 and S^{6+} having coordination number 4, the hexacoordinated S^{6+} in crystals have ionic radius 0.29Å; four naturally-occurring stable isotopes: S-32 (95.02%), S-33 (0.75%), S-34 (4.21%), S-36 (0.02%); thirteen artificial radioactive isotopes in the mass range 27, 29–31, 35, 37–44; the longest-lived radioisotope is the beta-emitter S-35, $t_{1/2}$ 87.2 days.

History, Occurrence, and Uses

Sulfur was known to the alchemists from ancient times as brimstone. Lavoisier in 1772 proved sulfur to be an element. The element derived its name from both the Sanskrit and Latin names *Sulvere* and *Sulfurium*, respectively. Sulfur is widely distributed in nature, in earth's crust, ocean, meteorites, the moon, sun, and certain stars. It also is found in volcanic gases, natural gases, petroleum crudes, and hot springs. It is found in practically all plant and animal life. Most natural sulfur is in iron sulfides in the deep earth mantle. The abundance of sulfur in earth's crust is about 350 mg/kg. Its average concentration in seawater is estimated to be about 0.09%. Sulfur occurs in earth's crust as elemental sulfur (often found in the vicinity of volcanoes), sulfides, and sulfates. The most important sulfur-containing ores are iron pyrite, FeS_2; chalcopyrite, $CuFeS_2$; sphalerite, ZnS; galena, PbS; cinnabar HgS; gypsum $CaSO_4 \cdot 2H_2O$; anhydrite $CaSO_4$; kieserite, $MgSO_4 \cdot H_2O$; celestite, $SrSO_4$; barite, $BaSO_4$; and. stibnite, Sb_2S_3.

Important sulfur compounds include sulfuric acid, sulfur dioxide, hydrogen sulfide, sulfur trioxide, and a number of metal sulfides and metal oxo- salts such as sulfates, bisulfates, and sulfites. Numerous organic compounds contain sulfur, such as mercaptans, thiophenes, thiophenols, sulfate esters, sulfones, and carbon disulfide.

Elemental sulfur is used for vulcanizing rubber; making black gunpowder; as a soil conditioner; as a fungicide; preparing a number of metal sulfides; and producing carbon disulfide. It also is used in matches; bleaching wood pulp, straw, silk, and wool; and in synthesis of many dyes. Pharmaceutical grade precipitated and sublimed sulfurs are used as scabicides and as antiseptics in lotions and ointments.

Physical Properties

Sulfur exists in several allotropic forms; at ordinary temperatures it exists as thermodynamically stable alpha-cyclooctasulfur (S_8). The cyclooctasulfur also has two other modifications, the beta and the gamma forms.

Alpha cyclooctasulfur or the alpha-sulfur is yellow orthorhombic crystalline solid; refractive index 1.957; density 2.07 g/cm^3 at 20°C; stable at ordinary temperatures; converts to monoclinic beta form at 94.5°C.

Beta-sulfur is pale-yellow, opaque needle-like crystals; monoclinic structure; brittle; stable between 94.5 to 120°C; converts to orthorhombic form on standing; density 1.96 g/cm^3; melts at 115.2°C.

Gamma-sulfur is a second monoclinic form of cyclooctasulfur; pale-yellow amorphous solid; density 1.92 g/cm^3; melts around 120°C.

There are also various other forms of sulfur including cyclohexa-(S_6), cyclohepta-(S_7), cyclonona-(S_9), cyclodeca-(S_{10}) and cyclododeca(S_{12}) sulfur. Polymeric amorphous sulfur of molecular weight about 200,000 also is known.

Liquid sulfur consists of cyclic S_8 molecules below 159°C. Above this temperature, the cyclic molecules break down forming linear polymers of varying chain lengths. Also, liquid sulfur possibly contains smaller S_6 rings.

Sulfur vapor consists of several small molecules from S_1 through S_4 and cyclic S_5 through S_{10}. At low pressures and temperatures above 1,500°C, sulfur occurs in vapor phase in monoclinic S_1 form. At temperatures between approximately 500 to 1,500°C and subatmospheric pressures, the diatomic oxygen-like S_2 form predominates. The S_3 and S_4 molecules of uncertain structures and the S_5 to S_{10} rings are usually minor components of sulfur vapors.

Sulfur vaporizes at 444.6°C. The element, particularly in its orthorhombic S_8 form, is insoluble in water but dissolves in carbon disulfide, anhydrous liquid ammonia, and methylene iodide. It is moderately soluble in benzene, toluene, chloroform, and acetone, solubility increasing with temperature. Solid polymeric sulfur is practically insoluble in all solvents.

Thermochemical Properties

$\Delta H_f°$ (orthorhombic)	0.0 kcal/mol
$\Delta H_f°$ (monoclinic)	0.08 kcal/mol
$\Delta H_f°$ (gas)	66.64 kcal/mol
$\Delta G_f°$ (orthorhombic)	0.0 kcal/mol
$\Delta G_f°$ (gas)	56.95 kcal/mol

S° (orthorhombic)	7.60 cal/deg mol
S° (gas)	40.08 cal/deg mol
C_ρ (orthorhombic)	5.41 cal/deg mol
C_ρ (gas)	5.66 cal/deg mol

Production

Elemental sulfur is recovered from its ore deposits found throughout the world. It is obtained commercially by the Frasch process, recovery from wells sunk into salt domes. Heated water under pressure is forced into the underground deposits to melt sulfur. Liquid sulfur is then brought to the surface. Sulfur is recovered by distillation. Often the ore is concentrated by froth flotation.

Elemental sulfur also is recovered as a by-product in processing natural gas and petroleum. Refining operations of natural gas and petroleum crude produce hydrogen sulfide, which also may occur naturally. Hydrogen sulfide is separated from hydrocarbon gases by absorption in an aqueous solution of alkaline solvent such as monoethanol amine. Hydrogen sulfide is concentrated in this solvent and gas is stripped out and oxidized by air at high temperature in the presence of a catalyst (Claus process).

Elemental sulfur also may be obtained by smelting sulfide ores with a reducing agent, such as coke or natural gas, or by reduction of sulfur dioxide.

Reactions

Sulfur forms two oxides, sulfur dioxide, SO_2, and the trioxide, SO_3. It burns in oxygen at about 250°C or in air above 260°C, forming sulfur dioxide. In excess oxygen the trioxide is obtained.

Sulfur reacts with hydrogen at 260 to 350°C forming hydrogen sulfide. The reaction is slow at this temperature and does not go to completion. The reaction is catalyzed by activated alumina.

Reactions with excess chlorine or fluorine yield sulfur tetrachloride, SCl_4, or hexafluoride, SF_6. These reactions occur under cold conditions.

Sulfur reacts with sulfur dioxide in an electric discharge to form disulfuroxide, S_2O.

Sulfur reacts with aqueous sulfide to form polysulfides:

$$S + Na_2S \rightarrow Na_2S_2$$

With aqueous solution of sulfite the product is thiosulfate:

$$S + SO_3^{2-} \rightarrow S_2O_3^{2-}$$

Thiosulfate also is obtained by heating sulfur with powdered sulfite:

$$S + Na_2SO_3 \rightarrow Na_2S_2O_3$$

When heated with alkali cyanide, thiocyanate salt is obtained:

$$S + KCN \rightarrow KSCN$$

A similar reaction occurs in the aqueous phase in which thiocyanate is obtained by evaporation and crystallization.

Sulfur combines with alkali metals, copper, silver, and mercury on cold contact with the solid, forming sulfides. Reactions with magnesium, zinc, and cadmium occur to a small degree at ordinary temperatures, but rapidly on heating. Sulfur reacts with phosphorus, arsenic, antimony, bismuth, and silicon at their melting points and with other elements at elevated temperatures forming binary sulfides. Sulfides of tellurium, gold, platinum, and iridium are difficult to obtain even at elevated temperatures. Sulfur does not react with inert gases, nitrogen, and iodine.

Analysis

Sulfur can be analyzed by x-ray, GC and GC/MS techniques. Alpha-octacyclosulfur is dissolved in benzene, toluene, or chloroform and analyzed for sulfur by GC using a flame photometric detector or by GC/MS. The characteristic mass ions for its identification are multiples of 32 (i.e. 32, 64, 128, and 256). Sulfur may be identified by mixing a little powder with copper, silver, or mercury at room temperature and identifying the metal sulfide from color change and various instrumental methods.

SULFUR CHLORIDE

[10025-67-9]
Formula S_2Cl_2; MW 135.04; linear Cl-S-S-Cl chain; S-S bond distance 1.95Å and S-Cl distance 2.05Å
Synonyms: disulfur dichloride; sulfur subchloride; sulfur monochloride

Uses

Sulfur chloride is a solvent for sulfur and a chlorinating agent. Other applications are vulcanizing rubber; an intermediate in making sulfur dyes, synthetic rubber, thionyl chloride, and several other compounds; pesticide formulations; hardening soft woods; and extracting gold.

Physical Properties

Yellowish red oily liquid; pungent penetrating odor; fumes in air; refractive index 1.670 at 20°C; density 1.69 g/mL; dipole moment 1.60; dielectric constant 4.9 at 22°C; freezes at –77°C; boils at 137°C; reacts with water; soluble in ethanol, benzene, ether, chloroform, and carbon tetrachloride: dissolves sulfur at ambient temperature (67 g/100 g sulfur chloride).

Thermochemical Properties

$\Delta H_f°$ (liq)	–14.2 kcal/mol

Preparation

Sulfur chloride is prepared as an orange liquid by passing chlorine gas through molten sulfur. If excess chlorine is passed and in the presence of a trace $FeCl_3$ or iodine as catalyst, an equilibrium mixture of about 85% dichloride, SCl_2 , and 15% S_2Cl_2 is obtained. The dichloride dissociates to sulfur chloride:

$$2SCl_2 \leftrightarrow S_2Cl_2 + Cl_2$$

Sulfur chloride is separated by fractional distillation.

Analysis

Elemental composition: S 47.48%, Cl 52.52%. Sulfur chloride is identified by its physical and chemical properties. It may be analyzed by GC-ECD or GC-FPD. For GC-ECD analysis, a non-chlorine solvent must be employed. The compound can be confirmed from mass spectra obtained from the GC/MS analysis.

Toxicity

Sulfur chloride is toxic and a lachrymator. The vapors can cause irritation of the eyes, nose, and respiratory tract.

SULFUR DIOXIDE

[7446-09-5]
Formula SO_2; MW 64.06
Synonyms: sulfurous oxide; sulfurous anhydride

Uses

Sulfur dioxide has a wide range of industrial applications, the most notable being as an intermediate in producing sulfuric acid. It is used to produce chlorine dioxide, sodium bisulfite, and sodium dithionate, which are all bleaching agents. Also, sulfur dioxide itself is a bleaching agent used in bleaching textile fibers, straw, glue, gelatin, and other substances. Sulfur dioxide is used extensively in the food industry to preserve vegetables and dry fruits such as apricots and cherries; as a bleach and steeping agent for grains; to prevent growth of bacteria in processing soy proteins; in refining sugar; as an additive to wine to destroy molds, bacterias, and undesired wild yeast; to prevent formation of nitrosamines in beer in the malting process; and in producing high-fructose corn syrups.

Sulfur dioxide is used in removing oxygen in petroleum recovery processes to prevent corrosion in piping and storage systems. Also, it is applied in water treatment to reduce residual chlorine. In clay processing it reduces iron compounds and other color-forming impurities. Other uses are extracting sulfide ores; casting magnesium; catalyst modifier in certain organic oxidation reactions; and colorimetric analysis of sulfite ion in aqueous samples. In the chemical industry, sulfur dioxide is used as a reducing agent in a number of preparative and analytical reactions. Liquid sulfur dioxide is used as a solvent for sulfur trioxide in sulfonation.

Sulfur dioxide occurs in nature in volcanic gases. It is found in the upper atmosphere at varying but trace concentrations resulting from natural processes and human activities. It occurs in the automotive exhausts and in many fire and stack emission gases. It is produced from burning sulfur–containing fuels, such as coal and oil. Also, it is produced in the petroleum refining process. Sulfur dioxide is partly responsible for causing acid rain.

Physical Properties

Colorless gas; pungent suffocating odor; gas density 2.927 g/L at 20°C; heavier than air, vapor density 2.263 (air=1); condenses to a colorless liquid at –10°C; density of liquid SO_2 1.434 g/mL; freezes at –72.7°C; critical temperature 157.65°C; critical pressure 77.78 atm; critical volume 122 cc/g; dielectric constant 17.27 at –16.5°C; dissolves in water forming sulfurous acid, solubility 22.97 g and 11.58 g/100mL water at 0° and 20°C, respectively, under atmospheric pressure; very soluble in acetone, methyl isobutyl ketone, acetic acid, and alcohol; soluble in sulfuric acid; liquid SO_2 slightly miscible in water.

Thermochemical Properties

$\Delta H_f°$ (gas)	–70.94 kcal/mol
$\Delta H_f°$ (liq)	–76.60 kcal/mol
$\Delta G_f°$ (gas)	–71.75 kcal/mol
S° (gas)	59.30 cal/deg mol
C_ρ (gas)	9.53 cal/deg mol
ΔH_{vap}	5.96 kcal/mol

Production

Sulfur dioxide is manufactured mostly by combustion of sulfur or its iron sulfide mineral, pyrite, FeS_2 , in air. The flame temperatures for such combustion of sulfur in the air are usually in the range 1,200 to 1,600°C. Many types of sulfur burners are available and are used to produce sulfur dioxide. They include rotary-kiln, spray, spinning-cup and air-atomizing sulfur burners. Selection and design of burners depend on quality of sulfur to be burned, and rate and concentration of sulfur dioxide to be generated. Pyrites or other metal sulfides may be burned in air in fluid-bed roasters to form sulfur dioxide.

Other sources of sulfur dioxide are flue gases and spent sulfuric acid. Sulfur dioxide may be recovered from stack gases in smelting or power plants. Similarly, SO_2 can be generated from spent sulfuric acid recovered from oil refineries. The spent acid is burned in a high temperature furnace above 900°C to form sulfur dioxide, water, and gaseous products.

Liquid sulfur dioxide can be produced by passing a stream of sulfur trioxide, SO_3, through molten sulfur:

$$2SO_3 + S \rightarrow 3SO_2$$

Trace sulfur trioxide in the product may be removed by passing the product sulfur dioxide through sulfuric acid.

Reactions

Sulfur dioxide combines with oxygen on heating and in the presence of a catalyst. This reaction proceeds at temperatures between 400 to 700°C with vanadium pentoxide catalyst to make sulfuric acid:

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$

In the upper atmosphere such oxidation of sulfur dioxide to its trioxide forming sulfuric acid or sulfate anion may occur at ambient temperature at a much slower rate in the presence of various free radicals.

Sulfur dioxide dissolves in water forming sulfurous acid that is stable only in solution:

$$SO_2 + H_2O \rightarrow H_2SO_3$$

The acid has never been isolated in pure form. It is a weak acid. The pK_{a1} and pK_{a2} values are 1.85 and 7.20, respectively. When concentrated acid solution is cooled, it crystallizes forming a hexahydrate of sulfur dioxide, $SO_2 \cdot 6H_2O$.

Reactions with chlorine or bromine yield sulfuryl chloride, SO_2Cl_2, or sulfuryl bromide, SO_2Br_2:

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2$$

Sulfur dioxide reacts with bases, such as alkali or alkaline-earth oxides and hydroxides to form corresponding metal sulfites and bisulfites:

$$SO_2 + MgO \rightarrow MgSO_3$$

$$SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$$

$$SO_2 + NaOH \rightarrow NaHSO_3$$

Such reactions occur with alkalies in solutions, slurries, or solid form. Products and yields depend on temperature and concentrations of reacting bases. At high concentrations and temperatures metabisulfites are produced:

$$SO_2 + Na_2SO_3 \rightarrow Na_2S_2O_5$$

When heated with hydrogen sulfide at 300°C, sulfur dioxide is reduced forming sulfur and water:

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O$$

In the presence of moisture or a catalyst, such as silica, or alumina, the reaction can occur at ambient temperature.

Sulfur dioxide also can be reduced by hydrogen, carbon, carbon monoxide, carbon disulfide, certain metals, metal hydrides, and sodium borohydride when heated at high temperatures:

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$$

$$SO_2 + C \rightarrow S + CO_2$$

$$SO_2 + CS_2 \rightarrow 3S + CO_2$$

$$2SO_2 + Zn \rightarrow ZnS_2O_4$$

$$SO_2 + CO \rightarrow COS + O_2$$

$$SO_2 + 2CO \rightarrow S + 2CO_2$$

Reduction with carbon monoxide at high temperatures can form either carbonyl sulfide or sulfur depending on the catalyst used. With cobalt molybdate, COS is the primary product. On the other hand, lanthanum titanate catalyzes the reaction to form sulfur.

Sulfur dioxide reacts with manganese dioxide to form manganese dithionate, which is an intermediate in the production of sodium dithionate:

$$MnO_2 + 2SO_2 \rightarrow MnS_2O_6$$

$$MnS_2O_6 + Na_2CO_3 \rightarrow MnCO_3 + Na_2S_2O_6$$

Sulfur dioxide serves as a reducing agent in many preparative reactions. It reduces sodium chlorate in sulfuric acid solution to form chlorine dioxide. The reaction is used to produce chlorine dioxide *in situ*, a bleaching agent in the pulp and paper industry:

$$SO_2 + 2NaClO_3 \rightarrow 2ClO_2 + Na_2SO_4$$

Sulfiur dioxide reduces hydrogen peroxide to form sulfuric acid:

$$SO_2 + H_2O_2 \rightarrow H_2SO_4$$

Sulfur dioxide is used as a reducing agent in many organic reactions. It reduces quinones, disulfides, nitroaromatics, and diazo compounds.

An organic reaction of interest is the Diels-Alder reaction that sulfur dioxide undergoes with butadiene and other acyclic dienes. With butadiene, the product is sulfolene, C_4H_6S , a five-membered S-heterocyclic ring compound which is hydrogenated to form sulfolane, C_4H_8S.

Sulfur dioxide undergoes sulfoxidation and sulfochlorination with alkanes.

When the gas is simultaneously passed along with oxygen through an alkane in the presence of light, a sulfonic acid forms:

$$2C_8H_{18} + 2SO_2 + O_2 \rightarrow 2C_8H_{17}SO_3H + H_2O$$

A similar sulfochlorination (or chlorosulfonation) reaction occurs when sulfur dioxide and chlorine are passed simultaneously through the hydrocarbon:

$$C_8H_{18} + SO_2 + Cl_2 \rightarrow C_8H_{17}SO_2Cl + HCl$$

With Grignard reagents, sulfur dioxide reacts to form sulfinic acid salts:

$$2SO_2 + 2RMgBr \rightarrow (RSO_2)_2Mg + MgBr_2$$

Analysis

Sulfur dioxide may be analysed by GC-FPD, GC-TCD, and GC/MS. The molecular ion for its GC/MS identification is 64. Also, the SO_2 may be measured by colorimetry. It is purged with nitrogen gas and trapped in an absorbing solution containing Fe^{3+} and 1,10-phenanthroline. The Fe^{3+} is reduced to Fe^{2+} forming an orange complex. After removing excess Fe^{3+} with ammonium bifluoride, absorbance of the orange complex is measured at 510 nm.

Toxicity

Sulfur dioxide is highly toxic. It causes severe irritation of eyes, skin, and respiratory tract. Effects are coughing, suffocation, and bronchial constriction.

SULFUR HEXAFLUORIDE

[2551-62-4]
Formula SF_6; MW 146.05

Uses

Sulfur hexafluoride is used as a gaseous insulator for electrical equipment and in electronic ultrahigh frequency devices.

Physical Properties

Colorless, odorless gas; density 6.41 g/L; about five times heavier than air; liquefies at –50.7°C (triple point); density of liquid 1.88 g/mL at –50.7°C; sublimes at –63.8°C; critical temperature 45.54°C; critical pressure 37.13 atm; critical volume 199 cm^3/mol; slightly soluble in water; soluble in ethanol.

Thermochemical Properties

$\Delta H_f°$	–289.0 kcal/mol
$\Delta G_f°$	–264.2 kcal/mol

S°	69.72 cal/deg mol
C_ρ	23.25 cal/deg mol

Preparation

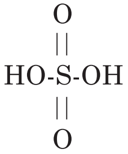
Sulfur hexachloride may be prepared by reacting fluorine with sulfur or sulfur dioxide.

Analysis

Elemental composition: S 21.95%, F 78.05%. The compound may be identified from its mass spectra. The characteristic mass ions are 146, 127, and 108.

SULFURIC ACID

[7664-93-9]
Formula H_2SO_4; MW 98.08
Structure



$$\begin{array}{c} O \\ \| \\ HO\text{-}S\text{-}OH \\ \| \\ O \end{array}$$

Synonym: oil of vitriol
The fuming sulfuric acid or oleum, $H_2SO_4 \bullet xSO_3$ [8014-95-7] is a mixture of sulfur trioxide dissolved in sulfuric acid. The SO_3 content may range between 15 and 30%.

Uses

Sulfuric acid probably is the most important industrial chemical of modern time. In production, it is the largest volume chemical produced in the United States. Most sulfuric acid manufactured in the USA is used by the fertilizer industry for making phosphoric acid and phosphate fertilizers. Sulfuric acid has numerous applications. Some major uses include extracting ores; pickling metal; making explosives; manufacturing dyes, glues, and parchment papers; producing nitric and other acids; purifying petroleum; preparing metal sulfates; and synthesizing many organics. Sulfuric acid also is used in lead storage batteries for automobiles. The lead storage battery was invented by Gaston Plante in 1859. Sulfuric acid is used heavily in sulfonation, estertification, oxidation, dehydration, and acid-base neutralization reactions. Sulfuric acid is a common laboratory reagent used for laboratory preparation of a large number of salts; as a dehydrating agent; as a component of chromic mixture for cleaning glassware; and in acid-base titration. The acid has been in wide usage in various industrial applications for more than two hundred years. Commercial concentrated acid has an assay of 95 to 98% H_2SO_4. Its normality is 36 N and density 1.834 to 1.836 g/mL.

Manufacture

Sulfuric acid is manufactured by two processes; namely, the chamber process and the contact process. The chamber process was discovered in 1746 and was used to produce sulfuric acid for over a century. This process was replaced by the contact process which has a lower production cost and yields a more concentrated acid needed for most industrial applications. The chamber process is obsolete now but for historical interest it is outlined below.

In the chamber process, nitric oxide catalyzes the oxidation of sulfur dioxide to trioxide:

$$2SO_2\,(g) + O_2\,(g) \xrightarrow{NO(g)} 2SO_3\,(g)$$

The reaction is homogeneously catalyzed by NO. Although the oxidation process is exothermic and spontaneous, the reaction is very slow without a catalyst. The mechanism of the reaction is as follows:

$$2NO + O_2 \rightarrow 2NO_2 \qquad \text{(fast)}$$

$$NO_2 + SO_2 \rightarrow NO + SO_3 \qquad \text{(fast)}$$

Practically all sulfuric acid is now made by the contact process. The starting material is sulfur dioxide, which is made by various methods, such as burning sulfur in dry air:

$$S\,(s) + O_2(\,g) \rightarrow SO_2\,(g)$$

or by burning pyrites or hydrogen sulfide:

$$4FeS_2(s) + 11O_2(g) \rightarrow 8SO_2\,(g) + 2Fe_2O_3\,(s)$$

$$2H_2S\,(g) + 3O_2\,(g) \rightarrow 2SO_2\,(g) + 2H_2O(g)$$

Sulfur dioxide produced is reacted with oxygen in the presence of a catalyst to form sulfur trioxide:

$$2SO_2\,(g) + O_2\,(g) \rightarrow 2SO_3\,(g)$$

Sulfur trioxide produced above by the contact process is absorbed in sulfuric acid to form pyrosulfuric acid, $H_2S_2O_7$, which is diluted with water to form sulfuric acid:

$$SO_3\,(g) + H_2SO_4(l) \rightarrow H_2S_2O_7\,(l)$$

$$H_2S_2O_7\,(l) + H_2O\,(l) \rightarrow 2H_2SO_4(l)$$

Sulfur trioxide also can be dissolved in water to form sulfuric acid. The dissolution of sulfur trioxide mist, however, is difficult to attain. Most plants employ sulfuric acid to dissolve SO_3 vapor which can be diluted to obtain sulfuric acid of desired concentration.

Conversion of sulfur dioxide to trioxide requires a suitable catalyst. Vanadium pentoxide, V_2O_5, is probably the most effective catalyst for the contact process. Vanadium and potassium salts supported on diatomaceous earth, platinized asbestos, platinized magnesium sulfate, and ferric oxide also have proved to be efficient catalysts.

Lead, tantalum, zirconium, and many specialty alloys are not attacked by concentrated acid even at moderate temperatures. Containers made of such materials can be used for handling, storage, and carrying out reactions.

Reactions

Sulfuric acid is a strong diprotic acid. In dilute aqueous solution, ionization of the first hydrogen is complete and the Ka value for the hydrogen sulfate ion, HSO_4^- at 25°C is 1.2×10^{-2}. It neutralizes bases forming corresponding salts and water. Thus, with caustic soda, sodium sulfate is obtained on evaporation of the solution:

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

Among some important industrial reactions of sulfuric acid is its reaction with potassium nitrate and distillation of nitric acid from the mixture:

$$KNO_3(s) + H_2SO_4\,(l) \xrightarrow{\Delta} KHSO_4(s) + HNO_3(g);$$

and the production of hydrogen chloride from its reaction with sodium chloride, discovered by Johann Glauber in 1648:

$$NaCl(s) + H_2SO_4\,(l) \rightarrow NaHSO_4(s) + HCl\,(g)$$

Sulfuric acid reacts with metal halides to form hydrogen halides. Thus, hydrogen fluoride is commercially made by the action of calcium fluoride with the acid:

$$CaF_2(s) + H_2SO_4\,(l) \xrightarrow{\Delta} CaSO_4(s) + 2HF(g)$$

Sulfuric acid reacts with bauxite to yield aluminum sulfate, another important industrial reaction:

$$Al_2O_3\cdot2H_2O\,(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3\,(aq) + 5H_2O(l)$$

Probably the most important commercial reaction of sulfuric acid involves making phosphoric acid from phosphate rock:

$$Ca_3(PO_4)_2\,(s) + 3H_2SO_4\,(aq) + 6H_2O\,(l) \rightarrow 2H_3PO_4\,(aq) + 3CaSO_4\cdot2H_2O(s)$$

Also, some phosphate rock can be converted directly to super–phosphate fertilizer, which is a mixture of $CaSO_4$ and $Ca(H_2PO_4)_2 \cdot H_2O$:

$$2Ca_5(PO_4)_3F\,(s) + 7H_2SO_4\,(aq) + 3H_2O\,(l) \xrightarrow{\Delta} 7CaSO_4(s) + 3Ca(H_2PO_4)_2 \cdot H_2O(s) + 2HF(g)$$

Concentrated acid is a powerful dehydrating agent. It forms hydrates $H_2SO_4 \cdot nH_2O$. It dehydrates and chars sugar.

In dilute aqueous solution, sulfuric acid is a nonoxidizing acid. However, when concentrated and hot, it is an oxidizing agent. Thus, hot and concentrated sulfuric acid oxidizes copper to Cu^{2+}, liberating sulfur dioxide. The net ionic equation is:

$$Cu(s) + 4H^+\,(aq) + SO_4^{2-}\,(aq) \rightarrow Cu^{2+}\,(aq) + SO_2(g) + 2H_2O\,(l)$$

Similar reactions occur with zinc, magnesium, aluminum, and iron. Concentrated sulfuric acid oxidizes iodide to iodine and bromide to bromine:

$$2I^- + HSO_4^- + 3H^+ \rightarrow I_2 + SO_2 + 2H_2O$$

Sulfuric acid does not manifest such oxidizing action with chloride ion. As mentioned above, reaction with solid sodium chloride forms hydrogen chloride gas, while no such hydrogen halide is produced with corresponding bromide or iodide salt.

Analysis

The normality or molarity of the acid can be determined by titration with a standard solution of sodium hydroxide using a color indicator, or by potentiometric titration using a pH meter or a millivoltmeter. The sulfate anion in dilute acid can be measured by precipitation with barium chloride or by ion chromatography.

Hazard

Sulfuric acid is a highly corrosive acid. Concentrated acid can cause severe burn on skin contact. Contact with eyes can damage vision.

SULFUROUS ACID

[7782-99-2]
Formula H_2SO_3; MW 82.08

Sulfurous acid is a solution of sulfur dioxide in water (about 6%). Although it yields sulfite salts, many of which are stable and can be readily prepared, sulfurous acid itself exists in solution only and cannot be isolated in solid crystalline form.

The acid is a colorless, clear solution of density about 1.03 g/mL. It emits a suffocating odor of sulfur dioxide and slowly oxidizes in air to sulfuric acid. It is used as an antiseptic and dental bleach solution.

SULFUROUS OXYCHLORIDE

[7719-09-7]
Formula $SOCl_2$; MW 118.97
Synonyms: thionyl chloride; sulfur oxychloride

Uses

Sulfurous oxychloride is used as a chlorinating agent for making sulfoxides and acyl chlorides. It also is used in pesticide formulations and to prepare anhydrous metal halides from their hydrated halides or hydroxides.

Physical Properties

Pale yellow to red fuming liquid; suffocating odor; refractive index 1.517 at 20°C; density 1.631 g/mL at 20°C; freezes at –101°C; boils at 75.6°C; decomposes at 140°C; decomposes in water; soluble in benzene, chloroform, and carbon tetrachloride.

Thermochemical Properties

$\Delta H_f°$ (liq)	–58.7 kcal/mol
$\Delta H_f°$ (gas)	–50.8 kcal/mol
$\Delta G_f°$ (gas)	–47.4 kcal/mol
S° (gas)	74.0 cal/deg mol
C_ρ (liq)	28.9 cal/deg mol
C_ρ (gas)	15.9 cal/deg mol
ΔH_{vap}	7.58 kcal/mol

Preparation

Sulfurous oxychloride can be prepared by oxidation of sulfur dichloride with sulfur trioxide:

$$SCl_2 + SO_3 \rightarrow SOCl_2 + SO_2$$

Also, the compound can be prepared by reacting sulfur dioxide with phosphorus pentachloride:

$$SO_2 + PCl_5 \rightarrow SOCl_2 + POCl_3$$

Reactions

Sulfurous oxychloride is rapidly and violently hydrolyzed in water forming sulfur dioxide and hydrogen chloride:

$$SOCl_2 + H_2O \rightarrow SO_2 + 2HCl$$

The compound decomposes above 140°C to form sulfur dioxide, chlorine and disulfur dichloride:

$$4SOCl_2 \rightarrow 2SO_2 + S_2Cl_2 + 3Cl_2$$

Reaction with hydrofluoric acid forms sulfurous oxyfluoride (thionyl fluoride), SOF_2:

$$SOCl_2 + 2HF \rightarrow SOF_2 + 2HCl$$

Similar halogen exchange reaction occurs with metal halides.

Sulfurous oxybromide is obtained with hydrogen bromide at 0°C:

$$SOCl_2 + 2HBr \rightarrow SOBr_2 + 2HCl$$

The compound forms several adducts.

Analysis

Elemental composition: S 26.95%, Cl 59.60%, O 13.45%. The compound may be identified by its physical and chemical properties. A solution in benzene or toluene may be analyzed by GC-ECD or GC-FPD or by the GC/MS, the GC/MS being the most reliable test. For the GC/MS analysis a halogenated solvent such as methylene chloride or chloroform may be used.

Toxicity

Liquid and vapor are highly corrosive to skin and the eye. Vapors are strongly irritating to mucous membranes.

SULFUR TRIOXIDE

[7746-11-9]
Formula SO_3; MW 80.064
Synonym: sulfuric anhydride

Uses

Sulfur trioxide is an intermediate in manufacturing sulfuric acid. It is used for sulfonation of organic compounds and in manufacturing explosives.

Physical Properties

Colorless liquid at ambient temperature and atmospheric pressure; fumes in air.

Sulfur trioxide tends to polymerize, particularly in the presence of traces of water or sulfuric acid. The rate of its polymerization, however, decreases greatly as its freezing point is approached. Solid (polymeric) sulfur trioxide exists in three polymorphic phases: alpha-, beta- and gamma- modifications.

The alpha phase is made up of ice-like needles having polymeric cross-linked structure. It melts at 62.3°C and has a vapor pressure of 73 torr at 25°C.

The beta phase is a metastable allotrope with white, asbestos-like, lustrous needles consisting of polymeric molecules, melting at 32.5°C, and with vapor pressure 344 torr at 25°C.

The gamma modification at ordinary temperatures can exist in solid or liquid form. In solid form it is a colloidal ice-like mass melting at 16.8°C. In the liquid form it has a density of 1.9224 g/mL, boiling at 44.8°C. It has a vapor pressure of 433 torr at 25°C. The gamma phase consists of both cyclic trimer and monomer molecules. When solid sulfur trioxide melts, it converts to its gamma phase which on solidification changes to alpha modification.

Critical temperature of SO_3 is 217.8°C; critical pressure 80.97 atm; critical density 0.63 g/cm^3; the dielectric constant of liquid SO_3 at 18°C is 3.11.

Sulfur trioxide dissolves in water forming sulfuric acid and generating large heat.

Thermochemical Properties

$\Delta H_f°$ (cry)	–108.63 kcal/mol
$\Delta H_f°$ (liq)	–105.41 kcal/mol
$\Delta H_f°$ (gas)	–94.58 kcal/mol
$\Delta G_f°$ (cry)	–88.19 kcal/mol
$\Delta G_f°$ (liq)	–88.04 kcal/mol
$\Delta G_f°$ (gas)	–88.69 kcal/mol
S° (cry)	12.50 cal/deg mol
S° (liq)	22.85 cal/deg mol
S° (gas)	61.34 cal/deg mol
C_ρ (gas)	12.11 cal/deg mol
ΔH_{fus} (alpha)	77.4 kcal/mol
ΔH_{fus} (beta)	36.2 kcal/mol
ΔH_{fus} (gamma)	22.5 kcal/mol

Production

Sulfur trioxide is produced as an intermediate in manufacturing sulfuric acid by the contact process (See Sulfuric Acid). The process involves catalytic oxidation of sulfur dioxide to trioxide.

Sulfur trioxide is prepared in the laboratory by heating fuming sulfuric acid, condensing its vapors, and collecting in a cool receiver. When vapors are condensed below 27°C in the presence of trace moisture, all three polymorphic phases of SO_3 are produced. They can be separated by fractional distillation. Condensation of the vapors above 27°C forms the liquid variety of gamma-sulfur trioxide.

Analysis

Sulfur trioxide is cautiously dissolved in water under cooling to form sulfuric acid. Molarity of the acid is measured by titration with a standard solution of sodium hydroxide. Its vapors may be diluted with helium and analyzed by GC-FPD or GC/MS using a polar column.

Toxicity

Both liquid and vapors are highly corrosive to skin, eyes and mucous membranes.

SULFURYL CHLORIDE

[7791-25-5]
Formula: SO_2Cl_2; MW 134.97
Synonyms: sulfonyl chloride; sulfuric chloride; sulfuric oxychloride

Uses

Sulfuryl chloride is used as a chlorinating and sulfonating agent in organic synthesis. It also is used in military gas.

Physical Properties

Colorless, mobile liquid; turns yellow on standing; very pungent odor; refractive index 1.4437 at 20°C; density 1.667 g/mL at 20°C; vapors heavier than air, vapor density 4.7 (air=1); melts at –51°C; boils at 69.4°C; sparingly soluble in water, decomposing slowly to sulfuric and hydrochloric acids; forms a hydrate $SO_2Cl_2 \cdot 15H_2O$ with ice-cold water; miscible with benzene, toluene, chloroform, carbon tetrachloride, and glacial acetic acid; decomposed by alkalies (violent reaction occurs)

Thermochemical Properties

$\Delta H_f°$ (liq)	–94.19 kcal/mol
$\Delta H_f°$ (gas)	–86.00 kcal/mol
$\Delta G_f°$ (gas)	–76.48 kcal/mol
S°(gas)	74.54 cal/deg mol
C_ρ (liq)	32.03 cal/deg mol
C_ρ (gas)	18.40 cal/deg mol
ΔH_{vap}	7.50 kcal/mol

Preparation

Sulfuryl chloride is prepared by reacting sulfur dioxide with chlorine in the presence of a catalyst, such as activated carbon or camphor. Both the gases should be in dry form and passed over the catalyst:

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2$$

Also, the compound can be obtained by heating chlorosulfonic acid in the presence of a catalyst:

$$2ClSO_3H \rightarrow SO_2Cl_2 + H_2SO_4$$

Analysis

Elemental composition: S 23.76%, Cl 52.54%, O 23.70%. The compound can be dissolved in an organic solvent, such as toluene, and analyzed by GC using an ECD or FPD type detector or by the GC/MS (a confirmatory analysis). Also, a small amount of compound is decomposed in water (slow reaction) and the products, HCl and H_2SO_4, are measured by ion chromatography or by wet methods

Toxicity

Sulfuryl chloride is highly corrosive to skin, eyes and mucous membranes. Reactions with alkalies, lead dioxide, phosphorus and dimethyl sulfoxide can be violent.

TANTALUM

[7440-25-7]
Symbol Ta; atomic number 73; atomic weight 180.95; a Group VB (Group 5) transition metal in vanadium subgroup; electron configuration $[Xe]4f^{14}5d^36s^2$; valence state +5; atomic radius 1.46Å; ionic radius of Ta^{5+} is 0.64Å for a coordination number 6 in crystals; standard electrode potential, E° for $Ta^{3+} + 3e^- \leftrightarrow Ta$ is –0.6V; two natural isotopes: Ta-181 (99.988%), Ta-180 (0.012%), Ta-180 is radioactive with a half-life over 1.2×10^{15} years; twenty-nine known artificial radioactive isotopes in the mass range 156-179, 182-186.

History, Occurrence and Uses

Tantalum was discovered by the Swedish chemist Anders Ekeberg in 1802, although for a long time after his discovery many chemists believed tantalum and niobium were the same element. In 1866, Marignac developed a fractional crystallization method for separation of tantalum from niobium. Ekeberg named the element in honor of Tantalus, who was Niobe's father in Greek mythology.

Tantalum is never found in nature in free elemental form. The most important mineral is columbite-tantalite (Fe,Mn) $(Nb,Ta)_2O_6$. Tantalum also is found in minor quantities in minerals pyrochlore, samarskite, euexenite, and fergusonite. The abundance of tantalum in the earth's crust is estimated as 2 mg/kg.

Tantalum and its alloys have high melting points, high strength and ductility and show excellent resistance to chemical attack. Tantalum carbide graphite composite is one of the hardest substances ever made and has a melting point over 6,700°C. The pure metal is ductile and can be drawn into fine wire, which is used as filament for evaporating aluminum and other metals. Tantalum filaments were used in incandescent lamp bulbs before tungsten replaced them. At temperatures below 150°C, tantalum is attacked only by hydrofluoric acid, fluoride ion in acidic solutions, and free sulfur trioxide. It also is attacked, but slowly, by alkalies. Tantalum and its alloys, therefore, are used to build reactors, vessels, and cruicibles for preparing and carrying out reactions involving many reactive intermediates. The metal and its alloys are used to construct furnace parts, electrolytic capacitors, aircraft and missile parts, chemical process equipment, and nuclear reactors. Being nonreactive to body fluids and a nonirritant to body tissues, tantalum is used in making surgical appliances. Plate and sheet tantalum are applied in bone repair, foil and wire for nerve repair, and plate, gauge, and sheet for repair of abdominal muscle. Tantalum oxide is used to produce optical glasses of high refractive index. The oxide film on the metal makes it a rectifier for converting alternating current to direct current.

Physical Properties

Gray, heavy, and very hard metal; malleable and ductile; body-centered cubic lattice structure; the density of the metal 16.65 g/cm^3 at 20°C and that of powder 14.40 g/cm^3; melts at 2,996°C; vaporizes around 5,458°C; electrical resistivity 13.1 microhm-cm at 25°C; modulus of elasticity 27×10^{-6} psi; Poisson's ratio 0.35; magnetic susceptibility 0.849×10^{-6} cgs units at 25°C; insoluble in water, alcohol and practically all acids; soluble in hydrofluoric acid

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	186.9 kcal/mol
$\Delta G_f°$ (gas)	176.7 kcal/mol
S° (cry)	9.92 cal/deg mol
S° (gas)	44.3 cal/deg mol
C_ρ (cry)	5.00 cal/deg mol
C_ρ (gas)	6.91 cal/deg mol
ΔH_{fus}	8.74 kcal/mol
Thermal conductivity (27°C)	0.575 W/cmK
Coefficient of linear expansion (25°C)	6.3×10^{-6} /°C

Production

Tantalum is mined using techniques such as hydraulic washing and dredging. The ore is crushed, milled, and concentrated by gravity, magnetic, or electrostatic separation or a combination of many wet or dry processes. Ore concentrates consist of tantalum and niobium oxides at varying ratios along with iron, manganese, and small amounts of silica, tin, and titanium. Isolation of tantalum from niobium is usually a tedious and cumbersome process because of their similar chemical properties.

Liquid-liquid extraction is a relatively simple and efficient process compared to Marignac's older fractional crystallization method. Ore concentrate in its finely-ground form is heated with hydrofluoric acid to dissolve the oxides of tantalum and niobium and separate them from associated impurities.

Separation of tantalum from niobium in hydrofluoric acid is carried out by solvent extraction due to solubility difference, using a suitable organic solvent such as methyl isobutyl ketone. At low acidity tantalum partitions from water into immiscible organic solvent leaving behind niobium in the aqueous HF extract. Tantalum is thus separated from this aqueous HF solution. The acidity of the aqueous HF solution is now increased and the solution again extracted with fresh methyl isobuty ketone to recover niobium, which partitions into the organic solvent, leaving any impurity that may remain dissolved in the HF solution.

The organic extract containing tantalum is treated with pure water upon which tantalum partitions into the aqueous phase as a water-soluble salt.

The aqueous solution on neutralization with ammonia forms tantalum pentoxide, $Ta_2O_5 \cdot nH_2O$ Alternatively, treating the aqueous extract with potassium fluoride yields potassium fluotantalate, K_2TaF_7.

Marignac's original process has undergone several modifications over the years. Although it has been applied commercially in producing tantalum, the application is very limited. This process can produce tantalum. However, pure niobium cannot be obtained this way. Separation of tantalum from niobium is achieved through fractional crystallization and is based on the solubility difference of potassium fluotantalate, K_2TaF_7, and potassium pentafluoroniobate, K_2NbOF_5, in dilute hydrofluoric acid solution. The tantalate is less soluble than the niobate in dilute HF. In the above process, ore concentrate is fused with caustic soda. The fused mass is treated with hot water and then with hydrochloric acid and filtered. While all impurities are solubilized and remain in the filtrate, the residue essentially consists of hydrated tantalum and niobium oxides. The residue is dissolved in hydrofluoric acid solution and to this solution a potassium salt, usually the hydroxide, fluoride, or carbonate is added. Upon cooling, potassium fluotantalate precipitates from solution.

Tantalum metal is prepared from potassium fluotantalate or tantalum pentoxide produced from the ore concentrate by solvent extraction or fractional crystallization as described. The metal is produced industrially by Balkes electrolysis process. Fused potassium fluotantalate is electrolyzed at 900°C in a cast iron pot. While the latter serves as a cathode, a graphite rod is used as the anode. A small amount of tantalum oxide is added to the melt. The unreduced potassium fluotantalate is separated from the tantalum metal produced by leaching with water. Impurities are removed from the metal by acid wash.

Another electrolysis process involves electrodeposition of dense, high-purity tantalum metal. In this electrolysis, electrolyte consists of potassium fluotantalate and potassium fluoride and the anode is made of tantalum upon which electrodeposition from the fused salt occurs.

Thermal reduction processes have been applied successfully in making the metal from salts. In one such process, potassium fluotantalate is reduced with sodium metal at high temperatures to form tantalum powder of high purity and small particle size. Also, tantalum oxide can be reduced at high temperatures in vacuum with aluminum, silicon, or tantalum carbide. When the oxide is reduced by tantalum carbide, a metal sponge is obtained which can be embrittled with hydrogen to form powder metal.

Reactions

The most common oxidation state of tantalum is +5 and its aqueous solution chemistry is that of its pentavalent ion Ta^{5+}. Ta metal forms a pentavalent oxide, tantalum pentoxide, Ta_2O_5, on heating with oxygen. However, at ordinary temperatures a thin layer of oxide covering the metal surface protects tantalum from most chemical attacks. The metal is attacked by hydrofluoric acid below 150°C. It also is dissolved by hot fuming sulfuric acid. It reacts with fluorine and chlorine on heating, forming tantalum pentafluoride, TaF_5, and pentachloride, $TaCl_5$, respectively. The metal is immune to dilute aqueous alkalies but is attacked slowly by concentrated fused alkalies. It combines with molecular hydrogen above 250°C. The hydride formed decomposes on heating above 800°C in vacuum. Tantalum forms alloys with several metals.

Analysis

Tantalum may be digested with a mixture of hydrofluoric acid and nitric acid, the solution diluted, and analyzed by flame AA or ICP-AES. Also, tantalum can be identified by x-ray methods and neutron activation analysis.

TANTALUM PENTACHLORIDE

[7721-01-9]
Formula: $TaCl_5$; MW 358.21; shows a dinuclear structure, Ta_2Cl_{10}, but in vapor phase it exists as a mononuclear, $TaCl_5$, having a trigonal bipyramidal shape.
Synonyms: tantalum chloride; tantalic chloride

Uses

Tantalum pentachoride is used to make pure metal and other tantalum salts. Also, it is used for chlorination of organic substances.

Physical Properties

Yellow monoclinic crystals; hygroscopic; density 3.68 g/cm³; melts at 216°C; vaporizes at 239.4°C; critical temperature 494°C; critical volume 402 cm³/mol; can be sublimed without decomposition in chlorine atmosphere; reacts with water; soluble in ethanol, ether and carbon tetrachloride.

Thermochemical Properties

$\Delta H_f°$	–205.3 kcal/mol
ΔH_{fus}	8.39 kcal/mol
ΔH_{vap}	13.1 kcal/mol

Preparation

Tantalum pentachloride is prepared by heating tantalum metal with excess chlorine:

$$2Ta + 5Cl_2 \rightarrow 2TaCl_5$$

Reactions

Tantalum pentachloride is hydrolyzed by water to form hydrous tantalum pentoxide, $Ta_2O_5 \cdot nH_2O$ and hydrochloric acid:

$$2TaCl_5 + 5H_2O \rightarrow Ta_2O_5 + 10HCl$$

Reaction with hydrofluoric acid yields tantalum pentafluoride:

$$TaCl_5 + 5HF \rightarrow TaF_5 + 5HCl$$

Tantalum pentachloride forms adducts with donor solvent molecules. Also, it forms several complexes and organometallic derivatives.

Reactions with alcohols in the presence of an amine forms dinuclear alkoxides. Thus, with ethanol in the presence of diethylamine, the dinuclear tantalum ethoxide, $Ta_2(OC_2H_5)_{10}$, is obtained.

Reaction with dimethylzinc forms dichlorotrimethyl tantalum, in which three chlorine atoms are substituted with methyl groups:

$$2TaCl_5 + 3Zn(CH_3)_2 \rightarrow 2(CH_3)_3TaCl_2 + 3ZnCl_2$$

Reaction with cyclopentadienyl sodium yields bis(cyclopentadienyl) tantalum trichloride:

$$TaCl_5 + 2C_5H_5\ Na \rightarrow (C_5H_5)_2TaCl_3 + 2NaCl$$

Analysis

Elemental composition: Ta 50.50%, Cl 49.50%. Tantalum content in an acid extract ($HF–HNO_3$ extract) can be determined by various instrumental techniques. The pentachloride is hydrolyzed to HCl, which can be measured by acid-base titration. Also, the compound can be identified from its physical and x-ray properties.

TANTALUM PENTOXIDE

[1314-61-0]
Formula Ta_2O_5; MW 441.89
Synonyms: tantalum oxide; tantalic acid anhydride

Uses

Tantalum pentoxide is used in making high refractive index optical glass; as a dielectric film on tantalum for its use as a capacitor component and rectifier; and for preparing tantalum metal, its carbide, and many other tantalum compounds.

Physical Properties

White orthorhombic crystal or powder; density 8.20 g/cm^3; melts at

1,785°C; insoluble in water, ethanol and practically all acids; soluble in hydrofluoric acid; solubilized by fusion with caustic potash or potassium hydrogen sulfate.

Thermochemical Properties

$\Delta H_f°$	–489.0 kcal/mol
$\Delta G_f°$	–456.8 kcal/mol
S°	34.2 cal/deg mol
C_ρ	32.3 cal/deg mol
ΔH_{fus}	28.7 kcal/mol

Preparation

Tantalum pentoxide is obtained as an intermediate in extracting tantalum from the columbite-tantalite series of minerals. Also, the oxide can be made by heating Ta metal in oxygen or air at elevated temperatures.

Analysis

Elemental composition: Ta 81.89%, O 18.11%. The oxide may be identified by x-ray methods. It may be dissolved in hydrofluoric and nitric acid, diluted and analyzed by AA, ICP and other instrumental techniques.

TECHNETIUM

[7440-26-8]
Symbol Tc; atomic number 43; atomic weight 98; a Group VIIB (Group 7) manganese group metallic element; the first artificially-produced radioactive element; electron configuration [Kr]$4d^5\ 5s^2$; valence states 0, +2, +4, +5, +6, +7; most stable oxidation state +7; atomic radius 1.36Å; all isotopes are radioactive; twenty-eight artificially produced isotopes are known in the mass range 86–113; three have long half-lives; Tc-97, $t_{1/2}$ 2.6×10^6 year; Tc-98, $t_{1/2}$ 4.2×10^6 year; and Tc-99, $t_{1/2}$ 2.13×10^5 year.

History, Occurrence and Uses

Existence of technetium was predicted from the vacant position in the Periodic Table between manganese and rhenium. Noddack, Tacke, and Berg reported its discovery in 1925 and named it "masurium." The metal actually was never isolated from any source by these workers. Its existence, therefore, could not be confirmed. Perrier and Segre in 1937 produced this element by bombarding molybdenum metal with deuterons in a cyclotron. They named the element technetium derived from the Greek word *technetos*, meaning artificial.

Technetium has not been found to exist on earth. However, it has been detected in certain stars. Long-lived technetium-99 isotope of half-life 2.15×10^5 years is found in relatively significant quantities in fission products of uranium-235. Every 1g of uranium-235 yields about 0.027g of technetium-99 from its fission.

Technetium metal does not have much commercial application. Its short-lived metastable istopes Tc-99m with a half–life of 6 hours is used to locate tumors in liver, brain, spleen, and thyroid by scintillation scanning. It also is used in research. Tc is an excellent corrosion inhibitor for steel and can be used to protect steel. The steel may be confined to a closed system and to prevent any exposure to radiation.This property, however, has not yet been utilized in commerical practice. Also, technetium and its alloys exhibit excellent superconducting properties. They can be used to produce magnetic fields at a low temperature.

Physical Properties

Silvery-gray metal; slowly tarnishes in moist air; crystallizes in hexagonal close-packed structure; density 11.49 g/cm^3 (calculated); melts at 2,172°C; vaporizes at 4,265°C; Young's (elastic) modulus 3.76×10^6 kg/cm; Poisson's ratio 0.293; thermal neutron absorption cross-section 22 barns; superconductor below 11°K; insoluble in water and hydrochloric acid; dissolves in nitric acid, concentrated sulfuric acid and aqua regia.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	162.0 kcal/mol
$\Delta G_f°$ (cry)	0.0
S° (gas)	43.25 cal/deg mol
C_ρ (cry)	4.97 cal/deg mol
ΔH_{fus}	7.96 kcal/mol
Thermal conductivity	0.506 W/cm K
Coefficient of linear expansion	$8.06\text{x}10^{-6}$ / °C

Preparation

Technetium isotopes are prepared by bombardment of molybdenum with protons and neutrons. A few nuclear reactions are shown for the three long-lived isotopes:

$${}^{97}_{42}\text{Mo} + {}^{2}_{1}\text{d} \longrightarrow {}^{97m}_{43}\text{Tc} + 2{}^{1}_{0} + \gamma$$

$${}^{97m}_{43}\text{Tc} \longrightarrow {}^{97}_{43}\text{Tc} + \gamma$$

($t_{1/2}$ 2.6 x10^6 year)

$${}^{98}_{42}\text{Mo} + {}^{1}_{1}\text{p} \longrightarrow {}^{98}_{43}\text{Tc} + {}^{1}_{0}\text{n}$$

$${}^{98}_{42}\text{Mo} + {}^{1}_{0}\text{n} \longrightarrow {}^{99}_{42}\text{Mo} + \gamma$$

$${}^{99}_{42}\text{Mo} + \xrightarrow{\beta^-} {}^{99m}_{43}\text{Tc} \xrightarrow{\gamma} {}^{99}_{43}\text{Tc}$$

($t_{1/2}$ 2.15 x10^5 year)

Technetium-99 also is a fission product of uranium-235.

Pure technetium metal may be prepared by reducing ammonium pertechnate, NH_4TcO_4, with hydrogen at high temperatures. Hydrogen reduction at about 200°C first forms the oxide, TcO_2, which is reduced to Tc metal at 600 to 800°C.

Reactions

Most chemical properties of technetium are similar to those of rhenium. The metal exhibits several oxidation states, the most stable being the heptavalent, Tc^{7+}. The metal forms two oxides: the black dioxide TcO_2 and the heptoxide Tc_2O_7. At ambient temperature in the presence of moisture, a thin layer of dioxide, TcO_2, covers the metal surface. The metal burns in fluorine to form two fluorides, the penta- and hexafluorides, TcF_5 and TcF_6. Binary compounds also are obtained with other nonmetallic elements. It combines with sulfur and carbon at high temperatures forming technetium disulfide and carbide, TcS_2 and TcC, respectively.

Technetium dissolves in dilute or concentrated nitric acid to form nitrate, $Tc(NO_3)_2$. Reaction with concentrated sulfuric acid yields the sulfate $TcSO_4$. Technetium is oxidized by hydrogen peroxide in alkaline solution to form soluble pertechnetate, TcO_4^- anion. Such pertechnatate anion forms complexes with tertiary or quarternary amines, pyridine and its methyl-substituted derivatives.

Analysis

Technetium can be measured by spectrophotmetric methods. It forms two characteristic peaks with absorption maxima at 247 and 285 nm. Also, it can be measured by polarographic methods. All technetium isotopes are radioactive. The element can be identified from its specific activity using a scintillation counter.

TELLURIC ACID

[7803-68-1]
Formula: H_6TeO_6 or $Te(OH)_6$; MW 229.64; hydrogen-bonded octahedral molecules
Synonyms: orthotelluric acid; telluric (VI) acid; hydrogen tellurate

Uses

No commercial application of this compound is known. It is used in preparing certain tellurium complexes and tellurates.

Physical Properties

White crystals; dimorphic solid; exists in both cubic and monoclinic crystalline forms; density 3.07g/cm^3; melts at 136°C; tends to polymerize (similar to stannic acid); forms polymetatelluric acid $(H_2TeO_4)_n$ on strong heating; soluble in water, about 33g/100 mL at 30°C; the solubility decreases as the molecule polymerizes and becomes colloidal; a very weak dibasic acid, pK_{a1} 7.68 and pK_{a2} 11.0 at 18°C; soluble in dilute nitric acid and alkalies.

Preparation

Telluric acid can be prepared by reducing barium tellurate with sulfuric acid:

$$BaTeO_4 + H_2SO_4 + 2H_2O \rightarrow H_6TeO_6 + BaSO_4$$

Also, telluric acid can be prepared by oxidation of tellurium or tellurium dioxide with a strong oxidizing agent such as hydrogen peroxide, sodium peroxide, chromic acid, or potassium permanganate in nitric acid. Molecular equations for overall reactions are shown below:

$$Te + 3H_2O_2 \rightarrow H_6TeO_6$$

$$TeO_2 + H_2O_2 + 2H_2O \rightarrow H_6TeO_6$$

$$Te + 2CrO_3 + 3H_2O \rightarrow H_6TeO_6 + Cr_2O_3$$

At cold temperatures at about 1°C, telluric acid crystallizes as tetrahydrate.

Analysis

Elemental composition: Te 55.57%, H 2.63%, O 41.80%. An aqueous solution or a dilute nitric acid solution is analyzed for tellurium by AA or ICP techniques. Aqueous solution also may be analyzed by colorimetric methods (See Tellurium below).

TELLURIUM

[13494-80-9]
Symbol Te; atomic number 52; atomic weight 127.60; a Group VI A (Group 16) metallic element in the oxygen group placed between selenium and polonium; electron configuration $[Kr]4d^{10}5s^25p^4$; valence states +2, +4, +6; atomic radius 1.42 Å; ionic radii of Te^{+4} and Te^{+6} in crystals, 0.97 Å and 0.56 Å, respectively, for coordination number 6; electronegativity 2.1; eight naturally-occurring isotopes: Te-120 (0.096%), Te-122 (2.603%), Te-123 (0.908%), Te-124 (18.952%); Te-125 (7.139%), Te-126 (18.952%), Te-128 (31.687%), Te-130 (33.799%); two of these naturally–occurring isotopes are radioactive with very long half-lives, Te-130 ($t_{1/2}$ $2.5x10^{21}$ year) and Te-123 ($t_{1/2}$ $1.3x10^{13}$ year); twenty-five artificial radioactive isotopes in the mass range 106–119, 121, 127, 129, 131–138.

History, Occurrence, and Uses

The element was discovered by Muller von Reichenstein in 1782 while investigating a bluish-white ore of gold. The element was isolated from this ore by Klaproth in 1798, who suggested the name “tellurium” after the Latin word *tellus*, meaning earth. Tellurium occurs in nature only in minute quantities. It is found in small amounts in many sulfide deposits. One of the more common tellurium minerals is calaverite, $AuTe_2$, in which the metal is combined with gold. Some other tellurium minerals are altaite, PbTe; sylvanite, $(Ag,Au)Te_2$; rickardite, Cu_4Te_3; tetradymite, Bi_2Te_2S; petzite, Ag_3AuTe_2 and coloradoite, HgTe. The metal is found in the native state and also in the form of its dioxide, tellurite, TeO_2. The abundance of tellurium in the earth’s crust is estimated to be about 1 µg/kg.

Small amounts of tellurium are added to stainless steel and copper to improve their machinability. It enhances the strength and hardness of lead and protects lead from the corrosive action of sulfuric acid. Tellurium also is a strong chilling agent in iron castings. It controls the chill and imparts a tough abrasion resistance to the surface. Tellurium is a curing agent for natural and synthetic rubber. It improves mechanical properties of the rubber imparting resistance to heat and abrasion. Tellurium is a coloring agent in glass, ceramics, and enamels. Traces of tellurium incorporated into platinum catalysts make the catalytic hydrogenation of nitric oxide favorable to forming hydroxylamine.

A major application of tellurium is in semiconductor research. Tellurides of lead and bismuth are used in thermoelectric devices for power generation and refrigeration.

Physical Properties

Silvery-white lustrous metal when pure or dark gray amorphous powder; orthorhombic crystals; hardness 2.3 Mohs; density 6.25 g/cm^3; melts at 452°C; vaporizes at 990°C; modulus of elasticity 6.0x10^6 psi; thermal neutron absorption cross section 4.7 ± 0.1 barns; insoluble in water, carbon disulfide, and benzene; also insoluble in HCl; soluble in sulfuric acid, nitric acid, and aqua regia; also soluble in caustic potash and in solutions of alkali metal cyanides.

Thermochemical Properties

$\Delta Hf°$ (cry)	0.0
$\Delta Hf°$ (gas)	47.02 kcal/mol
$\Delta Gf°$ (cry)	0.0
$\Delta Gf°$ (gas)	37.55 kcal/mol
S° (cry)	11.88 cal/deg mol
S° (gas)	43.65 cal/deg mol
C_ρ (cry)	6.15 cal/deg mol
C_ρ (gas)	4.97 cal/deg mol
ΔH_{fus}	4.18 kcal/mol
ΔH_{vap}	27.0 kcal/mol
Coefficient of linear expansion	16.75x10^{-6}/°C
ΔH_{vap}	27.3 kcal/mol

Production

Tellurium is recovered from the anode slimes produced in electrolytic refining of copper. Other metals present in these slimes are gold, silver, and selenium, which are all recovered as by-products in the extraction of tellurium. Tellurium is leached with caustic soda solution and the leachate upon neutralization precipitates tellurium dioxide, TeO_2, in crude and impure form. A part of tellurium remaining in the slimes can be recovered during extraction of gold and silver. In this gold and silver recovery process, tellurium incorporates into the soda slag obtained from roasting the slimes in a furnace. Soda slag is produced when leached with a solution of caustic soda. The liquor is neutralized to form a crude precipitate of tellurium dioxide.

Crude tellurium dioxide is dissolved in a strong solution of caustic soda to form sodium tellurite. Electrolysis of sodium tellurite solution deposits tellurium metal on the stainless steel cathode.

Also, the tellurium metal can be prepared by thermal reduction of dioxide. However, prior to reduction crude dioxide is refined by successive caustic leaching and neutralization steps mentioned above.

Refined tellurium contains traces of lead, copper, iron, selenium, and other impurities. Highly pure tellurium can be obtained either by distilling refined tellurium in vacuum or by the zone melting process. The last traces of selenium can be removed as hydride by treating molten tellurium with hydrogen.

Reactions

Tellurium burns in air with a greenish-blue flame. The combustion product is dioxide, TeO_2, the most stable oxide of the metal. Tellurium also forms other oxides; the monoxide, TeO, the trioxide, TeO_3, and the pentoxide, Te_2O_5. Monoxide has not yet been obtained in solid form. Like sulfur and selenium, tellurium forms oxyacids. Such oxyacids include orthotelluric acid, H_6TeO_6 and tellurous acid, H_2TeO_3, in which the metal is in +6 and +4 valence states respectively.

Tellurium combines with halogens forming halides at different oxidation states. While with fluorine, direct fluorination of the metal produces tellurium hexafluoride, TeF_6, a colorless gas with a repulsive odor:

$$Te + 3F_2 \rightarrow TeF_6$$

With chlorine and bromine, products are tellurium tetrachloride, $TeCl_4$, a white, very hygroscopic crystalline solid, and tellurium tetrabromide, $TeBr_4$, an orange crystalline solid:

$$Te + 2Cl_2 \rightarrow TeCl_4$$

$$Te + 2Br_2 \rightarrow TeBr_4$$

Tellurium also forms a black dichloride and a brown dibromide usually by its reaction with dichlorodifluoromethane and trifluorobromomethane, respectively:

$$Te + 2CCl_2F_2 \rightarrow TeCl_2 + C_2F_4$$

$$Te + 2CBrF_3 \rightarrow TeBr_2 + C_2F_6$$

Tellurium forms many sulfides and oxysulfides. The metal reacts with sulfides of zinc, cadmium, or mercury, forming tellurium sulfide:

$$Te + ZnS \rightarrow TeS + Zn$$

The higher sulfides of tellurium such as TeS_2 and TeS_3, are obtained from tellurite solutions by precipitation with hydrogen sulfide or sodium sulfide. Tellurium reacts with concentrated sulfuric acid to form red oxysulfide of the composition, $TeSO_3$. With nitric acid, the metal is oxidized to dioxide, TeO_2. Oxidation of tellurium with chromic acid or potassium permanganate in nitric acid yields orthotelluric acid (H_6TeO_6).

Tellurium forms binary tellurides with several metals. The reaction is carried out by heating tellurium with a metal in stoichiometric amounts in the absence of air in an evacuated ampoule. Tellurium reacts with halides of several metals, when heated in a stream of hydrogen, to produce metal tellurides.

Analysis

Tellurium and its compounds can be analysed by AA, ICP-AES and other spectrophotometric methods. Also, the metal can be identified by volumetric, gravimetric, and simple colorimetric measurements.

Tellurium metal, its alloys, minerals or the tellurides may be dissolved in warm concentrated sulfuric acid or cold fuming sulfuric acid to form a red color, the intensity of which is proportional to the tellurium content in the substance. When this red solution is poured into water, black elemental tellurium metal precipitates out of solution. Oxidized tellurium does not respond to this test.

An acidic solution of tellurium (IV) or tellurium (VI) is treated with sulfur dioxide and hydrazine hydrochloride. Tellurium precipitated from solution can be estimated by gravimetry. Selenium interferes with this test. A volumetric test involves converting tellurium to tellurous acid and oxidizing the acid with excess ceric sulfate in hot sulfuric acid in the presence of Cr^{3+} ion as catalyst. The excess ceric sulfate is measured by titration with a standard solution of ferrous ammonium sulfate.

Tellurium can be measured by neutron activation analysis.

Toxicity

Human exposure to tellurium causes “garlic breath” due to dimethyl telluride which persists for a considerable period after exposure. The toxic effects of tellurium are nausea, giddiness, headache, metallic taste, and dryness in the throat.

TELLURIUM DIOXIDE

[7446-07-3]
Formula: TeO_2; MW 159.60
Synonym: tellurous acid anhydride

Uses

Tellurium dioxide is used to prepare tellurium metal, telluric acid, and many tellurium salts.

Physical Properties

White crystals; dimorphic; exists in tetragonal and orthorhombic forms; density 5.75 g/cm^3 (tetragonal), 6.04 g/cm^3 (orthorhombic); melts at 733°C forming a deep yellow liquid; vaporizes at 1,245°C; insoluble in water; soluble in acids and alkalies.

Thermochemical Properties

$\Delta Hf°$	–77.1 kcal/mol
$\Delta Gf°$	–64.6 kcal/mol
S°	19.0 cal/deg mol
ΔH_{fus}	7.0 ± 0.5 kcal/mol
ΔH_{vap}	51.7 kcal/mol

Production

Tellurium dioxide in its orthorhombic form occurs in nature as mineral tellurite. It is mined from natural deposits. Also, tellurium dioxide is produced as an intermediate during recovery of tellurium metal from anode slimes of electrolytic copper refining (See Tellurium, Production). The dioxide also is prepared by treating tellurium metal with hot nitric acid to form $2TeO_2 \cdot HNO_3$. The product then is heated to drive off nitric acid.

Analysis

Elemental composition: Te 79.95%, O 20.05%. The compound can be identified by its physical and x–ray properties. Tellurium content may be measured by digesting the dioxide in HCl or aqua regia, diluting the solution, and analyzing by AA or ICP.

TERBIUM

[7440-27-9]
Symbol Tb; atomic number 65; atomic weight 158.925; a lanthanide series element; an inner-transition rare earth metal; electron configuration [Xe]$4f^96s^2$; valence states +3, +4; mean atomic radius 1.782Å; ionic radii, Tb^{3+}

0.923Å and 1.04Å corresponding to CN 6 and 8, respectively; standard electrode potential, E° for $Tb^{3+} + 3e^- \leftrightarrow Tb$ is –2.28V; one naturally-occurring stable isotope, Tb-159 (100%); twenty-five artificial radioactive isotopes in the mass range 140–158, 160–165; the longest-lived radioisotope, Tb-158, $t_{1/2}$ 180 years; shortest-lived isotope, Tb-142, $t_{1/2}$ 0.60 sec.

History, Occurrence, and Uses

The element was discovered in 1843 by Carl Gustav Mosander. He determined that the oxide, known as yttria, was actually a mixture of at least three rare earths which he named as yttria—a colorless oxide, erbia—a yellow oxide, and terbia— a rose–colored earth. Mosander separated these three oxides by fractional precipitation with ammonium hydroxide. Pure terbia was prepared by Urbain in 1905. The element was named terbium for its oxide, terbia, which was named after the Swedish town, Ytterby.

Terbium occurs in nature associated with other rare earths. It is found in minerals; xenotime, a rare earth phosphate consisting of 1% terbia; and in euxenite, a complex oxide containing about 1.3% terbia. It also is found in cerite, monazite, and gadolinite. Also, the element has been detected in stellar matter. Abundance of terbium in the earth's crust is estimated to be 1.2 mg/kg.

The metal or its salts do not have any important uses at present.

Physical Properties

Silvery-gray metal; hexagonal crystal structure; malleable, ductile, and soft enough to be cut with a knife; density 8.223 g/cm^3; melts at 1,359°C; vaporizes at 3,221°C; resistivity 116×10^{-6} ohm-cm at 25°C; Young's modulus 5.75×10^{11} dynes/cm^2 (from velocity of sound measurements); shear modulus 2.28 dynes/cm^2; Poisson's ratio 0.261; thermal neutron absorption cross section, 46 barns; insoluble in water; soluble in acids.

Thermochemical Properties

$\Delta Hf°$ (cry)	0.0
$\Delta Hf°$ (gas)	92.9 kcal/mol
$\Delta Gf°$ (cry)	0.0
$\Delta Gf°$ (gas)	83.6 kcal/mol
S° (cry)	17.5 cal/deg mol
S° (gas)	48.6 cal/deg mol
C_ρ (cry)	6.91 cal/deg mol
C_ρ (gas)	5.87 cal/deg mol
ΔH_{fus}	2.43 kcal/mol
Thermal conductivity	0.111 W/cm K
Coefficient of linear expansion	10.3×10^{-6}/°C

Preparation

Terbium is recovered from the minerals, monazite, xenotime, and euxenite. The recovery processes are quite similar to those of other lanthanide elements (See individual lanthanide elements). The metal is separated from other rare earths by ion exchange methods, which are relatively easy and faster than fractional crystallization techniques.

Terbium metal is obtained from its anhydrous trifluoride, TbF_3, or trichloride, $TbCl_3$, by thermal reduction with calcium, carried out in a tantalum crucible. Terbium produced by such methods may contain traces of calcium and tantalum. High purity metal can be prepared by various methods such as vacuum remelting, distillation, amalgam formation, floating zone melting, and various chemical processes.

Compounds

The most common valence state in solid compounds is +3. A +4 valence state is known for the metal in its dioxide, TbO_2, and tetrafluoride, TbF_4. Terbium also forms several nonstoichiometric oxides of approximate composition Tb_4O_7.

In solution the metal exists only in trivalent state, $[Tb(H_2O)_n]^{3+}$. The standard electrode potential for $Tb \rightarrow Tb^{3+} + 3e^-$ is calculated to be about 2.39V.

Terbium forms binary compounds with a number of elements including hydrogen, halogens, nitrogen, phosphorus, sulfur, carbon, silicon, selenium, tellurium, boron, arsenic, and antimony. A few well-characterized binary compounds include the four oxides—the cubic crystalline TbO_2, the body-centered cubic crystalline sesquioxide Tb_2O_3, the rhomobohedral Tb_7O_{12}, and the triclinic $Tb_{11}O_{20}$; the hydrides—a cubic dihydride, TbH_2 and a hexagonal trihydride, TbH_3; and the cubic crystalline sulfide, nitride, phosphide, selenide, and telluride of compositions TbS, TbN, TbP, TbSe, and TbTe respectively. Halide compounds include orthorhombic trifluoride, TbF_3; monoclinic tetrafluoride, TbF_4; and the hexagonal triiodide, TbI_3. Also, several borides and carbides of hexagonal, tetragonal, and cubic structures are known.

Among Tb oxo salts are the monoclinic nitrate hexahydrate $Tb(NO_3)_3 \cdot 6H_2O$, the tetragonal oxychloride, TbOCl, and the rhombohedral oxyfluoride, TbOF.

Analysis

Terbium may be identified by various instrumental techniques including atomic absorption and emission spectrophotometry and neutron activation analysis.

THALLIUM

[7440-28-0]

Symbol Tl; atomic number 81; atomic weight 204.38; a Group III A (Group 13) metallic element placed below indium; electron configuration $[Xe]4f^{14}5d^{10}6s^26p^1$; valence state +1, +3; atomic radius 1.70Å; standard electrode potential, E° for $Tl^{3+} + 3e^- \leftrightarrow Tl$ is 0.741 V; two naturally-occurring stable isotopes: Tl-203 (29.524%), Tl-205 (70.476%), twenty-eight artificial radioisotope in the mass range 179, 182-202, 204, 206–210; longest-lived isotope, Tl-204, $t_{1/2}$ 3.78 year; shortest-lived isotope, Tl-179 $t_{1/2}$ 0.2 sec.

History, Occurrence, and Uses

Thallium was discovered spectroscopically by Sir William Crookes in 1861. While searching for tellurium, he observed a beautiful green line in the spectrum of residues of a German sulfuric acid manufacturing plant. He named this element after the Latin word *thallos* meaning the budding green twig. In the following year, in 1862, both Crookes and Lamy independently isolated the metal.

Thallium occurs in nature in potash minerals and many sulfide ores. It is found in pyrites from which the metal is recovered. The metal also occurs in the minerals cooksite, lorandite, and hutchinsonite. The average concentration of thallium in the earth's crust is estimated to be 0.85 mg/kg.

Thallium and its compounds have limited applications. It is used in insecticides and rodenticides. Thallium-mercury alloys are used for switches and closures for use at sub-zero temperatures. Another application is in making low melting glasses for electronic encapsulation. Thallium sulfide is used in photocells.

Physical Properties

Metallic luster when freshly cut but attains a bluish-gray tinge on exposure to air resembling lead in appearance; tetragonal crystals; density 11.85 g/cm^3 at 20°C; melts at 303.5° C; vaporizes at 1473° C; electrical resistivity 18 microhm–cm at 0°C and 74 microhm–cm at 303°C; tensile strength 1300 psi; surface tension at 327°C, 401 dynes/cm; insoluble in water; soluble in nitric and sulfuric acids; slightly soluble in hydrochloric acid.

Thermochemical Properties

$\Delta Hf°$ (cry)	0.0
$\Delta Hf°$ (gas)	43.55 kcal/mol
$\Delta Gf°$ (cry)	0.0
$\Delta Gf°$ (gas)	35.24 kcal/mol
S° (cry)	15.45 cal/deg mol
S° (gas)	43.22 cal/deg mol
C_p (cry)	6.29 cal/deg mol
C_p (gas)	4.97 cal/deg mol
ΔH_{fus}	4.02 kcal/mol
Thermal conductivity at 27°C	0.461 W/cm K
Coefficient of linear expansion (at 25°C)	29.9×10^{-6}/°C

Production

Thallium is recovered from roasting pyrites as a by-product of making sulfuric acid. Also, it is obtained from smelting lead and zinc ores. Lead and zinc concentrates contain small quantities of thallium. During smelting operation at high temperatures thallium compounds volatilize. Thallium compounds, usually oxide and sulfate, are collected in flue dusts along with other metals including selenium, tellurium, cadmium, and indium.

Separating thallium compounds from other substances in flue dust is based on differences in solubility. Solubility differences of thallium salts from those of other metal salts of the same anions in water, acids, and alkalies, are fully utilized in all separation processes. Two industrial processes are briefly mentioned below (Howe, H.E. 1968. *Thallium*. In *An Encyclopedia of Chemical Elements*, ed. C. E. Hempel, New York, Reinhold Book Corporation). In general, thallium compounds are separated and obtained as by-products during processing and recovery of associated metals in flue dust. For example, thallium is obtained as a by-product in recovering cadmium. In this process, crude flue dust is treated with sulfuric acid which converts both cadmium and thallium to their sulfates. Impurity metals are removed from this solution as their sulfides. The solution then is electrolyzed to form a deposit of cadmium-thallium alloy containing less than 20% thallium. The alloy is treated with boiling water. Thallium is converted to its soluble hydroxide. Any cadmium present in the solution is removed by precipitation with sodium carbonate. Insoluble cadmium carbonate is filtered leaving thallium carbonate in solution. Treating this solution with sodium sulfide precipitates thallium sulfide. The precipitate is dissolved in sulfuric acid to form pure thallium sulfate. The solution then is electrolyzed. Thallium is electrodeposited as sponge on aluminum cathodes.

In another industrial process, flue dusts from smelting lead and zinc concentrates are boiled in acidified water. Thallium dissolves and is separated from insoluble residues by filtration. Dissolved thallium in solution then is precipitated with zinc. Thallium is extracted from the precipitate by treatment with dilute sulfuric acid which dissolves the metal. The solution may also contain zinc, cadmium, lead, copper, indium, and other impurities in trace amounts. These metals are precipitated with hydrogen sulfide. The pure thallium sulfate solution then is electrolyzed to yield thallium.

Reactions

Thallium forms all its compounds in two valence states, +1 (thallous) and +3 (thallic). The metal oxidizes slowly in air at ambient temperature but rapidly on heating, forming thallous oxide, Tl_2O. This oxide oxidizes further on heating to form thallic oxide, Tl_2O_3. When exposed to air at ambient temperatures for several days thallium forms a heavy oxide crust.

Thallium reacts with water containing oxygen to form thallous hydroxide, TlOH, which is a relatively strong base, absorbing carbon dioxide and attacking glass.

The metal dissolves in nitric and sulfuric acid. The solution on evaporation crystallizes to yield thallous nitrate and sulfate. Reaction with hydrochloric acid is very slow.

Thallium burns in fluorine with incandescence. Reactions with other halogens form halides. Thallium combines with several elements forming binary compounds.

Analysis

Thallium may be analyzed by flame- and furnace- AA spectrophotometric methods and also by the ICP-AES methods. For the flame-AA analysis, an air-acetylene flame is satisfactory. The ICP- AES measurement may be carried out at wavelength 190.86 nm or at 377.57 nm.

Toxicity

Thallium and its compounds (particularly soluble salts) can cause serious or fatal poisoning from accidental ingestion or external application. Acute symptoms are nausea, vomiting, diarrhea, weakness, pain in extremities, convulsions, and coma. Chronic effects are weakness, pain in extremities, and rapid loss of hair. Thallium and its compounds are listed under Federal toxics regulations. It is listed by the US EPA as a priority pollutant metal in the environment.

THALLIUM CHLORIDE

[7791-12-0]
Formula: TlCl; MW 239.84
Synonym: thallous chloride

Uses

Thallium chloride is a catalyst in chlorination reactions.

Physical Properties

White crystalline powder; turns violet on exposure to light; density 7.004 g/cm^3 at 20°C; melts at 430°C; vaporizes at 720°C; vapor pressure 20 torr at 550°C; slightly soluble in water, 0.29 g/mL at 15.6°C; sparingly soluble in boiling water, 2.4 g/100mL; insoluble in alcohol, acetone and ammonium hydroxide.

Thermochemical Properties

$\Delta Hf°$ (cry)	–48.8 kcal/mol
$\Delta H f°$ (gas)	–16.2 kcal/mol
$\Delta G f°$ (cry)	–44.2 kcal/mol
S° (cry)	26.6 cal/deg mol
C_ρ (cry)	12.2 cal/deg mol
ΔH_{fus}	4.25 cal/deg mol
ΔH_{vap}	24.4 cal/deg mol

Preparation

Thallium chloride may be prepared by heating the metal with chlorine.

Analysis

Elemental composition: Tl 85.22%, Cl 14.78%. A small amount of the salt is dissolved in water (it is slightly soluble in water at room temperature) and the solution analyzed for chloride ion by ion chromatography or by titration with a standard solution of silver nitrate using potassium chromate indicator. The salt is digested with nitric acid, diluted, and analyzed for thallium metal by flame or furnace AA or ICP-AES (see Thallium).

Toxicity

Thallium chloride is highly toxic. Acute toxic effects are those of thallium poisoning.

THALLIUM FLUORIDE

[7789-27-7]
Formula: TlF; MW 223.38
Synonym: thallous fluoride

Uses

The compound is used in preparing fluoro esters.

Physical Properties

Hard shiny crystals; orthorhombic structure; density 8.23 g/cm^3 at 4°C; melts at 327°C; begins to sublime at 300°C; vaporizes at 655°C; very soluble in water, 78.6 g/100mL at 15°C; decomposes in hot water; slightly soluble in alcohol.

Thermochemical Properties

$\Delta Hf°$ –18.5 kcal/mol

Preparation

Thallium fluoride is prepared by reacting thallium carbonate with hydrofluoric acid. Also, the compound can be made by reacting thallium metal with fluorine.

Analysis

Elemental composition: Tl 91.49%, F 8.51%. An appropriately diluted aqueous solution may be analyzed for thallium by AA or ICP methods (See Thallium) and for the F^- ion by the fluoride ion-specific electrode or by ion chromatography.

Toxicity

Highly toxic (See Thallium).

THALLIUM NITRATE

[10102-45-1]
Formula: $TlNO_3$; MW 266.39
Synonyms: thallous nitrate; thallium(I) nitrate.

Uses

The salt is an analytical reagent for measuring iodine in the presence of chlorine and bromine. Also, it is used in pyrotechnics and producing green fire for signaling at sea.

Physical Properties

White crystals; exists in three allotropic modifications: a rhombohedral gamma form that transforms to trigonal beta form at 75°C, the trigonal converting to a cubic alpha form at 145°C.

Density of the salt is 5.56 g/cm^3; melts at 206°C; vaporizes at 450°C with decomposition; moderately soluble in water, 9.55 g/100mL at 20°C; insoluble in alcohol.

Thermochemical Properties

$\Delta Hf°$	–58.3 kcal/mol
$\Delta Gf°$	–36.4 kcal/mol
S°	38.4 cal/deg mol
$C\rho$	23.8 cal/deg mol
ΔH_{fus}	2.29 kcal/mol

Preparation

Thallium nitrate is prepared by reacting thallium metal, thallous oxide, Tl_2O or thallous hydroxide, TlOH, with nitric acid followed by crystallization:

$$Tl_2O + 2HNO_3 \rightarrow 2TlNO_3 + H_2O$$

$$TlOH + HNO_3 \rightarrow TlNO_3 + H_2O$$

Analysis

Elemental composition: Tl 76.72%, N 5.26%, O 18.02%. An aqueous solution of the salt is analyzed for thallium metal by AA or ICP methods and nitrate ion by electrode, ion chromatography or colorimetric methods.

THALLIUM OXIDE

[1314-12-1]
Formula: Tl_2O; MW 424.707
Synonyms: thallous oxide; thallium (I) oxide

Uses

Thallium oxide is used in manufacturing high coefficient of refraction optical glass (thallium flint glass). Also, the oxide is used to make synthetic gems.

Physical Properties

Black powder; orthorhombic crystals; hygroscopic; density 9.52g/cm^3; melts at 596°C; vaporizes at about 1,080°C; soluble in water, alcohol and acids.

Thermochemical Properties

$\Delta Hf°$	–42.7 kcal/mol
$\Delta Gf°$	–35.2 kcal/mol
S°	30.0 cal/deg mol

Preparation

Thallium oxide can be made by heating Tl metal in air or oxygen. The brown-black thallic oxide, Tl_2O_3 , that may also form begins to lose oxygen at about 100°C converting to thallium oxide, Tl_2O.

Thallium oxide also can be prepared by thermal dissociation of thallium hydroxide, TlOH or thallium carbonate, Tl_2CO_3. Thallium oxide dissolves in water forming thallous hydroxide, TlOH. It reacts with carbon dioxide to form thallous carbonate, Tl_2CO_3.

Reactions

Thallium oxide slowly oxidizes to thallic oxide, Tl_2O_3 on exposure to air, gradually becoming insoluble in aqueous solution.

Analysis

Elemental composition: Tl 96.23%, O 3.77%. Thallium may be measured by various instrumental methods on an aqueous or acid solution of the metal oxide. Also, the compound can be identified by its physical and x-ray properties. Thallic oxide reverts to thallium oxide on heating above 100°C.

THORIUM

[7440-29-1]
Symbol Th; atomic number 90; atomic weight 232.04; an actinide series radioactive element; electron configuration $[Rn]6d^27s^2$; valence state +4; atomic radius 1.80 Å; ionic radius, Th^{4+} 1.05 Å for coordination number 8; standard electrode potential, E° for $Th^{4+} + 4e^- \leftrightarrow Th$ is –1.899V; all isotopes are radioactive; the only naturally-occurring isotope, Th-232, $t_{1/2}$ 1.4×10^{10} year; twenty-six isotopes are known in the mass range 212-237.

History, Occurrence, and Uses

The element was discovered by Berzelius in 1828. He named it thorium after Thor, the ancient Scandinavian god of war. An important application of thorium came in 1884 when Auer von Welsbach developed the incandescent gas light mantle using thorium oxide as the primary ingredient. The mantle emitted brilliant white light. With this discovery, the mantle industry saw a dramatic growth and a search for new thorium deposits, and thorium production increased sharply. Around the first quarter of the 20th century, electricity had almost replaced the gaslights causing a decline in thorium production. With development of atomic energy in the early 1940s and the use of thorium as nuclear fuel, thorium production has gone up tremendously.

Large thorium deposits have been found in many parts of the world. It occurs in minerals thorite, $ThSiO_4$, and thorianite, $ThO_2 \cdot UO_2$. Thorium also is found in mineral monazite which contains between 3 to 9% ThO_2. ThO_2 is the principal source of commercial thorium. Abundance of thorium in earth's crust is estimated at about 9.6 mg/kg. Thorium and uranium are believed to have contributed much of the internal heat of the earth due to their radioactive emanations since earth's formation.

The principal use of thorium is as a nuclear fuel. When bombarded with excess neutrons it converts to fissionable uranium-235. Another major application is the Welsbach incandescent mantle mentioned earlier. Such mantles are used as portable gaslights. Thorium alloyed with magnesium imparts high strength and creep resistance to magnesium at elevated temperatures. Such alloys are used in vehicles and aerospace equipment. Thorium oxide coated tungsten filaments are used in incandescent lamps, and rods are employed as electrodes in arc-melting. Other uses are in photoelectric cells; as a target in x-ray tubes; and as a reducing agent in metallurgy. Thorium oxide has several industrial applications (See Thorium Oxide).

Physical Properties

Grayish-white lustrous metal; soft when pure; quite ductile and malleable; can be shaped by cold or hot rolling, swaging or drawing; dimorphic, face-centered cubic crystals changing to body-centered cubic structure at 1,400°C; density 11.72 g/cm^3; melts at 1,750°C; vaporizes at 4,788°C; electrical resistivity 14 microhm-cm; Young's modulus 10.3×10^6 psi; shear modulus 4.1×10^6 psi; Poisson's ratio 0.27; soluble in hydrochloric and sulfuric acids, and aqua regia; slightly soluble in nitric acid; insoluble in water.

Thermochemical Properties

ΔHf° (cry)	0.0
ΔHf° (gas)	143.0 kcal/mol
ΔGf° (cry)	0.0
ΔGf° (gas)	133.26 kcal/mol
S° (cry)	12.76 cal/deg mol
S° (gas)	45.42 cal/deg mol
C_ρ (cry)	6.53 cal/deg mol
C_ρ (gas)	4.97 cal/deg mol
ΔH_{fus}	3.30 kcal/mol
ΔH_{vap}	140 kcal/mol
Thermal conductivity (at 27°C)	0.540 W/cmK
Coefficient of linear expansion	11.0×10^{-6}/°C

Production

Thorium is recovered mostly from monazite, which is a phosphate mineral of the light-weight rare earths. Monazite occurs as sand associated with silica and a few other minerals in smaller proportions.

The first step in the recovery process involves breaking down or opening up the ore. This usually is done by one of two methods: (1) digesting with hot concentrated sulfuric acid or (2) treatment with hot concentrated sodium hydroxide. In the acid digestion process, finely-ground monazite is treated with hot sulfuric acid. Thorium and rare earths dissolve in the acid. Phosphoric acid is released from monazite (a phosphate mineral) by reacting phosphates with sulfuric acid. Insoluble residues are removed by filtration. In the caustic digestion process, monazite, on heating with a concentrated solution of sodium hydroxide, breaks down to form soluble trisodium phosphate and an insoluble residue containing hydrated oxides of thorium and rare earths. Thus, in the caustic process, trisodium phosphate is recovered as a by-product. The hydrated oxides are dissolved in sulfuric acid.

Thorium sulfate, being less soluble than rare earth metals' sulfates, can be separated by fractional crystallization. Usually, solvent extraction methods are applied to obtain high purity thorium and for separation from rare earths. In many solvent extraction processes, an aqueous solution of tributyl phosphate is the extraction solvent of choice.

There are several processes for commercial thorium production from monazite sand. They are mostly modifications of the acid or caustic digestion process. Such processes involve converting monazite to salts of different anions by combination of various chemical treatments, recovery of the thorium salt by solvent extraction, fractional crystallization, or precipitation methods. Finally, metallic thorium is prepared by chemical reduction or electrolysis. Two such industrial processes are outlined briefly below.

Finely-ground monazite is treated with a 45% NaOH solution and heated at 138°C to open the ore. This converts thorium, uranium, and the rare earths to their water-insoluble oxides. The insoluble residues are filtered, dissolved in 37% HCl, and heated at 80°C. The oxides are converted into their soluble chlorides. The pH of the solution is adjusted to 5.8 with NaOH. Thorium and uranium are precipitated along with small quantities of rare earths. The precipitate is washed and dissolved in concentrated nitric acid. Thorium and uranium are separated from the rare earths by solvent extraction using an aqueous solution of tributyl phosphate. The two metals are separated from the organic phase by fractional crystallization or reduction.

In one acid digestion process, monazite sand is heated with 93% sulfuric acid at 210°C. The solution is diluted with water and filtered. Filtrate containing thorium and rare earths is treated with ammonia and pH is adjusted to 1.0. Thorium is precipitated as sulfate and phosphate along with a small fraction of rare earths. The precipitate is washed and dissolved in nitric acid. The solution is treated with sodium oxalate. Thorium and rare earths are precipitated from this nitric acid solution as oxalates. The oxalates are filtered, washed, and calcined to form oxides. The oxides are redissolved in nitric acid and the acid solution is extracted with aqueous tributyl phosphate. Thorium and cerium (IV) separate into the organic phase from which cerium (IV) is reduced to metallic cerium and removed by filtration. Thorium then is recovered from solution.

Thorium metal may be produced from its salts—usually the oxide or a halide—by several methods that include electrolysis and reduction with calcium. In the calcium reduction process, thorium oxide is heated in a closed vessel at 950°C. The product is cooled and leached with water and dilute acid and then washed and vacuum-dried to form a free-flowing powder.

Thorium metal also can be prepared by thermal reduction of its halides with calcium, magnesium, sodium, or potassium at elevated temperatures (950°C), first in an inert atmosphere and then in vacuum. Fluoride and chloride thorium salts are commonly employed. Berzelius first prepared thorium by heating tetrachloride, $ThCl_4$, with potassium. Magnesium and calcium are the most common reductant. These metals are added to thorium halides in excess to ensure complete reduction. Excess magnesium or calcium is removed by heating at elevated temperatures in vacuum. One such thermal reduction of halides produces thorium sponge, which can be converted into the massive metal by melting in an electron beam or arc furnace.

Thorium can be obtained from its halides by electrolysis. A fused salt bath of $NaCl–KCl–ThCl_4$ or $NaCl–KCl–KF–ThF_4$ or similar eutectic mixtures is employed in electrolysis. The electrolysis may be carried out in a graphite crucible, and thorium is deposited as a coarse powder on the electrode, which is made of molybdenum or other suitable material.

Reactions

Thorium combines with practically all nonmetallic elements except noble gases, forming binary compounds. The most stable oxidation state is +4. Heating the metal in air or oxygen forms the oxide, ThO_2. Heating the metal in hydrogen at 600°C yields the dihydride ThH_2. Also, higher halides of thorium are known. They are produced by heating the dihydride in hydrogen at 250°C. Thorium hydrides are pyrophoric.

Thorium combines with nitrogen at elevated temperatures to form nitrides ThN and Th_2N_3. Reaction with carbon at elevated temperatures forms the carbides ThC and ThC_2.

Thorium reacts with all halogens forming tetrahalides.

Thorium also forms inter-metallic compounds with iron, copper, aluminum, selenium, nickel, cobalt, manganese, bismuth, and many other metals at elevated temperatures.

Nuclear Reactions

Thorium undergoes radioactive disintegration through several decay steps ending by forming stable lead-208. The decay series involves six alpha and four beta emission steps. Radon-220 (thoron), an alpha emitter, is one of the disintegration products in the series.

Neutron bombardment converts thorium-232 to its isotope of mass 233. The thorium-233 formed undergoes two successive beta decays to form uranium-233, a fissionable material, similar to uranium-235 and plutonium-239.

Toxicity

All thorium isotopes are radioactive. Also all its intermediate decay products including radon-220 are radioactive and present radiation hazard. Exposure can cause cancer.

THORIUM DIOXIDE

[1314-20-1]
Formula: ThO_2; MW 264.04
Synonyms: thorium oxide; thorium anhydride; thoria

Occurrence and Uses

Thorium dioxide occurs in nature as mineral thorianite. Thorium dioxide is used in gaslight mantles, in tungsten filaments for incandescent lamps, to improve efficiency of electronic tubes, and in thoriated tungsten rods as electrodes in arc melting. An important application of this compound is hardening nickel to impart high strength and corrosion resistance at high temperatures. It also is used in making nonsilicate optical glass of high refractive index and low dispersion, and in special refractory crucibles. Thorium dioxide is a catalyst in many chemical reactions including petroleum cracking, conversion of ammonia to nitric acid, and preparation of sulfuric acid.

Physical Properties

White cubic crystals; refractive index 2.200 (thorianite); density 10.0 g/cm^3; hardness 6.5 Mohs; melts at 3,390°C; vaporizes at 4,400°C; insoluble in water or alkalis; soluble in acids with difficulties.

Thermochemical Properties

$\Delta Hf°$	–293.1 kcal/mol
$\Delta Gf°$	–279.4 kcal/mol
S°	15.6 cal/deg mol
C_ρ	14.8 cal/deg mol

Preparation

Thorium dioxide is obtained as an intermediate in the production of thorium metal from monazite sand (See Thorium).

The compound also can be prepared by many other methods including thermal decomposition of thorium oxalate, hydroxide, carbonate, or nitrate. Heating thorium metal in oxygen or air, and hydrolysis of thorium halides also yield thorium dioxide.

Analysis

Elemental composition: Th 87.88%, O 12.12%. The oxide may be identified by x-ray methods. Thorium dioxide may be analyzed by AA or ICP after digestion in aqua regia and appropriate dilution in water.

THORIUM NITRATE

[13823-29-5]
Formula: $Th(NO_3)_4$; MW 480.06; forms a stable tetrahydrate, $Th(NO_3)_4 \cdot 4H_2O$

[33088-16-3], MW 552.12, the commercial form of the nitrate; also exists as hexa- and dodecahydrates, $Th(NO_3)_4 \cdot 6H_2O$ and $Th(NO_3)_4 \cdot 12H_2O$, respectively.

Uses

Thorium nitrate is a reagent for measuring fluorine and for making thoriated tungsten filaments. Thorium nitrate containing 1% cerium nitrate is the impregnating liquid in making incandescent gas mantles.

Physical Properties

The tetrahydrate is a white crystalline mass; hydgroscopic; decomposes at about 500°C; very soluble in water; soluble in ethanol.

Preparation

Thorium nitrate is obtained as an intermediate in making thorium metal from monazite sand. Also, the salt is prepared by heating thorium metal or its oxide or hydroxide with nitric acid, followed by evaporation of the solution and crystallization.

Analysis

Elemental composition (in anhydrous salt): Th 48.33%, N 11.67%, O 40.00%. The aqueous solution may be analyzed for thorium (See Thorium) and for nitrate ion by ion chromatography, nitrate ion-specific electrode, and colorimetric methods. The water of crystallization can be determined by DTA, TGA, and other gravimetric methods.

Toxicity

Thorium nitrate is highly toxic by ingestion and other routes of exposure. The compound also is a radiation hazard.

THULIUM

[7440-30-4]

Symbol Tm; atomic number 69; atomic weight 168.93; a lanthanide series element; a rare earth metal; electron configuration [Xe]$4f^{13}6s^2$; valence +2, +3; atomic radius 1.73 Å; ionic radius, Tm^{3+} 1.09 Å for coordination number 7; one stable, natural isotope Tm-169 (100%); thirty radioisotopes in the mass range 146-168, 170-176; $t_{1/2}$ 1.92 years.

History, Occurrence, and Uses

Thulium was discovered in 1879 by Cleve and named after Thule, the earliest name for Scandinavia. Its oxide thulia was isolated by James in 1911. Thulium is one of the least abundant lanthanide elements and is found in very small amounts with other rare earths. It occurs in the yttrium-rich minerals: xenotime, euxenite, samarskite, gadolinite, loparite, fergusonite, and yttroparisite. Also, it occurs in trace quantities in minerals monazite and apatite. Abundance of thulium in earth's crust is estimated to be 0.52 mg/kg. The metal has very few commercial applications because of its high cost and low relative abundance. Thulium metal pellets containing natural isotope 169 and radioactive Tm-170 are used in portable x-ray equipment as medical and dental diagnostic tools. These pellets also are used to detect flaws in small, inaccessible parts of mechanical and electrical devices. Radioactive thulium-171 is a beta emitter with a half-life of two years and potentially is useful as an energy source. Natural thulium is used in ceramic magnetic materials (ferrites) for microwave devices.

Physical Properties

Silvery-white lustrous metal; hexagonal close-packed structure; density 9.321 g/cm^3 at 25°; melts at 1,545°C; vaporizes at 1,947°C; electrical resistivity 79 microhm-cm; compressibility 2.6x10^6 cm^2/kg; effective magnetic moment 7.62 Bohr magneton; insoluble in water; dissolves in concentrated acids.

Thermochemical Properties

$\Delta Hf°$ (cry)	0.0
$\Delta Hf°$ (gas)	55.5 kcal/mol
$\Delta Gf°$ (cry)	0.0
$\Delta Gf°$ (gas)	47.2 kcal/mol
S° (cry)	17.7 cal/deg mol
S° (gas)	45.4 cal/deg mol
C_ρ (cry)	6.46 cal/deg mol
C_ρ (gas)	4.97 cal/deg mol
ΔH_{fus}	4.02 kcal/mol
Thermal conductivity (at 27°C)	0.169 W/cmK
Coefficient of linear expansion	13.3x10^{-6}/°C

Production

Thulium is recovered from xenotime, gadolinite, euxenite, samarskite, and other minerals. The first step of recovery involves opening the ores. If xenotime, (Y)PO_4 is the starting material, the mineral is heated with an excess of sulfuric acid (95%). The product mixture is treated with cold water to separate water-soluble sulfates from unreacted mineral, silica, and other insoluble residues. The solution is filtered and yttrium and the individual rare earths are separated from this solution by ion exchange. The tripositive lanthanide metal ions and yttrium are absorbed on an appropriate cation exchange column and eluted with ammonium ethylenediamine tetraacetic acid (EDTA) at pH 8.4. The cation-exchange resin is pretreated with an equimolar mixture (1 M) of copper sulfate-sulfuric acid. The various eluate fractions are collected, and are treated with oxalic acid. The metals are precipitated as oxalates. Precipitate from the thulium fraction is calcined at 800°C to convert oxalate into oxide, Tm_2O_3.

If thulium is to be recovered from gadolinite, $Be_2Fe(Y)_2Si_2O_{10}$, pulverized mineral is opened by digesting with hot nitric acid-hydrochloric acid mixture.

Insoluble silica residues are removed by filtration. The solution now contains beryllium, iron, yttrium, and the rare earths. The solution is treated with oxalic acid to precipitate yttrium and the rare earths. The precipitate is calcined at 800°C to form rare earth oxides. The oxide mixture is dissolved in an acid from which yttrium and the rare earths are separated by the ion-exchange as above. Caustic fusion may be carried out instead of acid digestion to open the ore. Under this condition silica converts to sodium silicate and is leached with water. The insoluble residue containing rare earths and yttrium is dissolved in an acid. The acid solution is fed to an ion exchange system for separating thulium from other rare earths.

Thulium metal is prepared from its oxide by reduction with lanthanum at its melting point of 1,545°C. Thulium is separated from lanthanum by sublimation in vacuum. The metal vapor is condensed into crystalline metal in purified form free from lanthanum.

Reactions

The most stable oxidation state of thulium is +3. Only the tripositive Tm^{3+} ion is encountered in aqueous media. The metal also forms compounds in +2 and +4 valence states, but there is no evidence of Tm^{2+} and Tm^{4+} existing in aqueous phase. Thulium is relatively stable in air at ambient temperature. However, it combines with oxygen on heating forming its sesquioxide, Tm_2O_3.

Reactions with halogens are slow at ordinary temperatures, but vigorous above 200°C, forming trihalides.

Thulium reacts with concentrated mineral acids forming corresponding salts and liberating hydrogen.

The metal forms binary compounds when heated at elevated temperatures. Such binary compounds of thulium are known with many nonmetallic and metallic elements having varying stoichiometric compositions, such as TmN, TmS, TmC_2, Tm_2C_3, TmH_2, TmH_3, $TmSi_2$, $TmGe_3$, TmB_4, TmB_6, and TmB_{12}.

Analysis

Thulium may be determined by atomic absorption and emission spectrophotometry. The metal and its compounds are dissolved in acids and diluted appropriately before analysis. Thulium also can be measured by neutron activation analysis.

TIN

[7440-31-5]

Symbol Sn; atomic number 50; atomic weight 118.69; a Group IV A (Group 14) metallic element of carbon family; electron configuration [Kr] $4d^{10}5s^25p^2$; valence states +2, +4; atomic radius 1.41Å; electronegativity 1.7; standard electrode potential, E° for $Sn^{2+} + 2e^- \leftrightarrow Sn$ is –0.1375 V; ten naturally-occurring stable isotopes: Sn-112 (0.97%), Sn-114 (0.65%), Sn-115 (0.34%), Sn-116 (14.54%), Sn-117 (7.68%), Sn-118 (24.22%), Sn-119 (8.59%), Sn-120 (32.59%), Sn-122 (4.63%), Sn-124 (5.79%); twenty-five radioisotopes in the mass range 100-111, 113, 121, 123, 125-134; the longest-lived isotope, Sn-126, $t_{1/2}$ 1.0×10^5 years.

History, Occurrence and Uses

Tin is known from ancient times. Its alloy, bronze, containing 10 to 15% tin has been in use in weapons and tools for millennia.

The most important mineral of tin is cassiterite, SnO_2. It occurs in the form of alluvial sand. Also, it is found embedded in granite rocks. Other tin-bearing minerals are stannite and tealite. Abundance of tin in the earth's crust is estimated to be 2.3 mg/kg. Tin is used for plating steel to make "tin cans" for preserving food. Also, tin is coated over other metals to prevent corrosion. An important application of tin is to produce float glass, made by floating molten glass on molten tin which is used for windows. A number of tin alloys have wide industrial applications and include bronze, solder, Babbit metal, White metal, type metal, fusible metal, and phosphor bronze. A tin-niobium alloy that is superconducting at low temperatures is used in constructing super magnets. Tin also is in wrapping foil and collapsible tube.

Physical Properties

Silvery-white metal at ordinary temperature; slowly changes to gray below 13.2°C; soft, malleable, and somewhat ductile; Brinell hardness 2.9.

Tin has two allotropic forms: (1) white tin, the beta form, and (2) gray tin, the alpha form. The white tin (beta form) has a tetragonal structure. When cooled below 13.2°C, its color slowly changes from white to gray, the beta allotrope converting to alpha (gray tin). The presence of small amounts of antimony or bismuth prevents this transformation from white to gray tin. Other impurities such as zinc or aluminum promote change from white to gray tin.

Some other physical properties are: density 7.28 g/cm^3 (white), 5.75 g/cm^3 (gray) and 6.97 g/cm^3 (liquid at the melting point); melts at 231.9°C; vaporizes at 2,602°C; electrical resistivity 11.0 and 15.5 microhm-cm at 0 and 100°C, respectively; viscosity 1.91 and 1.38 centipoise at 240 and 400°C, respectively; surface tension 5.26 and 5.18 dynes/cm at 300 and 400°C, respectively; modulus of elasticity $6 - 6.5\times10^6$ cgs psi; magnetic suspectibility 0.027×10^{-6} cgs units; thermal neutron absorption cross section 0.625 barns; insoluble in water; soluble in HCl, H_2SO_4, aqua regia, and alkalies; slightly soluble in dilute nitric acid

Thermochemical Properties

$\Delta H_f°$(cry)(white)	0.0
$\Delta H_f°$(cry)(gray)	–0.50kcal/mol
$\Delta H_f°$(gas)	72.2kcal/mol
$\Delta G_f°$ (cry)(white)	0.0
$\Delta G_f°$ (cry)(gray)	0.03 kcal/mol
$\Delta G_f°$ (gas)	63.9 kcal/mol
S°(cry)(white)	12.32 cal/deg mol

S°(cry)(gray)	10.55 cal/deg mol
S°(gas)	40.24 cal/deg mol
C_ρ(cry)(white)	6.45 cal/deg mol
C_ρ (cry)(gray)	6.16 cal/deg mol
C_ρ (gas)	5.08 cal/deg mol
ΔH_{fus}	1.68kcal/mol
Thermal conductivity(at 27°C)	0.666W/cmK
Coefficient of linear expansion (at 25°C)	$22.0 x 10^{-6}$/°C

Production

Tin is produced commercially from mineral cassiterite, SnO_2. The mineral is mined from alluvial sand deposits by different techniques, such as various dredging (usually applied to low-grade deposits), gravel-pump mining (on level ground), and open-pit mining. The ore is broken up mechanically by blasting and drilling. It then is crushed and ground to produce finely divided material that can be separated by gravity concentration and froth flotation. Tin concentrates so obtained require removal of sulfide before smelting. This is done by roasting concentrates at high temperatures which removes both sulfur and arsenic. Lead sulfide is converted to lead sulfate but all other associated metal sulfides, such as those of iron, copper, zinc, and bismuth, are converted to oxides

Tin is produced from oxide by heating at high temperatures with carbon. Small amounts of limestone and sand are added to coal for this reduction and to promote removal of impurities. Primary smelting is carried out in a reverbaratory furnace at a temperature between 1,200 to 1,300°C. Electric arc furnaces also are used. The molten tin collected at the bottom is cast into slabs. The slags are resmelted at a higher temperature, up to 1,480°, in the same type of furnaces to recover more tin that is combined as silicates.

Tin obtained above contains small amounts of impurities. It is purified by resmelting in a small reverberatory furnace at a temperature just above the melting point of tin. The molten tin is drawn out, separating iron, copper, arsenic, antimony, and other metals. Purified tin is further refined by boiling or polling processes to remove traces of impurity metals, such as lead and bismuth.

Reactions

At ordinary temperatures tin is stable in air. It actually forms a very thin protective oxide film. In powder form, and especially in the presence of moisture, it oxidizes. When heated with oxygen it forms tin(IV) oxide, SnO_2.Tin reacts with all halogens forming their halides. Reaction with fluorine is slow at ordinary temperatures; however, chlorine, bromine and iodine readily react with the metal

Tin is attacked by concentrated acids. With dilute acids the reaction may be slow or very slow. The metal readily reacts with hot concentrated hydrochloric acid and aqua regia but slowly with cold dilute hydrochloric acid. The reaction also is slow with hot dilute sulfuric acid, which dissolves the metal, particularly in the presence of an oxidizing agent. The reaction with nitric acid is generally slow. Hot concentrated acid converts the metal to an insoluble hydrated tin(IV) oxide. The reaction is rapid with moist sulfur dioxide or sulfurous acid, chlorosulfonic, and pyrosulfuric acids. Organic acids such as, acetic, oxalic, and citric acids react slowly with the metal, particularly in the presence of air or an oxidizing agent.

Strong alkaline solutions of caustic soda or caustic potash dissolve tin forming the stannate, Na_2SnO_3, or K_2SnO_3. The metal is stable in dilute solutions of ammonia or sodium carbonate.

Tin dissolves in solutions of oxidizing salts such as potassium chlorate or potassium persulfate. The metal does not react with neutral salts in aqueous solutions. In air, tin reacts slowly with neutral salts.

The metal does not combine directly with hydrogen, nitrogen or ammonia gas.

Analysis

Tin can be measured readily at trace concentrations in aqueous solutions by flame or furnace atomic absorption spectrophotometry. For flame AA measurement, air-acetylene flame is suitable. The metal can be identified accurately at 224.6 nm. Tin also can be measured by other instrumental techniques such as ICP-AES, ICP/MS and neutron activation analysis.

TIN(II) CHLORIDE

[7772-99-8]
Formula: $SnCl_2$; MW 189.62; forms a dihydrate $SnCl_2 \cdot 2H_2O$ [10025-69-1], MW 225.65
Synonyms: stannous chloride; tin dichloride; tin protochloride

Uses

Tin (II) chloride is a strong reducing agent and is used in many industrial processes, such as manufacturing dyes, phosphors, and polymers. The compound is a major ingredient in acid tin plating baths. Other uses are a mordant in dyeing; an additive to lubricating oil to prevent sludging; a stablizier for perfume in soaps; in removing ink stains; a sensitizing agent for glass, paper, and plastics; and a soldering flux. Tin(II) chloride is used for preparing a number of tin(II) salts. It is a catalyst in many organic reactions. It is a common laboratory reagent.

Physical Properties

White orthogonal crystal; density 3.90 g/cm³; melts at 247°C; vaporizes at 623°C; vapor pressure 1 torr at 316°C, 5 torr at 366°C and 20 torr at 420°C; soluble in water, ethanol, acetone and ether; insoluble in xylene and mineral spirits.

The dihydrate, $SnCl_2 \cdot 2H_2O$, is a white monoclinic crystalline substance; density 2.71 g/cm^3; absorbs oxygen from air forming an oxychloride; melts at 37°C on rapid heating; decomposes on strong heating; very soluble in water; forms an insoluble basic salt with excess water; very soluble in hydrochloric acid; soluble in caustic soda solution, ethanol and ethyl acetate.

Thermochemical Properties

$\Delta H_f°$	–77.7 kcal/mol
ΔH_{fus}	3.06 kcal/mol
ΔH_{vap}	20.7 kcal/mol

Preparation

Tin(II) chloride is prepared by dissolving tin in hydrochloric acid followed by evaporation of the solution and crystallization.

Analysis

Elemental composition: Sn 62.60%, Cl 37.40%. An aqueous solution is analyzed to measure tin content. Chloride ion can be measured by ion chromatography or by chloride ion-selective electrode. Also, as a strong reducing agent, concentration of Sn^{2+} ion in an aqueous solution can be measured by redox titration.

TIN(IV) CHLORIDE

[7646-78-8]

Formula: $SnCl_4$; MW 260.52; forms a pentahydrate, $SnCl_4 \cdot 5H_2O$ [10026-06-9], MW 350.60

Synonyms: stanic chloride; tin tetrachloride; tin perchloride

Uses

Tin(IV) chloride is a mordant for dying fabrics; a stabilizer for perfume in soap; used in weighting silk; in ceramic coatings; in manufacturing blue print papers; and to produce fuchsin. Also, tin(IV) chloride is used in preparing many organotin compounds.

Physical Properties

Colorless fuming liquid; corrosive; density 2.234 g/mL; freezes at –33°C; boils at 114.15°C; critical temperature 318.75°C; critical pressure 37.98 atm; critical volume 351 cm^3/mol; soluble in cold water, evolving heat; decomposed by hot water; soluble in alcohol, benzene, toluene, chloroform, acetone and kerosene

The pentahydrate is a yellowish-white crystalline solid or small, fused lumps; faint odor of HCl; density 2.04 g/cm^3; decmposes at 56°C; very soluble in water; soluble in ethanol

Thermochemical Properties

$\Delta H_f°$ (liq)	–122.2 kcal/mol
$\Delta H_f°$ (gas)	–112.7 kcal/mol
$\Delta G_f°$ (liq)	–105.2 kcal/mol
$\Delta G_f°$ (gas)	–103.3 kcal/mol
S°(liq)	61.8 cal/deg mol
S°(gas)	87.4 cal/deg mol
C_ρ (liq)	39.5 cal/deg mol
C_ρ (gas)	23.5 cal/deg mol
ΔH_{fus}	2.20 kcal/mol
ΔH_{vap}	8.34 kcal/mol

Preparation

Tin(IV) chloride is prepared by reacting tin or tin(II) chloride with chlorine:

$$Sn + 2Cl_2 \rightarrow SnCl_4$$

$$SnCl_2 + Cl_2 \rightarrow SnCl_4$$

Analysis

Elemental composition: Sn 45.56%, Cl 54.44%. The compound may be identified from its physical properties. An aqueous solution may be analyzed by AA, ICP and other techniques to determine tin content. The compound may be dissolved in toluene or carbon tetrachloride, diluted sufficiently, and analyzed by GC/MS.

TIN(II) OXIDE

[21651-19-4]
Formula: SnO; MW 134.71
Synonyms: stannous oxide; tin monoxide; tin protoxide

Uses

Tin(II) oxide is a reducing agent; and is used in preparing other tin(II) salts. Also, it is used to make soft abrasive putty powder.

Physical Properties

Bluish-black powder; tetragonal crystals; density 6.45 g/cm^3; decomposes at 1,080°C; insoluble in water; dissolves in acids to form Sn^{2+} and in base to form stannite ion, $Sn(OH)^{3-}$.

Thermochemical Properties

$\Delta H_f°$ (cry)	–67.1 kcal/mol
$\Delta H_f°$ (gas)	3.61 kcal/mol

$\Delta G_f°$ (cry)	–60.2 kcal/mol
$\Delta G_f°$ (gas)	–2.01 kcal/mol
S°(cry)	13.7 cal/deg mol
S°(gas)	55.5 cal/deg mol
C_ρ (cry)	10.6 cal/deg mol
C_ρ (gas)	7.55 cal/deg mol

Preparation

Tin(II) oxide is prepared by heating tin(II) hydroxide. The latter is obtained as a white precipitate by reacting Sn^{2+} ions with hydroxide ions:

$$Sn^{2+}(aq) + 2OH^{-}(aq) \rightarrow Sn(OH)_2\ (s)$$

$$Sn(OH)_2 \xrightarrow{\Delta} SnO(s) + H_2O(g)$$

Analysis

Elemental composition: Sn 88.12%, O 11.88%. Tin oxide is dissolved in nitric acid, diluted, and analyzed for tin (See Tin).

TIN(IV) OXIDE

[18282-10-5]
Formula: SnO_2; MW 150.71
Synonyms: stannic oxide; tin dioxide; tin peroxide; white tin oxide; stannic anhydride; flowers of tin

Occurrence and Uses

Tin(IV) oxide occurs in nature as mineral cassiterite. It is used to make specialty glasses, in manufacturing enamels and pottery, for polishing glass marbles, metals and decorative stones, as a mordant in dyeing and printing textiles, in perfumes, and nail polishes.

Physical Properties

White or grayish powder; tetragonal crystals; density 6.85 g/cm^3; refractive index 2.006; Mohs hardness 6.5; melts at 1,630°C; insoluble in water; soluble in hot concentrated alkalies

Thermochemical Properties

$\Delta H_f°$	–138.0 kcal/mol
$\Delta G_f°$	–123.3 kcal/mol
S°	11.7 cal/deg mol
C_ρ	12.6 cal/deg mol

Production

Tin(IV) oxide is mined from naturally-occurring cassiterite. Various techniques are employed in mining (See Tin). The ore is crushed, ground, and separated by gravity concentration and froth flotation. Sulfide impurities are removed by roasting the ore concentrates at high temperatures.

Tin(IV) oxide is prepared by precipitation from tin(IV) chloride solution by adding ammonium hydroxide. The overall reaction is:

$$SnCl_4 + 4NH_4OH \rightarrow SnO_2 + 4NH_4Cl + 2H_2O$$

The precipitate is washed with hot water.

Analysis

Elemental composition: Sn 78.77%, O 21.23%. Tin(IV) oxide can be identified by physical properties and x-ray diffraction. Tin content may be determined by various instrumental techniques in an acid solution of the oxide (See Tin). The compound is solubilized by digestion with nitric acid or aqua regia and diluted appropriately.

TIN(IV) SULFATE

[7488-55-77]
Formula: $SnSO_4$; MW 214.77
Synonyms: stannous sulfate; tin sulfate

Uses

Tin(II) sulfate is used for electroplating automobile pistons and in other tin plating. Also, the compound is a mordant for dyeing; and is used in preparing tin(II) salts.

Physical Properties

Heavy white crystals; orthorhombic structure; density 4.15 g/cm^3; decomposes at 378°C to SnO_2 and SO_2; soluble in water, reacting to form a basic sulfate that precipitates; soluble in dilute sulfuric acid.

Preparation

Tin(II) sulfate is prepared by reacting tin(II) oxide with sulfuric acid:

$$SnO + H_2SO_4 \rightarrow SnSO_4 + H_2O$$

Analysis

Elemental composition: Sn 55.27%, S 14.93%, O 29.80%. The compound is dissolved in sulfuric acid, diluted, and analyzed for tin (See Tin). The compound is determined gravimetrically by decomposing at 378°C. The SO_2 gas produced is analyzed by GC/MS or by colorimetry (See Sulfur Dioxide) and the residue SnO_2 is analysed by gravimetry:

$$SnSO_4 \xrightarrow{\Delta} SnO_2 + SO_2$$

TITANIUM

[7440-32-6]
Symbol Ti; atomic number 22; atomic weight 47.867; a Group IVB (Group 4) transition metal; electron configuration [Ar]$3d^24s^2$; valence +2, +3, +4; atomic radius 1.47Å; ionic radius, Ti^{3+} 0.67 Å and Ti^{4+} 0.61Å, respectively, corresponding to CN 6; standard electrode potential, E° for $Ti^{2+} + 2e^- \leftrightarrow Ti$ is –1.63 V and $Ti^{3+} + 3e^- \leftrightarrow Ti$ is –1.37 V; five naturally-occurring stable isotopes: Ti-46 (8.25%), Ti-47 (7.44%), Ti-48 (73.72%), Ti-49 (5.41%, Ti-50 (5.18%); fifteen artificial radioisotopes in the mass range 39-45, 51-58, the longest-lived isotope, Ti-44, $t_{1/2}$ 67 years.

History, Occurrence and Uses

Titanium was discovered in 1790 by English chemist William Gregor. Five years later in 1795, Klaproth confirmed Gregor's findings from his independent investigation and named the element titanium after the Latin name *Titans*, the mythical first sons of the Earth. The metal was prepared in impure form first by Nilson and Pettersson in 1887. Hunter, in 1910, prepared the metal in pure form by reducing titanium tetrachloride with sodium.

Titanium occurs in nature in the minerals rutile(TiO_2), ilmenite ($FeTiO_3$), geikielite, ($MgTiO_3$) perovskite ($CaTiO_3$) and titanite or sphene ($CaTiSiO_4(O,OH,F)$). It also is found in many iron ores. Abundance of titanium in the earth's crust is 0.565%. Titanium has been detected in moon rocks and meteorites. Titanium oxide has been detected in the spectra of M-type stars and interstellar space.

Titanium is found in plants, animals, eggs, and milk.

Many titanium alloys have wide industrial applications. Titanium forms alloys with a number of metals including iron, aluminum, manganese, and molybdenum. Its alloys are of high tensile strength, lightweight, and can withstand extreme temperatures. They are used in aircraft and missiles. The metal also has high resistance to sea water corrosion and is used to protect parts of the ships exposed to salt water. Also, titanium is used to combine with and remove traces of oxygen and nitrogen from incandescent lamps. Titanium compounds, notably the dioxide and the tetrachloride, have many uses (See Titanium Dioxide and Titanium Tetrachloride.)

Physical Properties

White lustrous metal; ductile when free of oxygen; low density high strength metal.

Titanium has two allotropic modifications: (1) alpha form and (2) beta modification. The alpha form has a close-packed hexagonal crystal structure; density 4.54 g/cm^3 at 20°C and stable up to 882°C. It converts very slowly to a body-centered cubic beta form at 882°C. The density of the beta form is 4.40 g/cm^3 at 900°C (estimated). The other physical properties are as follows:

The metal melts at 1,610 ±10°C; vaporizes at 3,287°C; electrical resitivity 42 microhm-cm; modulus of elasticity 15.5x10^6 psi at 25°C; tensile strength, ultimate 34,000 psi (at 25°C); tensile strength yield 20,000 psi (at 25°C); Vickers hardness 80-100; surface tension at the melting point 1427dynes/cm^3; superconductivity below 1.73°K; thermal neutron absorption cross section 5.8 barns; insoluble in water; soluble in dilute acids.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	112.3 kcal/mol
$\Delta G_f°$(cry)	0.0
$\Delta G_f°$(gas)	101.6 kcal/mol
S°(cry)	7.32 cal/deg mol
S°(gas)	43.1 cal/deg mol
C_ρ (cry)	5.98 cal/deg mol
C_ρ (gas)	5.84 cal/deg mol
ΔH_{fus}	3.38 kcal/mol
Thermal conductivity(at 27°C)	0.219 W/cm K
Coefficient of linear expansion (at 25°C)	8.6x10^{-6}/ °C

Production

The production of titanium always encounters difficulties because of a tendency to react with oxygen, nitrogen and moisture at elevated temperatures. Most high purity elemental titanium can be produced by the Kroll process from titanium tetrachloride. The tetrachloride is reduced with magnesium in a mild steel vessel at about 800°C under an inert atmosphere of helium or argon. The net reaction is as follows:

$$TiCl_4 + 2Mg \rightarrow Ti + 2\ MgCl_2$$

The reaction is highly exothermic providing heat needed to maintain high temperature required for reaction. The Kroll process is applied commercially to produce elemental titanium.

Sodium metal can be used instead of magnesium in thermally reducing titanium tetrachloride.

Titanium metal also can be produced by electrolytic methods. In electrolysis, fused mixtures of titanium tetrachloride or lower chlorides with alkaline earth metal chlorides are electrolyzed to produce metal. Also, pure titanium can be prepared from electrolysis of titanium dioxide in a fused bath of calcium-, magnesium- or alkali metal fluorides. Other alkali or alkaline metal salts can be substituted for halides in these fused baths. Other titanium compouds that have been employed successfully in electrolytic titanium production include sodium fluotitanate and potassium fluotitanate.

Very highly pure titanium metal can be prepared in small amounts by decomposition of pure titanium tetraiodide, (TiI_4) vapor on a hot wire under low pressure (Van Arkel–de Boer method).

Reactions

Titanium metal is very highly resistant to corrosion. It is unaffected by atmospheric air, moisture and sea water, allowing many of its industrial applications. The metal burns in air at about 1,200°C incandescently forming titanium dioxide TiO_2. The metal also burns on contact with liquid oxygen.

Titanium forms four oxides, all of which have been well described. It forms a weakly basic monoxide, TiO; a basic dititanium trioxide, Ti_2O_3; the amphoteric dioxide, TiO_2; and the acidic trioxide, TiO_3.

Titanium combines with nitrogen at about 800°C forming the nitride and producing heat and light. It is one of the few elements that burns in nitrogen.

Titanium reacts with all halogens at high temperatures. It reacts with fluorine at 150°C forming titanium tetrafluoride, TiF_4. Reaction with chlorine occurs at 300°C giving tetrachloride $TiCl_4$. Bromine and iodine combine with the metal at 360°C forming their tetrahalides.

Water does not react with Ti metal at ambient temperatures, but tianium reacts with steam at 700°C forming the oxide and hydrogen:

$$Ti + 2H_2O \rightarrow TiO_2 + 2H_2$$

Titanium is soluble in hot concentrated sulfuric acid, forming sulfate. It also reacts with hydrofluoric acid forming the fluoride.

Nitric acid at ordinary temperatures does not react with Ti metal, but hot concentrated nitric acid oxidizes titanium to titanium dioxide.

The metal is stable with alkalies.

Titanium combines with several metals, such as, iron, copper, aluminum, chromium, cobalt, nickel, lead and tin at elevated temperatures forming alloys.

Analysis

Titanium can be meaured at trace concentations by flame-AA using a nitrous oxide-acetylene flame. The measurement can be done at 365.3 nm. ICP-AES and ICP/MS techniques also are applicable. The metal or its compounds must be dissolved by digestion with HF and HCl and the solution diluted and analyzed instrumentally.

TITANIUM DIOXIDE

[13463-67-7]
Formula: TiO_2; MW 79.866
Synonyms: titanic oxide; titanic acid anhydride; titanium anhydride; titania; titanium white

Uses

Titanium dioxide is an extreme white and bright compound with high index of refraction. In paints it is a white pigment and an opacifying agent.It is in house paints, water paints, lacquers, enamels, paper filling and coating, rubber, plastics, printing ink, synthetic fabrics, floor coverings, and shoe whiteners. Also, it is used in colorants for ceramics and coatings for welding rods. A rutile form of the dioxide is used in synthetic gem stones.

Physical Properties

The naturally occurring dioxide exists in three crystal forms: anatase, rutile and brookite. While rutile, the most common form, has an octahedral structure. Anatase and brookite have very distorted octahedra of oxygen atoms surrounding each titanium atom. In such distorted octahedral structures, two oxygen atoms are relatively closer to titanium than the other four oxygen atoms. Anatase is more stable than the rutile form by about 8 to 12 kJ/mol (Cotton, F.A., Wilkinson, G., Murillo, C.A and M Bochmann. 1999. *Advanced Inorganic Chemistry*, 6th ed, p. 697, New York: John Wiley & Sons) Other physical properties are: density 4.23g/cm^3; Mohs hardness 5.8 g/cm^3 (anatase and brookite) and 6.2 g/cm^3 (rutile); index of refraction 2.488 (anatase), 2.583 (brookite) and 2.609 (rutile); melts at 1,843°C; insoluble in water and dilute acids; soluble in concentrated acids.

Thermochemical Properties

$\Delta H_f°$	–225.6 kcal/mol
$\Delta G_f°$	–212.4 kcal/mol
S°	12.1 cal/deg mol
C_ρ	13.1 cal/deg mol

Production

Titanium dioxide is mined from natural deposits. It also is produced from other titanium minerals or prepared in the laboratory. Pigment-grade dioxide is produced from the minerals, rutile and ilmenite. Rutile is converted to pigment grade rutile by chlorination to give titanium tetrachloride, $TiCl_4$. Anhydrous tetrachloride is converted back to purified rutile form by vapor phase oxidation.

Anatase form is obtained by hydrolytic precipitation of titanium(IV) sulfate on heating. The mineral ilmenite is treated with concentrated sulfuric acid. Heating the sulfate solution precipitates hydrous titanium oxide. The precipitate is calcined to expel all water.

Titanium dioxide also can be prepared by heating Ti metal in air or oxygen at elevated temperatures.

Analysis

Elemental composition: Ti 59.95%, O 40.05%. The oxide may be identified by its physical properties and by x-ray methods. Titanium content may be measured by AA or ICP. The compound is digested in nitric acid or aqua regia, solubilized, and diluted sufficiently for metal analysis.

TITANIUM HYDRIDE

[7704-98-5]
Formula: TiH_2; MW 49.883

Uses

Titanium dihydride is an additive in powder metallurgy. Other uses are producing foamed metals, making solder for metal-glass composites; a getter for oxygen and nitrogen in electronic tubes; a source of pure hydrogen; and a reducing agent.

Physical Properties

Grayish-black metallic powder; stable in air; density 3.75 g/cm^3; decomposes at 450°C with evolution of hydrogen; insoluble in water

Production

Titanium hydride is prepared by heating titanium dioxide with calcium hydride at 600°C in the presence of hydrogen.

Also, the hydride may be prepared by heating tianium metal with hydrogen at elevated temperatures.

Analysis

Elemental composition: Ti 95.95%, H 4.04%. A measured amount of hydride is decomposed at about 450°C and the volume of liberated hydrogen is measured. The hydride is digested cautiously in aqua regia, diluted and analyzed for titanium.

Hazard

Violent reaction can occur in contact with a strong oxidizing agent.

TITANIUM TETRACHLORIDE

[7550-45-0]
Formula: $TiCl_4$; MW 189.68
Synonym: titanium(IV) chloride

Uses

Titanium tetrachloride is used to prepare titanium dioxide and most other titanium compounds. It also is used in making iridescent glass; arificial pearls; and smoke screens. The compound is a polymerization catalyst.

Physical Properties

Colorless or yellow liquid; penetrating acid odor; absorbs moisture from air; produces dense white fumes; density 1.73 g/mL; freezes at –25°C; boils at 136.5°C; critical temperature 464.8°C; critical pressure 46.6 atm; critical volume 339 cm^3/mol; reacts with water forming TiO_2 and HCl; soluble in ethanol

Thermochemical Properties

$\Delta H_f°$(liq)	–192.2 kcal/mol
$\Delta H_f°$(gas)	–182.4 kcal/mol
$\Delta G_f°$ (liq)	–176.2 kcal/mol
$\Delta G_f°$ (gas)	–173.6 kcal/mol
S°(liq)	60.3 cal/deg mol
S°(gas)	84.4 cal/deg mol
C_ρ (liq)	34.7 cal/deg mol
C_ρ (gas)	22.8 cal/deg mol
ΔH_{vap}	3.65 kcal/mol

Preparation

Titanium tetrachloride is prepared by heating titanium dioxide or the ores ilmenite or rutile with carbon to red heat in a stream of chlorine. When ilmetite is used, ferric chloride also is produced. Titanium tetrachloride is separated from ferric chloride and other impurities by fractionation.

Analysis

Elemental composition: Ti 25.25%, Cl 74.75%. The compound is digested in acid, diluted and analyzed for titanium (See Titanium). A small amount of compound is weighed accurately and decomposed in hot water to form TiO_2 and HCl:

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$$

The product HCl is measured by acid-base titration. An aliquot of the product mixture is analyzed for chloride ion by ion chromatography or titration with a standard solution of silver nitrate. The compound can be identified from its physical properties.

TITANIUM TRICHLORIDE

[7705-07-9]
Formula: $TiCl_3$; MW 154.22
Synonyms: titanous chloride; titanium(III) chloride

Uses

Titanium trichloride is a reducing agent. It is used to analyse nitro groups, ferric ion, perchlorate, and other oxidizing analytes. The trichloride also is a stripping agent for removing stains in laundering.

Physical Properties

Red-violet hexagonal crystals; hygroscopic; density 2.64 g/cm^3; decomposes on heating above 425°C; also decomposes in water, evolving heat; soluble in alcohol, acetonitrile and certain amines; insoluble in hydrocarbons and ether

Thermochemical Properties

$\Delta H_f°$	–172.3 kcal/mol
$\Delta G_f°$	–156.2 kcal/mol
S°	33.4 cal/deg mol
C_ρ	23.2 cal/deg mol
ΔH_{vap}	29.6 kcal/mol

Preparation

Titanium trichloride may be prepared by reducing titanium tetrachloride with hydrogen at 600°C. The tetrachloride may alternatively be reduced with aluminum, zinc, magnesium, tin, or by electrolysis.

Analysis

Elemental composition: Ti 31.05%, Cl 68.95%. Because it is a strong reducing agent and its aqueous solution is stable, the trichloride can be measured by redox titration. Also, titanium can be analyzed by various instrumental methods after digestion in an acid.

TUNGSTEN

[7440-33-7]
Symbol W; atomic number 74; atomic weight 183.85; a Group IV B (Group 6) chromium-group transition metal element; electron configuration [Xe]$4f^{14}5d^46s^2$; valence 0, +2, +3, +4, +5, +6; atomic radius 1.39 Å; ionic radius 0.66 Å and 0.62 Å for W^{4+} and $^{5+}$ corresponding to CN6 and 0.42 Å for W^{6+} at CN4; standard electrode potential, E° for $W^{3+} + 3e^- \leftrightarrow W$ is 0.10 V; five naturally-occurring stable isotopes: W-180 (0.120%), W-182 (26.498%), W-183 (14.314%), W-184 (30.642%, W-186 (28.426%); twenty-eight artificial radioisotopes in the mass range 158–179, 181, 185, 187–190; longest-lived isotope, W-181 $t_{1/2}$ 121.2 days.

History, Occurrence and Uses

The discovery of tungsten occurred in the 1780's. Peter Woulfe, in 1779, while examining the mineral now known as wolframite, established that it contained a new substance. Around the same time, Swedish chemist Carl Wilhelm Scheele was investigating another mineral, scheelite. This mineral was known at that time as tungsen, which in Swedish meant heavy stone. Scheele, in 1781, determined that tungsen contained lime and a new acid similar to molybdic acid. This new acid was tungstic acid. Scheele and Bergman predicted that reduction of this acid could produce a new metal. Two years later in 1783, J. J. de Elhuyar and his brother F. deElhuyar of Spain first prepared metallic tungsten from wolframite. They derived an acid from wolframite which was similar to acid obtained by Scheele from tungsten (scheelite), and succeeded in producing a new metal by reduction of this acid with charcoal. Also, they determined that the mineral wolframite contained iron and manganese. The metal took over the old name of its mineral tungsten. Also the metal is known as wolfram, derived from the name of its other mineral, wolframite. The word wolfram originated from the wolf-like nature of the mineral that it devoured tin during the tin smelting operation causing low recoveries. The element was given the symbol W for its old name wolfram.

Tungsten is widely distributed in nature, occurring in several minerals. It is found in scheelite, $CaWO_4$; wolframite, $(Fe,Mn)WO_4$; huebnerite, $MnWO_4$; ferberite, $FeWO_4$; tungstite, H_2WO_4; and cuprotungstite, $CuWO_4$. Its abundance in the earth's crust is estimated to be 1.25 mg/kg and average concentration in seawater is about 0.1 μg/L

Industrially tungsten is a very important metal having wide applications. This is due to many outstanding physical properties. Among all the metals, tungsten has the highest melting point and the lowest vapor pressure. Also at high temperatures it has the highest tensile strength. The metal has an excellent resistance to corrosion and attack by mineral acids. Also it has a thermal expansion comparable to that of borosilicate glass.

Tungsten is extensively used in alloy steel to impart high strength and hardness to steel. Heavy metal alloys with nickel, copper and iron, produced by powder metallurgy, can be made machineable and moderately ductile for applications as high-density materials. Tungsten carbides are extremely hard and are excellent cutting materials. They are used extensivly in the tool and die industry for drilling and cutting tools, sand blasting nozzels, armor-piercing bullets, and studs to increase traction of tires.

Among the nonferrous tungsten alloys, its alloys with copper and silver are used as electrical contacts and switches and with molybdenum in aerospace components.

Unalloyed tungsten has several major applications. An important use is in the electric lamp filaments for light bulbs. Also, it is used as electrodes in arc-welding, in heating elements for high-temperature furnaces, in electron and television tubes, in glass-to- metal seals, and in solar energy devices.

Physical Properties

Grayish-white metal; body-centered cubic crystalline structure; density 19.3 g/cm^3; melts at 3,422°C; vaporizes at 5,555°C; vapor pressure 1 torr at 3,990°C; electrical resistivity 5.5 microhm-cm at 20°C; modulus of elasticity about 50 to 57 × 10^6 psi (single crystal); Poisson's ratio 0.17; magnetic susceptibilty +59 × 10^{-6}; thermal neutron absorption cross section 19.2 $\pm$ 1.0 barns (2,200m/sec); velocity of sound, about 13,000 ft/sec; insoluble in water; practically insoluble in most acids and alkalies; dissolves slowly in hot concentrated nitric acid; dissolves in saturated aqueous solution of sodium chlorate and basic solution of potassium ferricyanide; also solubilized by fusion with sodium hydroxide or sodium carbonate in the presence of potassium nitrate followed by treatment with water

Thermochemcial Properties

$\Delta H_f°$(cry)	0.0
$\Delta H_f°$(gas)	203.0 kcal/mol
$\Delta G_f°$(gas)	192.9 kcal/mol
S°(cry)	7.79 cal/deg mol
S°(gas)	41.6 cal/deg mol
C_ρ (cry)	5.81 cal/deg mol
C_ρ (gas)	5.09 cal/deg mol
ΔH_{fus}	12.5kcal/mol
Thermal conductivity	1.74W/cmK
Cofficient of linear expansion	4.5×10^{-6}/°C

Production

Tungsten is recovered mostly from mineral scheelite and wolframite. The recovery process depends on the mineral, the cost, and the end use; i.e., the commercial products to be made. Typical industrial processes have been developed to convert tungsten ores to tungsten metal and alloy products, tungsten steel, non-ferrous alloys, cast and cemented tungsten carbides, and tungsten compounds. A few processes are mentioned briefly below.

The first step in recovery is opening the ore. If the ore is scheelite, $CaWO_4$, it is digested with hydrochloric acid:

$$CaWO_4 + 2HCl \rightarrow H_2WO_4 + CaCl_2$$

Tungstic acid, H_2WO_4 precipitates out. The precipitate is washed and dissolved in sodium or ammonium hydroxide solution during heating:

$$H_2WO_4 + 2NaOH \rightarrow Na_2WO_4 + 2H_2O$$

Sodium tungstate is crystallized, separated from any impurities in the solution, and digested again with hydrochloric acid to form tungstic acid in purified form. The pure acid is dried, ignited and reduced with carbon to form tungsten powder from which most non-ferrous alloys are made.

The tungstic acid may be dissolved in ammonium hydroxide solution instead of sodium hydroxide and evaporated to form ammonium paratungstate (APT) crystals, $5(NH_4)_2O \cdot 12WO_3 \cdot 11H_2O$. The APT crystals are washed, dried and calcined to obtain tungstic oxide, WO_3. The latter then is reduced with hydrogen at 1,100°C to form tungsten powder:

$$WO_3 + 3H_2 \rightarrow W + 3H_2O$$

The APT may directly be reduced with hydrogen to produce tungsten powder. The powder may be pressed, sintered and fabricated to produce tungsten metal and alloy products.The tungsten powder may be heated with carbon to form tungsen carbides which may be converted to cast carbides or certain grades of cemented carbides. Or the tungsten powder may be alloyed with specific metals to form various non-ferrous alloys.

If tungsten is recovered from the wolframite group mineral, the wolframite concentrate is boiled or pressure-digested with 50% caustic soda solution. Alternatively, they may be fused or sintered with caustic soda, caustic potash or sodium carbonate and the fused mass then leached with water. The solution is filtered to separate sodium tungstate solution. The filtrate is subjected to various treatments to remove molybdenum, phosphorus, and arsenic impurities. The filtrate at this point is essentially a solution of sodium tungstate and is treated in the same way as that obtained from the scheelite concentrate discussed above.

Commercial ferrotungsten is obtained by reducing wolframite, scheelite, ferberite or hybnerite with carbon in an electric furnace. Iron scrap is added in appropriate amounts to form a ferrotungsten alloy containing about 70 to 80% tungsten.

Reactions

Tungsten exhibits several oxidation states, +6 being most stable. Compounds of lower oxidation states show alkaline properties. They also are less stable than those produced in higher oxidation states. Tungsten exhibits remarkable stability to practically all substances at ambient temperature. The metal is not attacked by nonoxidizing mineral acid. Concentrated hydrochloric acid, dilute sulfric acid and hydrofluoric acid attack the metal very slightly even when heated to 100°C. Tungsten is stable to dilute or concentrated nitric acid under cold conditions. Cold acid passivates the surface forming a slight oxide film. Hot dilute nitric acid corrodes the metal, while hot concentrated acid slowly dissolves bulk metal but rapidly oxidizes metal in powder form. At room temperature, aqua regia oxidizes metal only on the surface forming tungsten trioxide. A hydrofluoric-nitric acid mixture rapidly oxidizes tungsten to its trioxide. Chromic acid-sulfuric acid mixture does not react with tungsten metal in ductile form at ambient temperatures.

Tungsten metal is not affected by aqueous alkalies at room temperature. In molten state, caustic soda and caustic potash slowly oxidize tungsten in the presence of air. Oxidation is more rapid in the presence of an oxidizing agent such as potassium nitrate, potassium chlorate, or lead dioxide. A similar reaction occurs with fused sodium or potassium carbonate. Tungsten dissolves slowly in molten salt but when an oxidizing agent is added to molten carbonate mixture, the reaction speeds up.

Although tungsten exhibits a high degree of resistance to most chemicals, it is readily oxidized by a number of oxidizing agents. A 30% solution of hydrogen peroxide dissolves metal powder slowly at room temperature. A similar reaction happens in a saturated solution of sodium or potassium chlorate.

Tungsten reacts with oxygen at high temperatures. The finely-divided powder is pyrophoric. But the bulk metal begins to oxidize at about 400°C. The metal oxidizes rapidly when heated in air or oxygen at red heat. Two simple oxides are known, a blue monoclinic dioxide, WO_2, and a lemon yellow trioxide, WO_3. The trioxide, WO_3, is the most stable oxide and the ultimate product of heating the metal in oxygen. Many other oxides also are known, but they are of nonstoichiometric compositions and are unstable. The metal also is oxidized by water vapor at red heat.

Tungsten reacts with all halogens. With fluorine, reaction occurs at room temperature forming a volatile hexafluoride, WF_6. Pure dry chlorine gas combines with the metal above 250°C to form purple tungsten hexachloride, WCl_6. In the presence of moisture, oxychlorides (or tungstic oxides) are formed. Tungsten reacts with bromine vapor at red heat forming brownish-black pentabromide, WBr_5. The metal reacts with iodine vapor at red heat to form black tetraiodide, WI_4. At a lower temperature of about 730°C, the product is orange diiodide, WI_2

Tungsten reacts with ammonia at elevated temperatures forming tungstic nitrides and amides. Tungsten ordinarily does not combine with nitrogen. At very high temperatures above 1,500°C nitrides, WN_2 and W_2N, are produced. These nitrides also are prepared at lower temperatures by reacting ammonia with tungsten powder.

Tungsten reacts with molten sulfur forming the disulfide, WS_2. In excess sulfur the trisulfide, WS_3 forms.

Tungsten forms a volating white crystalline hexacarbonyl, $W(CO)_6$ by reacting with carbon monoxide at 275 to 300°C under 200 atm CO pressure.

Tungsten forms a number of compounds with nonmetals and light metalloid elements. Many are important refractory materials in commerce. The most important are the carbides, WC and W_2C. They are made by heating tungsten and carbon together at about 1,500°C. The carbide, WC, in powder form is made by heating a mixture of tungsten powder and finely divided lamp black in hydrogen at about 1,500°C. Carbide for commercial uses is produced by ball milling with about 5 to 30% binder, such as cobalt. The mixture then is pressed, preheated at about 900°C in hydrogen, machined to final shape and sintered at about 1,300 to 1,400°C. Cast carbides are made by melting a mixture of tungsten powder (reduced by carbon) and a carbonaceous material at 3,000 to 3,200°C.

Tungsten also forms hard, crystalline refractory borides, such as WB_2, W_2B and WB when heated with boron in an electric furnace. Tungsten also forms a group of silicides, hard refractory compounds of compositions WSi_2, WSi_3 and W_2Si_3. These silicides are attacked by hydrofluoric-nitric acid mixture or by fused alkalies.

Analysis

Tungsten may be analyzed by flame AA and ICP-AES. For such analyses, the metal, its compounds, or alloys are solubilized by digestion with aqua regia, nitric acid-perchloric acid, or other acid combinations and diluted. Other instrumental techniques such as x-ray fluorescence and neutron activation analysis also are applicable.

TUNGSTEN HEXACARBONYL

[14040-11-0]
Formula: $W(CO)_6$; MW 351.90
Synonym: tungsten carbonyl

Uses

Tungsten hexacarbonyl is used to produce tungsten coatings on base metals. This is done by deposition of the carbonyl on the metal surface, which decomposes to leave a tungsten coating.

Physical Properties

White crystalline solid; density 2.65 g/cm^3; decomposes at 170°C without melting; sublimes; vapor pressure 0.1 torr at 20°C; insoluble in water; soluble in most organic solvents.

Preparation

Tungsten hexacarbonyl is produced by heating tungsten metal with carbon monoxide at high pressure. Also, carbonyl can be prepared by reducing the tungsten hexachloride by heating with iron powder under carbon monoxide pressure.

Analysis

Tungsten carbonyl may be dissolved in an organic solvent and analyzed by GC/MS. The compound should form mass spectra corresponding to the masses for $W(CO)_6$, CO and W. The compound may be decomposed thermally and product carbon monoxide transported with helium onto a GC column to be analyzed by GC-TCD or GC/MS. Residue tungsten metal is extracted with nitric acid-hydrofluoric acid, diluted with water, and analyzed (See Tungsten).

TUNGSTEN TRIOXIDE

[1314-35-8]
Formula: WO_3; MW 231.84
Synonyms: tungsten(VI) oxide; tungstic oxide; tungstic acid anhydride;

tungstic anhydride; wolframic acid, anhydrous

Uses

Tungsten trioxide is used for fireproofing fabrics and as a yellow pigment in ceramics. It is used to make tungstates for x-ray screens. Also, it serves as starting material for preparing many tungsten compounds and tungsten metal.

Physical Properties

Heavy yellow powder; turns dark orange on heating; reverts back to yellow on cooling; density 7.2 g/cm^3; melts at 1,472°C; insoluble in water; slightly soluble in acids; soluble in caustic alkalies

Thermochemical Properties

$\Delta H_f°$	–201.5 kcal/mol
$\Delta G_f°$	–182.6 kcal/mol
$S°$	18.1 cal/deg mol
C_ρ	17.6 cal/deg mol

Preparation

Tungsten trioxide is obtained as an intermediate in recovery of tungsten from its minerals (See Tungsten). In commerical processes tungstic acid, H_2WO_4, obtained from the mineral scheelite, may either be decomposed at high temperatures to form trioxide or dissolved in ammonium hydroxide solution and evaporated to yield ammonium paratungstate (APT) crystals, $5\,(NH_4)_2O \cdot 12WO_3 \cdot 11H_2O$. The APT crystals are then washed, dried, and calcined at elevated temperatures to form tungsten trioxide.

Tungsten trioxide, in general, can be made by heating metallic tungsten, its carbides, its lower oxides, or tungstic acid in air.

Analysis

Elemental composition: W 79.30%, O 20.70%. Tungsten trioxide may be identified by its physical properties or by x-ray diffraction methods. The oxide is either digested in aqua regia or dissolved in caustic alkalies, diluted, and analyzed for tungsten metal (See Tungsten).

TUNGSTIC ACID

[7783-03-1]
Formula: H_2WO_4; MW 249.85
Synonyms: orthotungstic acid; tungstic(VI) acid

Uses

Tungstic acid is used in preparing tungsten metal and many tungsten compounds. Also, it is a mordant for textiles.

Physical Properties

Yellow amorphous powder; density 5.59 g/cm^3; decomposes at 100°C; insoluble in water and most acids; soluble in hydrofluoric acid, caustic alkalies and ammonia solution. Freshly prepared tungstic acid containing a molecule of water of crystallization is moderately soluble in water.

Preparation

Tungstic acid is obtained as an intermediate in the recovery of tungsten from its minerals, scheelite and wolframite (See Tungsten). Also, the tungstic acid may be prepared by heating sodium tungstate with sulfuric acid or hydrochloric acid:

$$Na_2WO_4 + 2HCl \rightarrow H_2WO_4 + 2NaCl$$

$$Na_2WO_4 + H_2SO_4 \rightarrow H_2WO_4 + Na_2SO_4$$

Analysis

Elemental composition: W 73.59%, H 0.81%, O 25.61%. The compound is dissolved in hydrofluoric acid and the solution diluted with water and analyzed for tungsten (See Tungsten).

URANIUM

[7440-61-4]

Symbol U; atomic number 92; atomic weight 238.029; an actinide series radioactive element; heaviest naturally-occurring element; electron configuration [Rn]$5f^36d^17s^2$; valence states +2, +3, +4, +5, +6; ionic radii U^{3+} 1.03Å, U^{4+} 0.89Å, U^{5+} 0.76Å, for coordination number 6 and U^{6+} 0.45 Å and 0.81 Å for coordination numbers 2 and 7, respectively; standard electrode potential, E° for $U^{3+} + 3e^- \leftrightarrow U$ is –1.798V and $U^{4+} + e^- \leftrightarrow U^{3+}$ is –0.607V; twenty-two isotopes in the mass range 218–219, 222–240, 242; all isotopes are radioactive; Longest-lived isotope U-238, $t_{1/2}$ 4.46×10^9 years.

History, Occurrence and Uses

The element was discovered in the pitchblende ores by the German chemist M.S. Klaproth in 1789. He named this new element uranium after the planet Uranus which had just been discovered eight years earlier in 1781. The metal was isolated first in 1841 by Peligot by reducing the anhydrous chloride with potassium. Its radioactivity was discovered by Henry Becquerel in 1896. Then in the 1930's and 40's there were several revolutionary discoveries of nuclear properties of uranium. In 1934, Enrico Fermi and co-workers observed the beta radioactivity of uranium, following neutron bombardment and in 1939, Lise Meitner, Otto Hahn, and Fritz Strassmann discovered fission of uranium nucleus when bombarded with thermal neutrons to produce radioactive isotopes of lighter elements. Shortly after this, it was proved that only uranium-235 was fissionable while nonfissionable uranium-238 could be transmuted to a synthetic element, plutonium, by neutron irradiation. Plutonium also was fissionable by thermal neutrons like uranium-235. Fermi and his co-workers first successfully carried out a self-sustaining chain reaction in 1942. These investigations led to the first test of a nuclear explosive device in New Mexico in July 1945. This was followed by the first explosion of a nuclear bomb in Hiroshima, Japan in August 1945.

Uranium-235 is the most important uranium isotope for nuclear fuel. Uranium-238, although not fissionable itself, can be converted into the fissionable plutonium-239 in a breeder reactor by the following nuclear reaction:

$$^{238}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n} \longrightarrow ^{239}_{92}\mathrm{U} + \gamma \xrightarrow{\beta^-} ^{239}_{93}\mathrm{Np} \xrightarrow{\beta^-} ^{239}_{94}\mathrm{Pu}$$

Uranium-233, like uranium-235 and plutonium-239, forms a fissionable isotope used as nuclear fuel. This isotope can be made from natural thorium by irradiation with neutrons, as follows:

$$^{232}_{90}\mathrm{Th} + ^{1}_{0}\mathrm{n} \longrightarrow ^{233}_{90}\mathrm{Th} + \gamma \xrightarrow{\beta^-} ^{233}_{91}\mathrm{Pa} \xrightarrow{\beta^-} ^{233}_{92}\mathrm{U}$$

Uranium occurs in nature in many rocks, minerals and sediments. The principal uranium minerals are pitchblende, carnotite, uranitite, tobernite, uranophane, autunite, and davidite. Uranium also is found in very small quantities in monazite sand, phosphate rock, and lignite. Although uranium is present in very small quantites, these sources also are used for commercial recovery of the metal.

Abundance of uranium in the earth's crust is about 2.7 mg/kg. Its average concentration in seawater is 3.2 µg/L. The principal application of uranium is as nuclear fuel for reactors to generate electric power and to make nuclear explosives. Other uses are for making artifcial elements, x-ray targets for producing high-energy x-rays, and in inertial guidance devices. Uranium salts are used in making yellow vaseline glass and glazes.

Physical Properties

Silvery-white heavy metal; malleable and ductile; slightly paramagnetic; density 18.95 g/cm^3

The metal exists in three crystal forms: an orthorhombic alpha phase, density 18.97 g/cm^3 and stable to 667°C; a tetragonal beta phase of density 18.11 g/cm^3, stable between 688 to 776°C; and a body-centered cubic form of density 18.06 g/cm^3 and stable in the range 776 to 1,132°C. Other physical properties are listed below:

The metal melts at 1,132°C; vaporizes at 4,131°C; electical resistivity 28 microhm-cm; specific activity of total uranium (including the isotopes 238, 235 and 233) 1,501 disintegration/minute/mg; insoluble in water and alkalies; soluble in acids.

Thermochemical Properties

$\Delta H_f°$(cry)	0.0
$\Delta H_f°$(gas)	127.4 kcal/mol
$\Delta G_f°$(gas)	116.7 kcal/mol
S°(cry)	12.0 cal/deg mol
S°(gas)	47.8 cal/deg mol
C_ρ (cry)	6.62 cal/deg mol
C_ρ (gas)	5.66 cal/deg mol
ΔH_{vap}	2.18 kcal/mol
Thermal conductivity(at 27°C)	0.276 W/cm K
Coefficient of linear expansion (at 25°C)	$13.9\text{x}10^{-6}$/°C

Recovery

The ore is crushed and finely ground. Uranium in the ore is concentrated by leaching with either an acid or an alkali. Uranium as oxide,U_3O_8, is recovered from this leachate by ion exchange, solvent extraction or precipitation. The oxide is dissolved in concentrated nitric acid to form a solution of uranyl nitrate, $UO_2(NO_2)_2$. The uranyl nitrate is separated from associated impurities by solvent extraction using tributyl phosphate. Heating uranyl nitrate with hydrogen at elevated temperatures converts it to the oxide, UO_2. The oxide may be converted to uranium tetrafluoride, UF_4, upon heating with hydrogen fluoride.

Metallic uranium can be prepared from its oxides or halides by reduction at high temperature. Uranium dioxide, UO_2, or other oxides such as UO_3 or U_3O_8 may be reduced to uranium metal by heating with carbon, calcium or aluminum at high temperatures. Similarly, uranium tetrafluoride or other halides can be reduced to metal by heating with sodium, potassium, calcium, or magnesium at high temperatures. Alternatively, uranium tetrafluoride mixed with fused alkali chlorides is electrolyzed to generate uranium metal.

Reactions

In aqueous solution, uranium exists in four oxidation states: U^{3+}(red), U^{4+}(green) and its oxide ion UO_2^+ which is unstable, and the yellow uranyl ion, UO_2^{2+}. In solid compounds the metal exhibits several oxidation states.

Uranium forms several oxides. The main oxides are brown-black UO_2, orange yellow UO_3, and nonstoichiometric greenish black U_3O_8. The most stable oxide is dioxide, UO_2. Heating the metal in air or oxygen at 150 to 350°C forms UO_2 and U_3O_8. A trihydride, UH_3, is obtained when metal is heated in hydrogen at 250°C.

Uranium forms two stable fluorides, UF_4 and UF_6. When metal is heated with fluorine gas, hexafluoride, UF_6, is produced. Heating powdered metal with hydrogen fluoride gas at 350°C yields tetrafluoride, UF_4. Powdered metal is obtained by thermal decomposition of trihydride, UH_3. Uranium combines with chlorine at elevated temperature (at about 500°C) to form a mixture of various chlorides; namely, the tetrachloride, UCl_4, pentachloride, UCl_5, and hexachloride,UCl_6. Heating the metal with bromine vapor at 650°C forms tetrabromide, UBr_4. Uranium also forms tri-and pentabromides. With iodine vapor at 350°C, products are the triiodide, UI_3, and tetraiodide, UI_4.

Uranium forms three stable and well-known sulfides, US, US_2 and U_2S_3. While heating the metal with molten sulfur at 500°C forms the disulfide, US_2, all the three sulfides are obtained from reacting hydrogen sulfide with the metal, particularly in its powder form at 500°C.

Heating the metal with ammonia at elevated temperatures (at about 700°C) yields nitrides of nonstoichiometric compositions. With nitric oxide, uranium is oxidized at about 400°C, forming triuranium octaoxide, U_3O_8.

Both carbon monoxide and carbon dioxide oxidize uranium at 750°C forming uranium dioxide, UO_2, along with uranium carbide, UC.

The same carbide is produced by heating the powdered metal with methane at elevated temperatures. Uranium forms mono- and dicarbides and diuranium tricarbides, UC, UC_2, and U_2C_3, respectively when heated with carbon above 1,800°C

Uranium dissolves rapidly in nitric and hydrochloric acids. With hydrochloric acid, a black residue often remains. In sulfuric, hydrofluoric, and phosphoric acids, the metal dissolves slowly. Uranium is not affected by alkalies.

Uranium reacts with boiling water forming its dioxide, UO_2, and evolving hydrogen. The hydrogen produced combines with metal to form hydride.

Uranium reacts with dinitrogen tetroxide, N_2O_4, in acetonitrile to form an intermediate, $UO_2(NO_3)_2 \cdot N_2O_4 \cdot 2CH_3CN$, which on heating above 160°C yields uranyl nitrate, $UO_2(NO_3)_2$.

Analysis

Radioactivity of uranium can be measured by alpha counters. The metal is digested in nitric acid. Alpha activity is measured by a counting instrument, such as an alpha scintillation counter or gas-flow proportional counter. Uranium may be separated from the other radioactive substances by radiochemical methods. The metal or its compound(s) is first dissolved. Uranium is coprecipitated with ferric hydroxide. Precipitate is dissolved in an acid and the solution passed through an anion exchange column. Uranium is eluted with dilute hydrochloric acid. The solution is evaporated to near dryness. Uranium is converted to its nitrate and alpha activity is counted. Alternatively, uranium is separated and electrodeposited onto a stainless steel disk and alpha particles counted by alpha pulse height analysis using a silicon surface barrier detector, a semiconductor particle-type detector.

Hazard

Uranium and its compunds are highly toxic. These substances also present a radiation hazard. Finely-divided metal is pyrophoric.

URANIUM DIOXIDE

[1344-57-6]
Formula: UO_2; MW 270.03
Synonyms: uranium oxide; uranic oxide; urania; uranium(IV) oxide

Occurrence and Uses

Uranium dioxide occcurs in nature as mineral uraninite. It is used in nuclear fuel rods for reactors. Also it is used in large incandescent lamps for photography or motion pictures and is connected to the tungsten filaments to prevent sudden surges of current.

Physical Properties

Brown to black powder or cubic crystals; density 10.97 g/cm^3; Mohs hardness 5.5; melts at 2,827°C; insoluble in water and dilute acids; soluble in concentrated acids.

Thermochemical Properties

ΔH_f°(cry)	–259.3 kcal/mol
ΔH_f°(gas)	–111.3 kcal/mol
ΔG_f° (cry)	–246.6 kcal/mol
ΔG_f° (gas)	–112.7 kcal/mol
S°(cry)	18.4 cal/deg mol
S°(gas)	12.1 cal/deg mol
C_ρ (cry)	15.2 cal/deg mol
C_ρ (gas)	12.3 cal/deg mol

Preparation

Uranium dioxide occurs in mineral uraninite. Purified oxide may be obtained from uraninite after purification. The commercial material, however, also is recovered from other uranium sources. Uranium dioxide is obtained as an intermediate during production of uranium metal (See Uranium). Uranyl nitrate, $UO_2(NO_3)_2$, obtained from digesting the mineral uraninite or pitchblende with concentrated nitric acid and separated by solvent extraction, is reduced with hydrogen at high temperatures to yield the dioxide.

Analysis

Elemental composition: U 88.15%, O 11.85%. The compound is digested in nitric acid and alpha activity is measured by a gas-flow proportional counter, alpha scintillation counter or other counting instrument.

Hazard

See Uranium.

URANIUM HEXAFLUORIDE

[7783-81-5]
Formula: UF_6; MW 352.02
Synonym: uranium(VI) fluoride

Uses

The compound is used in the gaseous diffusion process to separate uranium isotopes

Physical Properties

White monoclinic crystals; density 5.09 g/cm^3; melts at 64°C (triple point); sublimes at 56.6°C; critical temperature 232.65°C; critical pressure 46 atm; critical volume 250 cm^3/mol; reacts with water forming UO_2F_2 and HF; soluble in chloroform, carbon tetrachloride and fluorocarbon solvents; soluble in liquid chlorine and bromine; dissolves in nitrobenzene to form a dark red solution that fumes in air.

Thermochemical Properties

$\Delta H_f°$(cry)	–525.1 kcal/mol
$\Delta H_f°$(gas)	–513.2 kcal/mol
$\Delta G_f°$(cry)	–494.4 kcal/mol
$\Delta G_f°$(gas)	–493.2 kcal/mol
S°(cry)	54.4 cal/deg mol
S°(gas)	90.3 cal/deg mol
C_ρ (cry)	39.9 cal/deg mol
C_ρ (gas)	31.0 cal/deg mol
ΔH_{fus}	4.59 kcal/mol

Preparation

Uranium hexafluoride is prepared by the reaction of fluorine on uranium metal, triuranium octafluoride, uranium pentachloride, or uranium carbide.

One preparative method involves heating triuranium octaoxide, U_3O_8, with hydrogen fluoride and fluorine. The product hexafluoride is separated and purified by fractional distillation.

Another preparative method involves converting triuranium octaoxide to uranyl nitrate, $UO_2(NO_3)_2$, by treatment with nitric acid. Uranyl nitrate then is decomposed to uranium trioxide, UO_3 , which is reduced to the dioxide, UO_2, with hydrogen. A fluidized bed of uranium dioxide is treated with hydrogen fluoride to produce uranium tetrafluoride, UF_4, which then is treated with fluorine to form hexafluoride. The preparation should be done in copper apparatus.

Analysis

Elemental composition: U 67.62%, F 32.38%. The compound may be identified by its physical properties. Alpha activity may be measured by an alpha counter or an alpha spectrometer (See Uranium). Flouride ion may be measured in an aqueous solution of the compound (reacts vigorously with water forming HF and UO_2F_2) by fluoride ion selective electrode or by ion chromatography.

Hazard

Uranium hexafluoride is a corrosive substance and also presents radiation hazard.

URANYL NITRATE

[10102-06-4]
Formula: $UO_2(NO_3)_2$; MW 394.04; exists as a stable hexahydrate
$UO_2(NO_2)_3 \cdot 6H_2O$
[13520-83-7] MW 502.13
Synonyms: uranium oxynitrate; yellow salt

Uses

Uranyl nitrate is used to prepare several uranium salts. Also it is used to make uranium glaze and decorative porcelain, and as an intensifier in photography. It is an analytical reagent (e.g., Redox titration).

Physical Properties

The hexahydrate is a yellow crystalline solid; orthogonal crystals; density 2.81 g/cm^3; hygroscopic; melts at 60°C; decomposes at 118°C; very soluble in water; soluble in alcohol and ether.

Preparation

Uranyl nitrate is obtained as an intermediate in recovering uranium from its minerals. The compound can be prepared by reacting triuranium octaoxide, U_3O_8, with nitric acid. It is separated and purified by extraction with ether.

Analysis

Elemental composition (anhydrous compound): U 60.41%, N 7.11%, O 32.48%. The compound may be identified by its physical properties and measured by gravimetric methods from its thermal decomposition to form uranium trioxide, UO_3. The radioactivity may be measured by an alpha counter.

Hazard

The compound is toxic and presents a radiation risk.

VANADIUM

[7440-62-2]
Symbol V; atomic number 23; atomic weight 50.942; a Group V B (Group 5)

transition metal; electron configuration $[Ar]3d^34s^2$; valence states +2, +3, +4, +5; atomic radius 1.34Å; ionic radius V^{2+}, V^{3+}, V^{4+}, and V^{5+} are 0.79Å, 0.64Å, 0.58Å, and 0.54Å,respectively for CN 6; standard electrode potential, E° for $V^{2+} + 2e^- \leftrightarrow V$ is –1.175V; two naturally-occurring isotopes: V-50 (0.25%), V-51 (99.75%); V-50 is radioactive with a $t_{1/2}$ of over 1.4×10^{17} year; sixteen artificial radioactive isotopes in the mass range 43-49, 52-60.

History, Occurrence, and Uses

Vanadium was discovered in 1801 by Mexican mineralogist Manuel del Rio in a lead ore in Hidalgo, Mexico. He named it *erythronium* because of the red color its salts when heated with acids. However, del Rio's discovery was mistakenly thought at that time to be a form of impure chromium. Swedish chemist Sefstrom in 1830 rediscovered this element detecting an unknown metal in the iron ores of Taberg, Sweden. He named it vanadium after the Scandinavian goddess Vanadis. Later in 1830, Wohler determined that del Rio's erythronium and Sefstrom's vanadium were the same element. Vanadium metal was prepared for the first time by Roscoe in 1867 in somewhat impure form, as a silvery-white powder, by reduction of vanadium chloride, VCl_2, with hydrogen. Hunter and Jones in 1923 prepared the metal at 99.5% purity as a fine gray powder by thermal reduction of vanadium trichloride with sodium in a steel bomb.

Vanadium is found in several minerals including roscoelite, a vanadium-bearing mica $[2K_2O \cdot 2Al_2O_3 \cdot (Mg, Fe)O \cdot 3V_2O_5 \cdot 10SiO_2 \cdot 4H_2O]$; carnotite, $K_2O \cdot 2U_2O_3 \cdot V_2O_5 \cdot 3H_2O$; vanadinite, $9PbO \cdot 3V_2O_5 \cdot PbCl_2$; patronite, a polysulfide $V_2S_5 \cdot nS$; cuprodesclozite, $4(Cu,Zn,Pb)O \cdot (V,As)_2O_5 \cdot H_2O$; hewettite, $CaO \cdot 3V_2O_5 \cdot 9H_2O$; and uvanite, $2UO_3 \cdot 3V_2O_5 \cdot 15H_2O$. Also, it is found in phosphate rocks, many iron ores, and in some crude oils. Abundance in earth's crust is about 120mg/kg. Vanadium has been found in meteorites.

Vanadium is added to steel for high resistance to oxidation and to stabilize carbide. Vanadium foil is used for cladding titanium to steel. Vanadium-gallium alloy is used in making superconductive magnets. An important compound of vanadium is pentoxide which has many commercial uses (See Vanadium Pentoxide).

Physical Properties

A bright white metal; soft and ductile; body-centered cubic structure; index of refraction 3.03; density 5.96 g/cm³; melts at 1,910°C; vaporizes at 3,407°C; electrical resistivity, 18.1 microhm-cm at 0°C and 20.1 microhm-cm at 25°C; magnetic susceptibility 1.4×10^{-6} cgs units; modulus of elasticity $18\text{-}19 \times 10^6$ psi; shear modulus 6.73×10^6psi; Poisson's ratio 0.36; thermal neutron absorption cross section 5 barns/atom; insoluble in water, dilute sulfuric acid, and hydrochloric acid at all concentrations; soluble in nitric acid, aqua regia, and concentrated sulfuric acid; insoluble in alkalies.

Thermochemical Properties

$\Delta Hf°$ (cry)	0.0
$\Delta Hf°$ (gas)	122.9 kcal/mol

$\Delta Gf°$ (cry)	0.0 kcal/mol
$\Delta Gf°$ (gas)	180.3 kcal/mol
S° (cry)	6.91 cal/deg mol
S° (gas)	43.5 cal/deg mol
C_ρ (cry)	5.95 cal/deg mol
C_ρ (gas)	6.22 cal/deg mol
ΔH_{fus}	5.14 kcal/mol
Thermal Conductivity (at 27°C)	0.307 W/cm K
Coefficient of linear expansion (at 25°C)	8.4×10^{-6}/°C

Recovery

Vanadium is recovered from several sources; vanadium minerals, vanadium-bearing phosphates, boiler residues, and spent vanadium catalysts. One major vanadium mineral is patronite, a greenish-black, amorphous sulfide ore used extensively for many years to produce vanadium. This mineral, found in Peru, has depleted gradually. The metal also is recovered commercially from carnotite and roscoelite.

Vanadium usually is recovered from its ores by one of two processes, (1) leaching raw mineral with hot dilute sulfuric acid, and (2) roasting ore with common salt to convert vanadium into water soluble sodium vanadates. In the sulfuric acid leaching process, vanadium is extracted from acid leach liquors by solvent extraction with an aliphatic amine or an alkyl phosphoric acid in kerosene. The organic solvent extract then is treated with an aqueous solution of ammonia in the presence of ammonium chloride to convert vanadium into ammonium metavanadate. Alternatively, the organic extract is treated with dilute sulfuric acid or an aqueous solution of soda ash under controlled conditions of pH. Vanadium is precipitated from this solution as a red cake of sodium polyvanadate.

Alternatively, ore is roasted with common salt and the residue leached with water or sodium carbonate solution. To this aqueous solution of sodium vanadates, sulfuric acid is added and pH is adjusted between 2 and 3. Vanadate precipitates as a red cake of sodium polyvanadate.

The sodium polyvanadate obtained above by either method is decomposed thermally at 700°C producing a melt of vanadium pentoxide, V_2O_5. Pentoxide obtained at this stage is in impure form. Purified vanadium pentoxide is obtained by dissolving the red cake in sodium carbonate solution to precipitate ammonium metavanadate. The metavanadate is decomposed at 320 to 430°C to form highly purified vanadium pentoxide.

Vanadium metal is prepared from pentoxide, V_2O_5, by reduction with calcium at elevated temperatures. Presence of iodine lowers calcium reduction temperature to 425°C because of heat of formation of calcium iodide. Pentoxide also may be converted to the trichloride, VCl_3, and the trichloride reduced with magnesium metal or magnesium-sodium mixture at high temperatures to form high purity ductile metal. Alternatively, a fused mixture of vanadium chloride, sodium chloride, and lithium chloride may be electrolyzed to produce the metal in high purity.

Reactions

Vanadium forms four oxides: the light grey monoxide, VO or (V_2O_2); the blue black dioxide, VO_2 (or V_2O_4); the black sesquioxide, V_2O_3; and the orange-red pentoxide, V_2O_5. The oxides are formed when the metal is heated in air or oxygen. Vanadium combines with chlorine on heating. Three chlorides are known: the green dichloride, VCl_2; the pink trichloride, VCl_3; and the brown-red tetrachloride, VCl_4. The more stable tetrachloride is formed when the metal is heated with chlorine at 180°C. The metal also forms three fluorides in valence states +3, +4, and +5. They are the green trifluoride, VF_3; a yellowish-brown tetrafluoride, VF_4, and the white pentafluoride, VF_5. When heated with bromine vapor vanadium forms the green-black tribromide, VBr_3. Vanadium forms two iodides, a violet-rose diiodide, VI_2, and a deliquescent triiodide, VI_3.

Vanadium combines with other nonmetals at elevated temperatures forming binary compounds. Such compounds include nitride, VN; carbide VC, and the sulfides, VS (or V_2S_2), V_2S_3, and V_2S_5.

Vanadium reacts with fused caustic soda and caustic potash to form water soluble vanadates with liberation of hydrogen. The metal, however, is stable in alkaline solutions.

Analysis

Trace quantities of vanadium in solid materials or water can be measured by flame-AA or ICP-AES methods. For such analysis the metal or its compounds or alloys have to be dissolved by digestion with nitric acid or aqua regia. Flame-AA measurement may be made at 318.4 nm using a nitrous oxide-acetylene flame. ICP-AES measurement may be made at 292.40nm. Other wavelengths may be substituted. Vanadium ions in solution can be measured by colorimetry using a spectrophotometer or a filter photometer at 415 nm. Color formation is based on catalytic effect of vanadium on reaction of gallic acid with persulfate ion in acid solution. An ammonium persulfate-phosphoric acid reagent solution may be used in the test. Many metal ions and halide ions may interfere in the test.

VANADIUM PENTOXIDE

[1314-62-1]
Formula V_2O_5; MW 181.88
Synonyms: vanadium(V) oxide; vanadic acid anhydride; vanadic anhydride.

Uses

The most important applications of vanadium pentoxide are in catalysis. It is a catalyst in manufacturing sulfuric acid by contact process. Also, it catalyzes conversion of ethanol to acetaldehyde, and many organic reactions. Other applications are in making yellow glass; as a depolarizer; as a developer in photography; inhibiting UV transmission in glass; and coloring ceramics. Vanadium pentoxide is used to prepare many vanadium compounds including ammonium vanadate used in making aniline black dye, and as a mordant for dyeing and printing fabrics.

Physical Properties

Brown-yellow orthorhombic crystals; density 3.35 g/cm^3; melts at 670°C; decomposes at 1,800°C; slightly soluble in water, 0.8g/100 mL at 20°C; soluble in concentrated acids forming an orange-yellow solution; soluble in alkalies forming vanadates.

Thermochemcial Properties

$\Delta Hf°$	–370.6 kcal/mol
$\Delta Gf°$	–339.3 kcal/mol
$S°$	31.3 cal/deg mol
C_ρ	30.5 cal/deg mol
ΔH_{fus}	15.4 cal/deg mol

Preparation

Vanadium pentoxide is an intermediate in recovering vanadium from minerals (See Vanadium). Sodium polyvanadate, obtained as a red cake in one of the steps in extracting vanadium from its ores is calcined at 700°C in air to form a melt of vanadium pentoxide. Pentoxide is prepared in purified form by dissolving red cake in sodium carbonate solution followed by addition of an aqueous solution of ammonia and ammonium chloride. Ammonium metavanadate is precipitated which on decomposition at 320 to 430°C forms vanadium pentoxide.

Reactions

Vanadium pentoxide may be reduced to vanadium tetraoxide, trioxide, or vanadium metal by various reducing agents including hydrogen, carbon, and oxalic acid. Pentoxide may be reduced to metal by heating at high temperatures with calcium or magnesium.

Pentoxide when heated with chlorine gas at 500°C in the presence of carbon forms vanadium oxytrichloride:

$$V_2O_5 + 3C + 3Cl_2 \rightarrow 2VOCl_3 + 3CO$$

At a higher temperature of 750°C vanadium tetrachloride is produced:

$$2V_2O_5 + 5C + 8Cl_2 \rightarrow 4VCl_4 + 5CO_2.$$

When sulfur dioxide is passed through a solution of vanadium pentoxide in sulfuric acid, the product is blue crystalline vanadyl sulfate:

$$V_2O_5 + H_2SO_4 + H_2O + SO_2 \rightarrow 2VOSO_4 + 2H_2O$$

Vanadium pentoxide reacts with caustic soda to form a series of water-soluble vanadates: sodium metavanadate, $NaVO_3$, sodium pyrovanadate, $Na_4V_2O_7$, and sodium orthovanadate, Na_3VO_4. The specific product depends on molar proportions of caustic soda:

$$V_2O_5 + 2NaOH \rightarrow 2NaVO_3 + H_2O$$

$$V_2O_5 + 4NaOH \rightarrow Na_4V_2O_7 + 2H_2O$$

$$V_2O_5 + 6NaOH \rightarrow 2Na_3VO_4 + 3H_2O$$

Analysis

Elemental composition: V 56.02%, O 43.98%. An acid solution is analyzed for vanadium (See Vanadium). Pentoxide in sulfuric acid may be converted to vanadyl sulfate by reduction with SO_2 (See Reactions) or ferrous ammonium sulfate (FAS). The excess FAS may be destroyed with ammonium persulfate. Vanadyl sulfate is then titrated with a standard solution of potassium permanganate:

$$10VOSO_4 + 2KMnO_4 + 22H_2O \rightarrow 10H_3VO_4 + K_2SO_4 + 2MnSO_4 + 7H_2SO_4$$

Toxicity

The compound is toxic by ingestion, inhalation, and contact. Inhalation can cause asthma, cough, dyspnea, and bronchial constriction. Ingestion can cause gastrointestinal tract disturbances. Other toxic symptoms are skin pallor, greenish-black tongue, and papular skin rash (Lewis, R.J. (Sr) 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed. New York: Van Nostrand Reinhold).

The oral LD_{50} for V_2O_5 dust in rats is 10 mg/kg and the inhalation LC_{LO} in rats is 70 mg/m^3/2hr.

VANADYL SULFATE

[27774-13-6]
Formula $VOSO_4$; MW 163.00; exists as a dihydrate, $VOSO_4 \cdot 2H_2O$.
Synonym: vanadium oxysulfate

Uses

The dihydrate is a mordant in dyeing and printing fabrics; used in preparing aniline black; a colorant in ceramics to form blue and green glazes; used in making colored glass; and a reducing agent.

Physical Properties

The dihydrate, $VOSO_4 \cdot 2H_2O$ is a blue black crystalline powder, soluble in water.

Preparation

Vanadyl sulfate is prepared by passing sulfur dioxide through a cold solution of vanadium pentoxide in sulfuric acid, followed by crystallization:

$$V_2O_5 + H_2SO_4 + H_2O + SO_2 \rightarrow 2VOSO_4 + 2H_2O$$

Analysis

Vanadyl sulfate may be analyzed by titration with a standard solution of potassium permanganate (See Vanadium Pentoxide, Analysis) or any suitable oxidizing agent. An aqueous solution may be analyzed for vanadium by AA or ICP (See Vanadium).

WATER

[7732-18-5]
Formula H_2O; MW 18.015; bent molecule; H–O–H bond angle 104.5°; H–O bond distance 0.9575 Å; bond dissociation energy of O–H bond 101.2 kcal/mol; intermolecular force: hydrogen bonding

Uses

Water is among the most important compounds on earth. It is the main constituent of the hydrosphere, which along with the mantle, crust, and the atmosphere are the four components of our planet. It is present everywhere on earth and is essential for sustenance of life. Water also determines climate, weather pattern, and energy balance on earth. It also is one of the most abundant compounds. The mass of all water on earth is 1.4×10^{21} kg and the total volume is about 1.4×10^{9} km^3, which includes 97.20% of salt water of oceans, 2.15% of fresh water in polar ice caps and glaciers, 0.009% in freshwater lakes, 0.008% in saline lakes, 0.62% as ground waters, 0.005% in soil moisture; 0.0001% in stream channels and 0.001% as vapors and moisture in the atmosphere.

Among the major industrial applications of water are generation of hydroelectric power, steam generation, industrial solvent, diluent, moderator in nuclear reactions, industrial coolant, washing and cleaning, textile processing, preparation of food and beverages, filtration processes, and generation of hydrogen by electrolysis. Also, water provides the aqueous phase to carry out innumerable chemical reactions in the production of myriads of chemical substances including mineral acids, alkalies and their salts.

Physical Properties

Colorless, odorless, tasteless liquid; refractive index 1.3330; exists in three allotropic forms: solid ice, liquid water, and gaseous steam (or vapor); density of water increases with temperature, becomes maximum 1.0000 g/mL at 3.98°C and then decreases with rise in temperatures; density at 25°C 0.997 g/cm^3; density of water at 100°C 0.9584 g/mL; density of steam 0.000596 g/mL at 100°C.

Water freezes to ice at 0°C; expands by about 10% on freezing; boils at 100°C; vapor pressure at 0°, 20°, 50°, and 100°C are 4.6, 17.5, 92.5, and 760 torr, respectively; dielectric constant 80.2 at 20°C and 76.6 at 30°C; dipole moment in benzene at 25°C 1.76; critical temperature 373.99°C; critical pressure 217.8 atm; critical density 0.322 g/cm^3; viscosity 0.01002 poise at 20°C; surface tension 73 dynes/cm at 20°C; dissolves ionic substances; miscible with mineral acids, alkalies; low molecular weight alcohols, aldehydes and ketones; forms an azeotrope with several solvents; immiscible with nonpolar solvents such as carbon tetrachloride, hexane, chloroform, benzene, toluene, and carbon disulfide.

Thermochemical Properties

$\Delta Hf°$ (liq)	–68.32 kcal/mol
$\Delta Hf°$ (gas)	–57.80 kcal/mol
$\Delta Gf°$ (liq)	–56.69 kcal/mol
$\Delta Gf°$ (gas)	–54.63 kcal/mol
S° (liq)	16.71 cal/deg mol
S° (gas)	45.10 cal/deg mol
C_ρ (liq)	17.99 cal/deg mol
C_ρ (gas)	8.025 cal/deg mol
ΔH_{fus}	1.436 kcal/mol
ΔH_{vap}	9.716 kcal/mol

Production

Water is produced by combustion of hydrogen with oxygen at high temperatures in the presence of a catalyst. Also, all combustion reactions of hydrocarbons (C, H compounds) or oxygenated hydrocarbons (C, H, O) yield water and carbon dioxide:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$2CH_3OH + 2O_2 \rightarrow 2CO_2 + 4H_2O$$

All acid-base neutralization reactions form water:

$$HCl + NaOH \rightarrow NaCl + 4H_2O$$

Organic condensation reactions eliminate a water molecule:

$$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$$

Many hydroxides dehydrate at high temperatures forming oxides and water:

$$Ca(OH)_2 \rightarrow CaO + H_2O$$

Water can be purified by distillation, ion exchange, filtration, carbon adsorption, and chlorination.

Reactions

Water undergoes autoionization to a small extent; the ionization constant at 25°C is 1.008×10^{-14}:

$$2H_2O(l) \leftrightarrow H_3O^+(aq) + OH^-$$

Water reacts both as an acid and a base. With bases it reacts as an acid:

$$NH_3(aq) + H_2O(l) \leftrightarrow NH_4^+(aq) + OH^-;$$

and with acids it reacts as a base:

$$HCl\ (aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

Water reacts with many metal oxides and nonmetal oxides forming bases and acids, respectively:

$$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(s)$$

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2\ (s)$$

$$N_2O_5(s) + H_2O(l) \rightarrow 2HNO_3(l)$$

$$P_4O_{10}(s) + 6H_2O\ (l) \rightarrow 4H_3PO_4(s)$$

Water also behaves both as an oxidizing and reducing agent. With alkali and alkaline earth metals, which are strong reducing agents, water acts as an oxidizing agent. Reactions occur violently or vigorously at ambient temperatures with all alkali metals and calcium, strontium, and barium forming their hydroxides with liberation of hydrogen:

$$2K(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2(g)$$

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$$

With less active metals, reactions occur at high temperatures. In such reactions oxides are formed instead of hydroxides, liberating hydrogen:

$$Mg(s) + H_2O(l) \rightarrow MgO(s) + H_2(g)$$

$$Ni(s) + H_2O\ (l) \rightarrow NiO(s) + H_2(g)$$

$$3Fe(s) + 4H_2O\ (l) \rightarrow Fe_3O_4(s) + 4H_2(g)$$

Water reacts with nonmetals and metalloid elements at very high temperatures forming oxides:

$$C(s) + H_2O(g) \xrightarrow{\Delta} CO(g) + H_2(g)$$

$$Ge(s) + 2H_2O(l) \xrightarrow{\Delta} GeO_2(s) + 2H_2(g)$$

Water behaves as a reducing agent in reactions with oxidizing agents:

$$2F_2(g) + 2H_2O(l) \rightarrow 4HF(aq) + O_2(g)$$

Water reacts with carbon monoxide at high temperatures (200 to 400°) in the presence of a catalyst to yield carbon dioxide and hydrogen. The reaction also is known as water-gas shift reaction:

$$CO(g) + H_2O(l) \leftrightarrow CO_2(g) + H_2(g)$$

Water reacts with metal hydrides liberating hydrogen. With the hydrides of sodium and potassium the reaction progresses with explosive violence:

$$NaH + H_2O \rightarrow NaOH + H_2$$

With alkali metal amides violent reactions occur, forming alkali hydroxides and ammonia:

$$NaNH_2 + H_2O \rightarrow NaOH + NH_3$$

Violent reactions occur with lithium aluminum hydride and similar compounds:

$$LiAlH_4 + 4H_2O \rightarrow LiOH + Al(OH)_3 + 4H_2$$

Sodium ethoxide decomposes in water forming sodium hydroxide and ethanol:

$$NaOC_2H_5 + H_2O \rightarrow NaOH + C_2H_5OH$$

Sulfuryl chloride, SO_2Cl_2, reacts with ice-cold water to form a hydrate, $SO_2Cl_2 \cdot 15H_2O$. However, at ambient temperature water decomposes sulfuryl chloride slowly forming sulfuric acid and hydrochloric acid:

$$SO_2Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$$

Water reacts with calcium carbide to form acetylene:

$$CaC_2 + H_2O \rightarrow C_2H_2 + CaO$$

Water forms hydrates with a large number of metal salts. Such hydrates are formed from absorption of moisture from air by anhydrous salts. Examples are $Na_2SO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, and $BaCl_2 \cdot 2H_2O$. In many salt hydrates, water molecules coordinate to the metal ions, e.g., $[Ni(H_2O)_6](NO_3)_2$. Organic esters are hydrolyzed to form corresponding organic acids and alcohol. The reaction is catalyzed by acids:

$$RCOOR' + H_2O \rightarrow RCOOH + R'OH$$

Analysis

Water can be identified from its physical properties. Also, trace amounts of water may be determined by Karl-Fischer analysis. The Karl-Fisher reagent is a solution of iodine, sulfur dioxide and pyridine in methanol or methyl cellosolve. Water of crystallization in hydrates can be measured by TGA and DTA methods. The presence of trace moisture in gases can be determined by mass spectrometry. The characteristic mass ion is 18.

XENON

[7440-63-3]
Symbol Xe; atomic number 54; atomic weight 131.29; a noble gas; a Group VIII A (Group 18) inert gas element; electron configuration $[Kr]4d^{10}5s^25p^6$; valence, usually 0, but known to form compounds with fluorine and oxygen; atomic radius 1.31Å; nine naturally-occurring stable isotopes: Xe-124(0.10%), Xe-126 (0.09%), Xe-128(1.91%), Xe-129(26.46%), Xe-130(4.11%), Xe-131(21.24%), Xe-132(26.95%), Xe-134(10.42%), Xe-136(8.91%); twenty-seven artificial radioactive isotopes in the mass range 110-123, 125, 127, 133, 135, 137-145; longest-lived radioisotope Xe-127, $t_{1/2}$ 36.4 days; shortest-lived radioisotope Xe-110, $t_{1/2}$ 0.2 second.

History, Occurrence, and Uses

Xenon was discovered by Ramsay and Travers in 1898 while purifying krypton by fractional distillation. The name is from the Greek word *zenos* meaning "Stranger."

Xenon occurs in the atmosphere at trace concentrations. It also occurs in gases from certain mineral springs. Xenon also is a fission product of uranium, plutonium, and thorium isotopes induced by neutron bombardment. The radioactive fission product, xenon-135, has a very high thermal neutron cross-section. The element has been detected in Mars' atmosphere.

Xenon is a filling gas for light bulbs in high-intensity lamps and in flash lamps for photography. It forms a beautiful blue glow under vacuum in an electric discharge tube. It also is used in lamps that excite ruby lasers to produce coherent light. Xenon gas is a filler in proportional radiation counters and liquid xenon bubble chambers. Xenon is an anesthetic gas in surgery.

Radioactive xenon is a biological tracer.

Physical Properties

Colorless, odorless, tasteless gas; density of the gas 5.761 g/L at STP; heavier than air, about 4.5 times heavier than air (air=1); liquefies at –108.04°C; density of liquid xenon 3.52 g/mL at its boiling point; freezes to a solid at –111.75°C; density of solid xenon 2.7 g/cm^3 at –140°C; critical pressure 57.64 atm; critical temperature 16.058°C; critical volume 118 cm^3/mol; solubility in water 203.2 mL/L at STP and 108.1 mL/L at 20°C.

Thermochemical Properties

$\Delta Hf°$	0.0
$\Delta Gf°$	0.0
S°	40.5 cal/deg mol
C_ρ	4.97 cal/deg mol
Thermal conductivity	5.5 mW/mK
ΔH_{fus}	1.436 kcal/mol
ΔH_{vap}	3.02 kcal/mol

Production

Xenon is recovered from air by liquefaction and fractional distillation. Usually it is obtained as a by-product of making other noble gases. It is collected in the liquid oxygen fraction along with krypton, acetylene, and other hydrocarbons that may be present in air. The xenon fraction is flash vaporized. Hydrocarbons present are separated by burning over a catalyst. Xenon is absorbed on silica gel at low temperatures. Finally, it is separated from krypton by selective absorption and desorption from charcoal.

Compounds

Although xenon has the stable octet configuration and is thought to be as inert as other noble gases, several xenon compounds have been prepared. The first xenon compound synthesized by N. Bartlett in 1962 was a red solid, $XePtF_6$, made by the reaction of xenon with platinum hexafluoride undergoing the following oxidation sequence (Cotton, F. A., Wilkinson G., Murillo, C. A. and M. Bochmann. 1999. *Advanced Inorganic Chemistry*, 6th ed., pp. 588. New York: John Wiley & Sons):

$$Xe + 2PtF_6 \xrightarrow{25°C} [XeF^+]\,[PtF_6^-] + PtF5 \xrightarrow{60°C} [XeF^+]\,[PtF_{11}^-]$$

Xenon forms three binary fluorides, XeF_2, XeF_4, and XeF_6. Fluorine is the only element with which xenon reacts directly forming XeF_2. Reactions occur with excess xenon under pressure:

$$Xe + F_2 \rightarrow XeF_2 \xrightarrow{F_1} XeF_4 \xrightarrow{F_2} XeF_6$$

Bartlett prepared xenon difluoride by the reaction of xenon with silver fluoride in hydrofluoric acid in the presence of boron trifluoride:

$$2AgF_2 + 2BF_3 + Xe \rightarrow XeF_2 + 2AgBF_4$$

Xenon tetrafluoride also can be prepared by oxidizing xenon with dioxygen difluoride, O_2F_2, or by photolysis of xenon-fluorine mixture.

All other compounds of xenon are made from xenon fluorides.

Compounds in oxidation states +2, +4, +6, and +8 are well known. The tetrafluoride and hexafluoride are readily hydrolyzed by water forming xenon trioxide, XeO_3, and the xenon tetraoxide, XeO_4, both of which are dangerously explosive. While the trioxide XeO_3 is a colorless crystalline solid, stable in solution, the tetraoxide XeO_4 is a colorless unstable gas.

The oxyfluoride, $XeOF_4$ is a stable colorless liquid produced by the reaction of xenon hexafluoride with sodium nitrate:

$$XeF_6 + NaNO_3 \rightarrow XeOF_4 + FNO_2 + NaF$$

The oxodifluoride, $XeOF_2$, dioxodifluoride, XeO_2F_2 and the trioxodifluoride, XeO_3F_2 all are unstable.

Xenon also forms many fluoroanions and their salts, mostly prepared from xenon tetrafluoride and hexafluoride. Such compounds include $Na^+XeF_5^-$ and $Cs^+XeF_7^-$ formed by reactions of xenon fluorides with sodium fluoride or cesium fluoride. The dicesium xenon octafluoride, Cs_2XeF_8, is a stable yellow solid that decomposes above 400°C.

Analysis

Xenon can be identified by GC-TCD or by the GC/MS. The latter is a confirmatory test. The mass ions for its identification are 132, 129, 131, 134, 136, and 130 in the order of abundance corresponding to xenon isotopes.

YTTERBIUM

[7440-64-4]
Symbol Yb; atomic number 70; atomic weight 173.04; a lanthanide series rare earth metal; electron configuration $[Xe]4f^{14}6s^2$; valence +2, +3; atomic radius 1.945Å; ionic radius, Yb^{3+} 0.868Å and 0.98Å for CN 6 and 8; respectively; standard electrode potential, E° for $Yb^{3+} + 3e^- \leftrightarrow Yb$ is –2.19V; seven naturally-occurring stable isotope: Yb-170 (3.05%), Yb-171 (14.32%), Yb-172 (21.93%), Yb-173 (16.12%), Yb-174 (31.84%), Yb-176 (12.72%); twenty-three artificial radioactive isotopes in the mass range 151-167, 169, 175, 177-180; the longest-lived radioisotope Yb-169, $t_{1/2}$ 32.03 days; shortest-lived radioisotope Yb-154, $t_{1/2}$ 0.40 second.

History, Occurrence, and Uses

Ytterbium was discovered in 1878 by J. C. G. de Marignac. He found a new component ytterbia in supposedly pure erbia or erbium oxide that had been isolated earlier by Mosander. The element got its name from the Swedish village Ytterby where this rare earth first was found. Urbain in 1907 separated ytterbia into two components, neoytterbia and lutecia, that are oxides of ytterbium and lutecium respectively. These two elements were discovered independently by von Welsbach around the same time. Klemm and Bommer in 1937 first prepared metallic ytterbium by reduction with potassium. The metal they prepared was impure, mixed with potassium chloride. Pure metal was prepared first by Daane, Dennison, and Spedding in 1953 in gram quantities.

Ytterbium occurs in minerals euxenite, a complex titanium niobotantalate; gadolinite, a rare earth iron beryllium silicate; monazite, a thorium-rare earth phosphate; and xenotime, also a rare earth-thorium phosphate. Abundance of ytterbium in the earth's crust is estimated to be 3.2 mg/kg.

The metal has very little commercial use. In elemental form it is a laser source, a portable x-ray source, and as a dopant in garnets. When added to stainless steel, it improves grain refinement, strength, and other properties. Some other applications, particularly in oxides mixed with other rare earths, are as carbon rods for industrial lighting, in titanate insulated capacitors, and as additives to glass. The radioactive isotope ytterbium-169 is used in portable devices to examine defects in thin steel and aluminum. The metal and its compounds are used in fundamental research.

Physical Properties

Silvery lustrous metal; soft, malleable and ductile; the metal exists in two allotropic forms: an alpha form, which has a face-centered cubic structure and is stable at room temperature, and a beta form, a body-centered cubic modification that forms when the alpha form is heated to 798°C. Density of the alpha modification is 6.98 g/cm^3 and that of beta form is 6.54 g/cm^3. Alpha phase exhibits metallic-type conductivity at ordinary temperatures and pressures, but becomes semi-conductive above 16,000 atm. At about 40,000 atm it again becomes metallic-type conductor. (In some texts, the term beta form refers to the alpha phase).

Ytterbium melts at 824°C; vaporizes at 1,194°C; electrical resistivity 25.0 microhm-cm; Vickers hardness 21 kg/mm^{2-}; Young's modulus 0.182x10^{-6} kg/cm^2; shear modulus 0.071x10^{-6} kg/cm^2; Poisson's ratio 0.284; magnetic susceptibility 71x10^6 emu/mol; thermal neutron absorption cross section 37 barns; reacts slowly with water; soluble in dilute acids and ammonia.

Thermochemical Properties

$\Delta Hf°$ (cry)	0.0
$\Delta Hf°$ (gas)	36.4 kcal/mol
$\Delta Gf°$ (gas)	28.3 kcal/mol
S° (cry)	14.3 cal/deg mol
S° (gas)	41.4 cal/deg mol
C_ρ (cry)	6.38 cal/deg mol
C_ρ (gas)	4.97 cal/deg mol
ΔH_{fus}	1.83 kcal/mol

Thermal Conductivity (at 27°C)	0.385 W/cm K
Coefficient of linear expansion(at 25°C)	26.3×10^{-6}/°C

Recovery

Recovery of ytterbium from ores involves several processes that are mostly common to all lanthanide metals. These are discussed individually under each rare earth metal. Recovery involves three major steps: (1) processing of ores, (2) separation of ytterbium from rare earth mixtures, and (3) preparation of the metal.

If the starting material is gadolinite, ore is digested with hydrochloric or nitric acid. Rare earths dissolve in acid. The solution is treated with sodium oxalate or oxalic acid to precipitate rare earths as oxalates. For euxenite, ore is opened either by fusion with potassium bisulfate or digestion with hydrofluoric acid. If monazite or xenotime is extracted, ore is either heated with sulfuric acid or digested with caustic soda solution at elevated temperatures.

Various processes separate rare earths from other metal salts. These processes also separate rare earths into specific subgroups. The methods are based on fractional precipitation, selective extraction by nonaqueous solvents, or selective ion exchange. Separation of individual rare earths is the most important step in recovery. Separation may be achieved by ion exchange and solvent extraction techniques. Also, ytterbium may be separated from a mixture of heavy rare earths by reduction with sodium amalgam. In this method, a buffered acidic solution of trivalent heavy rare earths is treated with molten sodium mercury alloy. Yb^{3+} is reduced and dissolved in the molten alloy. The alloy is treated with hydrochloric acid, after which ytterbium is extracted into the solution. The metal is precipitated as oxalate from solution.

After separation from other rare earths, ytterbium is usually obtained as its oxide, Yb_2O_3. If separated as oxalate, oxalate is converted into oxide by high temperature. Ytterbium oxide is reduced to metallic ytterbium by heating with lanthanum metal in high vacuum. The metal is purified by sublimation and collected over a condenser plate. Aluminum, zirconium, and cerium also are effective reducing agents and may be used instead of lanthanum.

Reactions

Ytterbium reacts with oxygen above 200°C. It forms two oxides, the monoxide, YbO, and more stable sesquioxide, Yb_2O_3.

The metal dissolves in dilute and concentrated mineral acids. Evaporation crystallizes salts. At ordinary temperatures, ytterbium, similar to other rare earth metals, is corroded slowly by caustic alkalies, ammonium hydroxide, and sodium nitrate solutions. The metal dissolves in liquid ammonia forming a deep blue solution.

Reactions with halogens are slow at room temperature but progress rapidly above 200°C forming ytterbium trihalides. All the trihalides; namely, the $YbCl_3$, $YbBr_3$, and YbI_3 with the exception of trifluoride, YbF_3, are hygroscopic and soluble in water.

Ytterbium forms many binary, metalloid, and intermetallic compounds with a number of elements when heated at elevated temperatures. When heated with hydrogen, nitrogen, sulfur, and carbon at high temperatures, the corresponding binary compounds are produced.

Analysis

The metal can be analyzed by flame-AA and ICP-AES methods. Ytterbium or its compounds are dissolved by acid digestion and diluted before such analysis. X-ray methods and neutron activation analysis are also applicable.

YTTERBIUM OXIDE

[1314-37-0]
Formula Yb_2O_3; MW 394.08
Synonyms: ytterbium (III) oxide; ytterbia

Uses

Ytterbium oxide is used in cored carbon rods for industrial lighting. The oxide also is used as an additive in special glasses. Other uses are in dielectric ceramics and special alloys.

Physical Properties

Colorless cubic crystals when pure; tinted brown or yellowish white in presence of thulia; density 9.2 g/cm^3; melts at 2,435°C; insoluble in water; soluble in hot dilute acids.

Thermochemical Properties

$\Delta H f°$	–433.7 kcal/mol
$\Delta G f°$	–412.7 kcal/mol
S°	31.8 cal/deg mol
C_ρ	27.6 cal/deg mol

Production

Ytterbium oxide is produced as an intermediate in recovering ytterbium from minerals (See Ytterbium). After opening the ore by digestion with concentrated sulfuric acid or caustic soda solution at high temperatures, rare earths are separated by ion exchange, solvent extraction, or fractional precipitation. Ytterbium fraction is treated with oxalic acid or sodium oxalate to precipitate ytterbium oxalate, which is ignited to yield ytterbium oxide.

Analysis

Elemental composition: Yb 87.82%, O 12.18%. Ytterbium oxide is dissolved in dilute acids and diluted for analysis by flame-AA or ICP-AES methods. The oxide may be characterized by x-ray.

YTTRIUM

[7440-65-5]
Symbol Y; atomic number 39; atomic weight 88.906; a Group III B (Group 3 transition metal; electron configuration $[Kr]4d^15s^2$; valence +3; atomic radius 1.80Å; standard electronic potentail, E° for $Y^{3+} + 3e \leftrightarrow Y$ is –2.372 V; one naturally-occurring stable isotope, Y-89 (100%); twenty-four artificial radioactive isotopes in the mass range 78-88, 90-102; the longest-lived radioisotope; Y-88, $t_{1/2}$ 106.6 days; shortest-lived radioisotope Y-98, $t_{1/2}$ 0.59 second.

History, Occurrence, and Uses

The element was discovered in 1794 by the Swedish chemist Gadolin. He named it after the small town Ytterby in Sweden where the mineral containing yttria was found. Mosander in 1843 determined that the yttria consisted of three oxides: yttria, erbia, and terbia. Yttrium occurs in all rare earths. It is recovered commercially from monazite sand, which contains about 3% yttrium. It also is found in bastnasite in smaller amounts of about 0.2%. Abundance of yttrium in earth's crust is estimated to be 33 mg/kg. The metal has been detected in moon rocks.

Yttrium alloys have many applications. The metal doped with rare earths such as europium is used as phosphor for color television receivers. When added to iron, chromium, vanadium, niobium, and other metals it enhances resistance of these metals and their alloys to high temperature oxidation and recrystallization. It is a deoxidizer for vanadium and other nonferrous metals. Yttrium-aluminum garnets are used in lasers and in jewelery gemstones. Yttrium-iron garnets are used as transmitters and as transducers of acoustic energy.

Physical Properties

Grayish lustrous metal; darkens when exposed to light; hexagonal close-packed crystals converting to body-centered cubic structure at 1,490°C; density 4.469 g/cm^3 at 25°C; Brinnel hardness 32; melts at 1,526°C; vaporizes at 3,336°C; electrical resistivity 59.6 microhm-cm at 25°C; compressibility 2.09×10^{-6} cm^2/kg; Young's modulus 9.62×10^6 psi; Poisson's ratio 0.265; reacts with water; soluble in dilute acids and alkalis.

Thermochemical Properties

$\Delta Hf°$ (cry)	0.0
$\Delta H f°$ (gas)	100.7 kcal/mol
$\Delta G f°$ (gas)	91.1 kcal/mol
S° (cry)	10.6 cal/deg mol
S° (gas)	42.9 cal/deg mol
C_ρ (cry)	6.19 cal/deg mol
C_ρ (gas)	6.38 cal/deg mol
ΔH_{fus}	2.72 kcal/mol
Thermal Conductivity (at 27°C)	0.172 W/cm K
Coefficient of linear expansion (at 25°C)	10.6×10^{-6}/°C

Recovery

Yttrium is recovered commercially from its two principal sources, xenotime and monazite. Ore is opened by digestion with hot sulfuric acid. Insoluble residues are filtered out and leachate solution containing yttrium and other rare-earths is loaded onto cation exchange resin beds for separation. Fractions are eluted with ethylenediamine tetraacetic acid (EDTA) buffered with ammonia at varying temperatures. Also, many other chelates are highly effective in eluting rare earths. Such temperature adjustments of resin beds enhance separation efficiency, particularly for separating yttrium. Separated rate earths including yttrium are converted into insoluble oxalates that precipitate when treated with oxalic acid or sodium oxalate.

Yttrium oxalate is then ignited to its oxide, Y_2O_3. The oxide is heated at 750°C in a stream of anhydrous hydrogen fluoride to yield yttrium fluoride, YF_3. Alternatively, the oxide is mixed with ammonium hydrogen fluoride NH_4HF_2 and heated at 400°C in a stream of dry air or helium. Yttrium metal may be produced from its fluoride either by metallothermic reduction or electrolysis. The more common metallothermic reduction involves reducing the fluoride with redistilled calcium in 10% excess over the stoichiometric amounts at elevated temperatures:

$$2YF_3 + 3Ca \rightarrow 2Y + 3CaF_2$$

In the electrolytic process, a fused bath of yttrium fluoride and lithium fluoride is heated to nearly 1,700°C and electrolyzed. The electrolysis is done in a graphite crucible using molybdenum cathodes at which yttrium is produced as molten metal.

Yttrium is purified by distillation at high temperatures under vacuum.

Reactions

The chemical properties of yttrium are more similar to those of rare earths than to scandium. However, unlike the rare earths, yttrium exhibits only one valence state, +3.

Yttrium combines with oxygen forming its only oxide, Y_2O_3. The reaction is much faster at high temperatures, particularly above 400°C. The metal, in the form of sponge or small particles, can ignite at this temperature. At ambient temperature the metal is slightly tarnished by oxygen or air, forming a very thin film of oxide that protects the metal from further oxidation.

Yttrium reacts with water vapor at high temperatures, usually above 750°C, forming a protective oxide coating.

The metal reacts with halogens above 200°C forming its trihalides. It combines with nitrogen above 1,000°C producing a nitride, YN. It combines at elevated temperatures forming binary compounds with most nonmetals and some metalloid elements such as hydrogen, sulfur, carbon, phosphorus, silicon, and selenium.

Analysis

The metal or its compounds can be analyzed at trace levels by flame-AA, ICP-AES, ICP/MS and neutron activation. ICP/MS is the most sensitive method. The metal is dissolved by acid digestion and diluted prior to analysis.

YTTRIUM OXIDE

[1314-36-9]
Formula Y_2O_3; MW 225.81
Synonym: yttria

Uses

The oxide is used in phosphors that form red color in color television tubes. Also, it is used in gas mantles and acetylene lights. Other uses are in yttrium-iron garnets for microwave filters in lasers, and as a stabilizer for high temperature in refractories.

Physical Properties

White powder; body-centered cubic structure; density 5.03 g/cm^3; melts at 2,436°C; insoluble in water; soluble in dilute acids.

Thermochemical Properties

$\Delta Hf°$	–455.4 kcal/mol
$\Delta Gf°$	–434.2 kcal/mol
S°	23.7 cal/deg mol
C_ρ	24.5 cal/deg mol
ΔH_{fus}	25.1 kcal/mol

Preparation

Yttrium oxide is produced as an intermediate in recovery of yttrium from xenotime and monazite (See Yttrium, Recovery). The oxide is produced after separation of rare earth sulfates obtained from digesting the mineral with sulfuric acid on a cation exchange bed, precipitating yttrium fraction as oxalate, and igniting the oxalate at 750°C.

Yttrium oxide also may be obtained by thermal decomposition of yttrium nitrate.

Analysis

Elemental composition: Y 78.74%, O 21.26%. Oxide is dissolved in nitric acid and the solution analyzed for yttrium (See Yttrium). Oxide may be characterized by x-ray diffraction.

YTTRIUM SULFATE

[7446-33-5]
Formula $Y_2(SO_4)_3 \cdot 8H_2O$; MW 610.125; prepared and sold as octahydrate

Uses

Yttrium sulfate is used in making many yttrium salts.

Physical Properties

Red monoclinic crystals; density 2.59 g/cm^3; loses all its water molecules at 120°C; decomposes at 700°C; sparingly soluble in water, less soluble in hot water; dissolves in concentrated sulfuric acid forming $Y(HSO_4)_3$; insoluble in alkalis; forms double salts with alkali sulfates.

Preparation

Yttrium sulfate is produced as an intermediate in recovering yttrium from monazite or xenotime (see Yttrium, Recovery). Rare earth sulfates are separated on a cation exchange resin bed. Yttrium fraction is purified by fractional crystallization. Alternatively, yttrium sulfate may be prepared by reacting yttrium oxide with sulfuric acid.

Analysis

Water of crystallization may be measured by thermogravitmetric analysis. The compound is dissolved in concentrated sulfuric acid, diluted, and analyzed for yttrium by flame-AA or ICP-AES.

ZINC

[7440-66-6]
Symbol Zn; atomic number 30; atomic weight 65.39; a Group II B (Group 12) metallic element; electron configuration [Ar]3d^{10}4s^2; valence +2; atomic radius 1.34Å; ionic radius 0.60Å (CN 4) and 0.74Å (CN 6); standard electrode potential, E° for $Zn^{2+} + 2e^- \leftrightarrow Zn$ is –0.7618 V; five naturally-occurring isotopes: Zn-64 (48.63%), Zn-66 (27.92%), Zn-67 (4.11%), Zn-68 (18.84%), Zn-70(0.61%); nineteen artificial radioactive isotopes in the mass range 57, 59-63, 65, 69, 71-81; the longest-lived radioisotope, Zn-65, $t_{1/2}$ 243.8 days; shortest-lived radioisotope, Zn-57, $t_{1/2}$ 0.04 second.

History, Occurrence, and Uses

Zinc is another earliest known metal. Use of its alloy, brass, dates back to prehistoric times. The metal was produced in India in the 13th century by reducing calamine (a silicate mineral of zinc) with wool. Marggraf produced the metal in 1746 by reducing calamine with charcoal. The element took its name from the German word *zink* meaning "of obscure origin." Lohneyes first used this name in 1697.

Zinc occurs in nature, widely distributed. The principal ores are sphalerite (and wurtzite) known as zinc blende, ZnS; gahnite, $ZnAl_2O_4$; calamine; smithsonite, $ZnCO_3$; franklinite, $ZnFe_2O_4$; and zincite, ZnO. Abundance in earth's crust is about 70 mg/kg and average concentration in sea water is about 10 µg/L.

Some important applications of zinc include galvanizing steel; to produce die castings; as a chemical additive in rubber and paints; in dry cells; in making electrodes; and as a reducing agent. Steel is galvanized by a thin coating of zinc to protect it from corrosion. Such galvanized steel is used in buildings, cars, and appliances. High-purity zinc is alloyed with aluminum at varying compositions, along with small amounts of copper and magnesium, to produce die castings. Such die castings are used extensively in automotive, hardware, and electrical industries. Zinc forms numerous alloys including brass, nickel silver, German silver, commercial bronze, soft solder, aluminum solder, and spring brass. The laboratory use of zinc includes preparating hydrogen gas and as a reducing agent in a number of chemical reactions. Zinc salts have numerous uses (See under specific compounds). Zinc is an essential nutrient element required for growth of animals.

Physical Properties

Bluish-white lustrous metal; brittle at room temperature; malleable between 100 to 150°C; hexagonal close-packed structure; density 7.14 g/cm^3; melts at 419.6°C; vaporizes at 907°C; vapor pressure 1 torr at 487°C, 5 torr at 558°C and 60 torr at 700°C; good conductor of electricity, electrical resistivity 5.46 microhm-cm at 0°C and 6.01 microhm-cm at 25°C; surface tension 768 dynes/cm at 600°C; viscosity 3.17 and 2.24 centipoise at 450 and 600°C, respectively; diamagnetic; magnetic susceptibility 0.139×10^{-6} cgs units in polycrystalline form; thermal neutron absorption cross-section 1.1 barns.

Thermochemical Properties

$\Delta H f°$ (cry)	0.0
$\Delta H f°$ (gas)	31.2 kcal/mol
$\Delta G f°$ (gas)	22.7 kcal/mol
S° (cry)	9.94 cal/deg mol
S° (gas)	38.5 cal/deg mol
C_ρ (cry)	6.07 cal/deg mol
C_ρ (gas)	4.97 cal/deg mol
ΔH_{fus}	1.75 kcal/mol
Thermal Conductivity (at 27°C)	1.16 W/cm K
Coefficient of linear expansion (at 25°C)	30.2×10^{-6}/°C

Recovery

Practically all zinc produced today comes from sulfide ores, sphalerite or blende. The ore is first roasted to form zinc oxide. The primary reaction is:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

Also, some zinc sulfate is produced in the roasting:

$$2ZnO + 2SO_2 + O_2 \rightarrow 2ZnSO_4$$

Two methods are employed broadly in producing zinc metal from its oxide.

One is distillation in which roasted zinc oxide is mixed with excess carbon or carbonaceous materials and reduced at elevated temperatures in a furnace.

$$ZnO(s) + C(s) \rightarrow Zn(g) + CO(g)$$

Reduction temperature is usually around 1,300°C. Zinc obtained as vapor is condensed and collected in vessels connected to the reduction retort.

Zinc also may be produced by electrolysis of zinc sulfate solution. The zinc oxide in the roasted concentrate is leached with sulfuric acid. The oxide is converted to soluble zinc sulfate. Impurity metals, such as iron, copper, cadmium, arsenic, tin, and cobalt are removed by precipitation, floc formation, and other methods. The purified zinc sulfate solution is electrolyzed using aluminum cathodes and lead anodes. Zinc is deposited on the cathode.

Reactions

Zinc exhibits a valence of +2 in all its compounds. It also is a highly electropositive metal. It replaces less electropositive metals from their aqueous salt solutions or melts. For example, a zinc metal bar put into Cu^{2+} solution acquires a brown-black crust of copper metal deposited on it. At the same time the blue color of the solution fades. Zinc reduces Cu^{2+} ions to copper metal. The overall reaction is:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

This spontaneous reaction was used first in 1830 to make a voltaic cell.

The metal is attacked by mineral acids. Reactions with sulfuric and hydrochloric acids produce hydrogen. With nitric acid, no hydrogen is evolved but the pentavalent nitrogen is reduced to nitrogen at lower valence states.

Zinc is attacked by moist air at room temperature. Dry air has no action at ambient temperatures but the metal combines with dry oxygen rapidly above 225°C.

Zinc reacts with carbon dioxide in the presence of moisture at ordinary temperatures forming a hydrated basic carbonate. The metal, on heating with dry halogen gases, yields zinc halides. However, in the presence of moisture the reaction occurs rapidly at ambient temperatures.

The metal dissolves in hot solutions of caustic alkalis to form zincates and evolves hydrogen:

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$$

Analysis

Zinc in trace amounts may be measured in solutions by flame-and furnace-AA, ICP-AES, and ICP/MS methods. It also can be identified by x-ray fluorescence and neutron activation analysis. Flame-AA measurement is done at 213.9nm using an air-acetylene flame. The ICP-AES measurement may be done at 213.86 nm or 206.20nm or alternative wavelengths. ICP/MS is the most sensitive method.

Zinc also can be identified in aqueous solutions by colorimetric methods. Two such methods, known as "dithizone" and "zincon" methods are applicable to analyze zinc in water (APHA, AWWA, and WEF. 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington, DC: American Public Health Association).

Toxicity

Zinc is an essential nutrient and is not regarded as toxic. However, the metal fumes, its oxide fumes, and chloride fumes can produce adverse inhalation effects. (See Zinc Oxide and Zinc Chloride, Toxicity) Ingestion of soluble salts can cause nausea.

ZINC ACETATE

[557-34-6]
Formula $Zn(C_2H_3O_2)_2$; MW 183.46; takes on water to become a stable dihydrate, $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ [5970-45-6], MW 219.51

Uses

Zinc acetate is used as a mordant in dyeing textiles; in preserving wood; in manufacturing glazes for painting on ceramics; and as an analytic reagent in measuring albumin, tannin, and phosphate. Other uses are as a crosslinking agent for polymers; and as a supplement in food. The compound is used in medicine as an astringent.

Physical Properties

The dihydrate $Zn(C_2H_3O_2) \cdot 2H_2O$ is a white lustrous powder; faint acetic acid odor; astringent taste; monoclinic crystals; density 1.735 g/cm^3; loses water at 100°C; decomposes at 237°C; readily dissolves in water, 43g/100 mL at 20°C; soluble in alcohol.

Preparation

Zinc acetate is prepared by the reaction of acetic acid with zinc oxide followed by crystallization (crystals of dihydrate obtained):

$$ZnO + 2CH_3COOH \rightarrow (CH_3COO)_2Zn + H_2O$$

Analysis

Water of crystallization is measured by thermogravimetric analysis. An aqueous solution is analyzed for zinc by AA or ICP.

ZINC BROMIDE

[7699-45-8]
Formula $ZnBr_2$; MW 225.19

Uses

Zinc bromide is used in preparing photographic emulsions, and in producing rayon. Concentrated solution is used as a shield in viewing windows for nuclear reactions.

Physical Properties

White crystalline powder; sharp metallic taste; orthorhombic structure; refractive index 1.5452; density 4.20 g/cm^3; very hygroscopic; melts at 394°C; vaporizes at 650°C; highly soluble in water 447g/100 mL at 20°C; aqueous solution acidic; very soluble in alcohol, ether, and acetone; soluble in alkali hydroxides and ammonia solution.

Thermochemical Properties

$\Delta Hf°$ ($ZnBr_2$)	–78.55kcal/mol
$\Delta Hf°$ ($ZnBr_2 \cdot 2H_2O$)	–224.0 kcal/mol
$\Delta Gf°$ ($ZnBr_2 \cdot 2H_2O$)	–191.1 kcal/mol
$\Delta Gf°$ ($ZnBr_2$)	–74.60 kcal/mol
S° ($ZnBr_2$)	33.1 cal/deg mol
S° ($ZnBr_2 \cdot H_2O$)	47.5 cal/deg mol

Preparation

Zinc bromide is prepared by mixing barium bromide and zinc sulfate solutions. The product barium sulfate is removed by filtration and the filtrate is evaporated to obtain crystals of zinc bromide:

$$BaBr_2 + ZnSO_4 \rightarrow ZnBr_2 + BaSO_4$$

Zinc bromide also may be prepared by the action of zinc with hydrobromic acid followed by crystallization.

Analysis

Elemental composition: Zn 29.03%, Br 70.97%

An aqueous solution is analyzed for zinc metal (see Zinc) by AA, ICP, and other methods, and for Br^- by ion chromatography.

ZINC CARBONATE

[3486-35-9]
Formula $ZnCO_3$; MW 125.39

Occurrence and Uses

Zinc carbonate occurs in nature as mineral smithsonite and zincspar. The compound is used in ceramics and fire proofing filler for rubber and plastics.

Also, it is used in lotions, ointments, cosmetics, and as a topical antiseptic.

Physical Properties

White crystalline solid; orthorhombic structure; refractive index 1.818; Mohs hardness 4.3; density 4.398 g/cm^3; decomposes at 300°C forming zinc oxide; practically insoluble in water, 10 mg/L at 15°C; soluble in acids, alkalis, and ammonium salt solutions.

Thermochemical Properties

$\Delta Hf°$	–194.3 kcal/mol
$\Delta Gf°$	–174.8 kcal/mol
S°	19.7 cal/deg mol
C_ρ	19.05 cal/deg mol

Production

Zinc carbonate is derived from its mineral smithsonite. Also, the compound may be prepared by the reaction of sodium bicarbonate with a soluble zinc salt:

$$ZnCl_2 + NaHCO_3 \rightarrow ZnCO_3 + NaCl + HCl$$

Analysis

Elemental composition: Zn 52.14%, C 9.58%, O 38.28%. Zinc carbonate is identified by effervescence produced upon adding dilute HCl. CO_2 evolved is identified by the lime water test or by GC or GC/MS. Characteristic mass for identification of CO_2 is 44. Zinc may be analyzed in an acid solution by AA, ICP, and other methods to measure zinc content of the compound.

ZINC CHLORIDE

[7646-85-7]

Formula $ZnCl_2$; MW 136.29

Uses

Zinc chloride is used as a wood preservative and in fireproofing timber. Other uses are as a deodorant in disinfecting fluids; in dental cements; in electroplating; in etching metals and glass; as flux for soldering; as a mordant in printing and dyeing textiles; in making dry batteries; in denaturing alcohols; in vulcanizing rubber; in manufacturing parchment; in making artificial silk; in making activated carbon and cold-water glues; and in refining petroleum. Also, zinc chloride is used as a dehydrating and condensing agent in organic syntheses. In medicine it is used as an astringent and antiseptic.

Physical Properties

White crystalline powder or granules; hygroscopic; density 2.907 g/cm^3; melts at 290°C; vaporizes at 732°C; vapor pressure 1 torr at 428°C and 20 torr at 536°C; highly soluble in water, 432 g/100mL at 25°C; aqueous solution acidic in litmus test; also soluble in ethanol, glycerol, and acetone.

Thermochemical Properties

$\Delta Hf°$ (cry)	–99.2 kcal/mol
$\Delta H\ f°$ (gas)	–63.6 kcal/mol
$\Delta G\ f°$ (gas)	–88.3 kcal/mol
S° (cry)	26.6 cal/deg mol
C_ρ (cry)	17.0 cal/deg mol
ΔH_{fus}	30.1 kcal/mol

Preparation

Zinc chloride is prepared by the reaction of zinc oxide or zinc metal with dilute hydrochloric acid, followed by crystallization:

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$$

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

Analysis

Elemental composition: Zn 47.97%, Cl 52.03%. The compound usually contains small amounts of oxychloride and water. An aqueous solution may be analyzed for zinc by AA, ICP, and other methods (See Zinc), and for chloride ion by titration against a standard solution of silver nitrate using potassium chromate indicator. Chloride ion also may be determined by ion chromatography after sufficient dilution.

Toxicity

Inhalation of zinc chloride fumes can injure lungs and respiratory tract. Dusts or fumes also cause dermatitis, boils, conjunctivitis, and gastrointestinal tract upset (Lewis(Sr), R.J. 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed. New York: Van Nostrand Reinhold).

LD_{50} oral (rat): 350mg/kg
LC_{LO} (inhalation): 1.960 g/m^3/10 min

ZINC CYANIDE

[557-21-1]
Formula $Zn(CN)_2$; MW 117.42

Uses

Zinc cyanide is used in electroplating; as an insecticide; and for separating ammonia from producer gas.

Physical Properties

White powder; orthorhombic crystals; density 1.852 g/cm^3; decomposes at

800°C; insoluble in water (about 5mg/L at 20°C); soluble in alkalies, potassium cyanide and ammonia solutions; insoluble in alcohol.

Thermochemical Properties

$\Delta Hf°$	22.9 kcal/mol

Preparation

Zinc cyanide is precipitated by mixing solutions of potassium cyanide and a soluble zinc salt, such as zinc chloride or sulfate:

$$Zn^{2+}(aq) + 2CN^{-}(aq) \rightarrow Zn(CN)_2(s)$$

Analysis

Elemental composition: Zn 55.68%, C 20.46%, N 23.86%. A small and measured amount is treated with dilute sulfuric acid. Hydrogen cyanide generated is swept with a purging gas and collected in sodium hydroxide solution. The solution is analyzed for cyanide by a colorimetric method using pyridine-barbituric acid reagent or by cyanide ion-specific electrode (See Hydrogen Cyanide, Analysis). The acid solution may be analyzed for zinc to measure its content in the compound.

Toxicity

The compound is toxic by oral and intraperitoneal routes. The intraperitoneal lethal dose in rat is 100 mg/kg.

ZINC FLUORIDE

[7783-49-5]

Formula ZnF_2; MW 103.39; forms a tetrahydrate, $ZnF_2 \cdot 4H_2O$ [13986-18-0], MW 175.45

Uses

Zinc fluoride is used in the manufacture of phosphors for fluorescent lights. It also is used in electroplating baths, in preservation of wood, in glazes and enamels for ceramics, and in fluorination reactions of organics.

Physical Properties

Anhydrous zinc fluoride is a white hygroscopic solid; tetragonal needles; density 4.9 g/cm^3; melts at 872°C; vaporizes at 1,500°C; vapor pressure 1 torr at 1,243°C and 5 torr at 1,328°C; practically insoluble in water, 5.2 mg/L; sparingly soluble in HCl, HNO_3 and ammonia solution.

The hydrated salt, $ZnF_2 \cdot 4H_2O$, is a white crystalline solid; rhombohedral crystals; density 2.30 g/cm^3; loses water of crystallization at 100°C; sparingly soluble in water, about 1.52 g/100mL at 20°C.

Thermochemical Properties

$\Delta Hf°$	–182.7 kcal/mol
$\Delta Gf°$	–170.5 kcal/mol
S°	17.6 cal/deg mol
C_ρ	15.7 cal/deg mol
ΔH_{vap}	45.4 kcal/mol

Preparation

Zinc fluoride may be prepared by heating zinc hydroxide or zinc carbonate with hydrogen fluoride:

$$Zn(OH)_2 + 2HF \rightarrow ZnF_2 + 2H_2O$$

$$ZnCO_3 + 2HF \rightarrow ZnF_2 + CO_2 + H_2O$$

Also, it can be precipitated by adding a solution of sodium fluoride to that of zinc acetate:

$$(CH_3COO)_2Zn + 2NaF \rightarrow ZnF_2 + 2CH_3COONa$$

Analysis

Elemental composition: Zn 63.24%, F 36.76%. ZnF_2 may be characterized from its x-ray and other physical properties. The water of crystallization in the tetrahydrate may be determined by thermogravimetric method. A small amount of compound is dissolved in water (anhydrous salt is very slightly soluble in water) and analyzed for fluoride ion by the electrode method or by ion chromatography. A diluted acid solution of the compound is analyzed for zinc by various instrumental methods (See Zinc).

ZINC HYDROXIDE

[20427-58-1]
Formula: $Zn(OH)_2$; MW 99.41

Uses

Zinc hydroxide is used in the preparation of other zinc compounds. Another application is as an absorbent in surgical dressings.

Physical Properties

Colorless orthorhombic crystals; density 3.053 g/cm^3; decomposes at 125°C; slightly soluble in water.

Thermochemical Properties

$\Delta Hf°$	–153.4 kcal/mol

$\Delta Gf°$	–132.3 kcal/mol
S°	19.4 cal/deg mol

Preparation

The compound is prepared by adding a strong alkali to a solution of zinc sulfate or chloride:

$$ZnSO_4 + 2NaOH \rightarrow Zn(OH)_2 + Na_2SO_4$$

Analysis

Zinc hydroxide is decomposed to form zinc oxide and water; the mass of oxide formed may be determined by gravimetry:

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

The oxide may be characterized by x-ray diffraction.

The zinc content in the hydroxide may be determined by flame- or furnace AA or by ICP-AES after acid digestion.

ZINC NITRATE

[7779-88-6]

Formula $Zn(NO_3)_2$; MW 189.40 obtained as hexahydrate, $Zn(NO_3)_2 \cdot 6H_2O$ [10196-18-6]; MW 297.49; also forms a stable trihydrate, $Zn(NO_3)_2 \cdot 3H_2O$

Uses

The compound is used as a mordant in dyeing and as a latex coagulant. It also is used as an acid catalyst and as an analytical standard for zinc.

Physical Properties

The hexahydrate, $Zn(NO_3)_2 \cdot 6H_2O$, is a colorless and odorless crystalline solid; tetragonal structure; density 2.065 g/cm^3 at 15°C; melts at 36.4°C; loses all its water of crystallization between 105 to 131°C; very soluble in water, about 184 g/100mL water at 20°C; the aqueous solution acidic, the pH of a 5% solution is about 5.1; also very soluble in alcohol.

The trihydrate, $Zn(NO_3)_2 \cdot 3H_2O$ consists of colorless needles; melts at 45.5°C; very soluble in water, 327 g/100mL at 40°C.

Thermochemical Properties

$\Delta Hf°$ [$Zn(NO_3)_2$]	–115.6 kcal/mol
$\Delta Hf°$ [$Zn(NO_3)_2 \cdot H_2O$]	–192.4 kcal/mol
$\Delta Hf°$ [$Zn(NO_3)_2 \cdot 2H_2O$]	–265.4 kcal/mol
$\Delta Hf°$ [$Zn(NO_3)_2 \cdot 4H_2O$]	–406.1 kcal/mol
$\Delta Hf°$ [$Zn(NO_3)_2 \cdot 6H_2O$]	–551.3 kcal/mol
$\Delta Gf°$ [$Zn(NO_3)_2 \cdot 6H_2O$]	–423.8 kcal/mol

S°	$[Zn(NO_3)_2 \cdot 6H_2O]$	109.2 cal/deg/mol
C_ρ	$[Zn(NO_3)_2 \cdot 6H_2O]$	77.2 cal/deg mol

Preparation

Zinc nitrate is prepared by reacting zinc metal, zinc oxide or zinc hydroxide with nitric acid followed by crystallization. The salt is obtained as hexahydrate:

$$Zn + 2HNO_3 \rightarrow Zn(NO_3)_2 + H_2$$

$$ZnO + 2HNO_3 \rightarrow Zn(NO_3)_2 + H_2O$$

$$Zn(OH)_2 + 2HNO_3 \rightarrow Zn(NO_3)_2 + 2H_2O$$

The salt also is sold commercially in the form of fused pieces and technical flakes containing about 20% and 25.6% water, respectively.

Analysis

Water of crystallization in hydrated salt can be measured by thermogravimetric analysis. Zinc can be measured in an aqueous solution by flame- or furnace- AA or ICP-AES (See Zinc). Nitrate anion can be measured in a diluted solution by ion-selective electrode or by ion chromatography.

ZINC OXIDE

[1314-13-2]
Formula: ZnO; MW 81.38
Synonyms: zinc white; zincite; flowers of zinc

Occurrence and Uses

Zinc oxide occurs in nature as mineral zincite. It is the most important zinc compound and has numerous industrial applications. Zinc oxide is the pigment in white paints. It is used to make enamels, white printing inks, white glue, opaque glasses, rubber products and floor tiles. It is used in cosmetics, soaps, pharmaceuticals, dental cements, storage batteries, electrical equipment, and piezoelectric devices. Other applications are as a flame retardant, as a UV absorber in plastics, and a reagent in analytical chemistry. A major application of zinc oxide is in the preparation of most zinc salts. In medicine, the compound is used as an antiseptic, an astringent and a topical protectant.

Physical Properties

White or yellowish-white powder; odorless; bitter taste; hexagonal crystal; refractive index 2.008; density 5.606 g/cm^3; melts at 1,975°C; practically insoluble in water, 1.6 mg/L at about 30°C; soluble in dilute acids, ammonia solution, and alkali hydroxides.

Thermochemical Properties

$\Delta Hf°$	–83.24 kcal/mol
$\Delta Gf°$	–76.08 kcal/mol
S°	10.43 cal/deg mol
C_ρ	9.62 cal deg/mol

Production

Zinc oxide is obtained as an intermediate in recovering zinc from minerals (See Zinc, Recovery). The oxide is prepared by vaporizing zinc metal and oxidation of the zinc vapors with preheated air (French process). The oxide can be produced by other processes. Another method involves roasting franklinite and other ores with coal and then oxidizing the product in air.

Reactions

Zinc oxide reacts with mineral acids to yield corresponding zinc salts when the solution is evaporated. Thus, with sulfuric acid it forms zinc sulfate (hydrated):

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$

Reactions with organic acids such as acetic or propionic acid yields zinc acetate, $(CH_3COO)_2Zn$, or zinc propionate, $(CH_3CH_2COO)_2Zn$, upon concentration.

Fusion of zinc oxide with fatty acids at elevated temperatures produces fatty salts. Thus, fusion with oleic or linoleic acid forms zinc oleate, $Zn(C_{17}H_{33}COO)_2$, or zinc linoleate, $Zn(C_{17}H_{31}COO)_2$.

Reaction with tellurium powder in alkaline solution yields red crystalline zinc telluride, ZnTe.

Zinc oxide reacts with potassium dichromate in solution in the presence of sulfuric acid to form a greenish-yellow pigment, zinc yellow or citron yellow [11103-86-9], $4ZnO \cdot 4CrO_3 \cdot K_2O \cdot 3H_2O$

Analysis

Elemental composition: Zn 80.34%, O 19.66%. The oxide is characterized by x-ray diffraction. Zinc content may be measured by dissolving the oxide in nitric acid, diluting and analyzing by AA or ICP (see Zinc).

Toxicity

Exposure to zinc oxide fumes from welding and other operations can cause metal fume fever. Its symptoms are chills, fever, cough, and tightness in the chest.

ZINC SULFATE

[7733-02-0]

Formula: $ZnSO_4$; MW 161.44; forms several hydrates; the commercial product

is heptahydrate, $ZnSO_4 \cdot 7H_2O$ [7446-20-0], MW 287.56; the monohydrate $ZnSO_4 \cdot H_2O$ [7446-19-7], MW 179.47
Synonyms: white vitriol; zinc vitriol.

Occurrence and Uses

Zinc sulfate occurs in nature as the mineral, zinkosite. The heptahydrate, $ZnSO_4 \cdot 7H_2O$ is the mineral, goslarite. The salt is used as a mordant in calico-printing, in making rayon, in preserving wood, in animal feeds, in electroplating, and in preparing many zinc compounds.

Physical Properties

The anhydrous sulfate is a colorless rhombohedral crystalline solid; refractive index 1.658; density 3.54 g/cm^3; decomposes at 600°C; soluble in water, methanol, and glycerol.

The heptahydrate, $ZnSO_4 \cdot 7H_2O$, is a colorless crystalline solid; metallic taste; rhombohedral crystals; effloresces; refractive index 1.457; density 1.957 g/cm^3 at 25°C; melts at 100°C; loses all its water molecules at 280°C; decomposes above 500°C; very soluble in water, 96.5 g/100mL at 20°C; soluble in glycerol, 40 g/100 mL; insoluble in alcohol.

The hexahydrate, $ZnSO_4 \cdot 6H_2O$ constitutes colorless monoclinic or tetragonal crystals; density 2.072 g/cm^3 at 15°C; loses five water molecules at 70°C; soluble in water.

Thermochemical Properties

$\Delta Hf°$ [$ZnSO_4$]	–234.9 kcal/mol
$\Delta Hf°$ [$ZnSO_4 \cdot H_2O$]	–311.8 kcal/mol
$\Delta Hf°$ [$ZnSO_4 \cdot 6H_2O$]	–663.8 kcal/mol
$\Delta Hf°$ [$ZnSO_4 \cdot 7H_2O$]	–735.6 kcal/mol
$\Delta Gf°$ [$ZnSO_4$]	–209.0 kcal/mol
$\Delta Gf°$ [$ZnSO_4 \cdot H_2O$]	–270.6 kcal/mol
$\Delta Gf°$ [$ZnSO_4 \cdot 6H_2O$]	–555.6 kcal/mol
$\Delta Gf°$ [$ZnSO_4 \cdot 7H_2O$]	–612.6 kcal/mol
S° [$ZnSO_4$]	28.6 cal/deg/mol
S° [$ZnSO_4 \cdot H_2O$]	33.1 cal/deg/mol
S° [$ZnSO_4 \cdot 6H_2O$]	86.9 cal/deg/mol
S° [$ZnSO_4 \cdot 7H_2O$]	92.9 cal/deg/mol
C_ρ [$ZnSO_4 \cdot 6H_2O$]	85.5 cal/deg mol
C_ρ [$ZnSO_4 \cdot 7H_2O$]	91.6 cal/deg mol

Production

Zinc sulfate is produced as an intermediate in recovering zinc from mineral zinc blende, ZnS (see Zinc, Recovery). The mineral is roasted at about 1,000°C to form zinc oxide and sulfur dioxide which, on prolonged heating in excess air, converts to zinc sulfate:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

$$2ZnO + 2SO_2 + O_2 \rightarrow 2ZnSO_4$$

In the zinc recovery process, roasted products are leached with sulfuric acid, whereupon zinc oxide is converted to sulfate.

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$

Also, zinc sulfate can be prepared by reacting metallic zinc with dilute sulfuric acid followed by evaporation and crystallization:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

Analysis

Water of crystallization in hydrated salts can be measured by thermogravimetric analysis. Zinc can be analyzed in an aqueous solution by AA or ICP. Sulfate can be identified by precipitation with barium chloride solution or by ion chromatography. The zinc content in the heptahydrate is determined by AA, ICP and other instrumental methods.

ZINC SULFIDE

[1314-98-3]
Formula ZnS; MW 97.46
Synonym: zinc blende

Occurrence and Uses

Zinc sulfide occurs in nature in two crystalline forms, the minerals, wurtzite, and sphalerite. Sulfide ore is the principal zinc mineral.

The most important use of this compound is as a pigment. As lithopone, a mixture with barium sulfate, it forms a low gloss interior house paint. The pigment, “mineral white” is made by combining zinc sulfide with zinc oxide. Zinc sulfide is incorporated into phosphors to produce luminescence when irradiated with light. It is used in making luminous dials, x-ray and television screens, and fluorescent lights. Also, it is used in making white and opaque glass and as a base for color lakes (which consist of an organic pigment with an inorganic carrier)..

Physical Properties

Zinc sulfide is white to gray-white or pale yellow powder. It exists in two crystalline forms, an alpha (wurtzite) and a beta (sphalerite). The wurtzite form has hexagonal crystal structure; refractive index 2.356; density 3.98 g/cm^3; melts at 1,700°C; practically insoluble in water, about 6.9 mg/L; insoluble in alkalis; soluble in mineral acids. The sphalerite form arranges in cubic crystalline state; refractive index 2.368; density 4.102 g/cm^3; changes to alpha form at 1,020°C; practically insoluble in water, 6.5 mg/L; soluble in mineral acids, insoluble in alkalis. When zinc sulfide contains water, it slowly oxidizes to sulfate on exposure to air.

Thermochemical Properties

ΔHf° [wurtzite]	–46.04 kcal/mol
$\Delta H f^\circ$ [sphalerite]	–49.23 kcal/mol
$\Delta G f^\circ$ [sphalerite]	–48.11 kcal/mol
S° [sphalerite]	13.8 cal/deg mol
C_ρ [sphalerite]	11.0 cal/ deg mol

Production

Zinc sulfide is mined from natural deposits and concentrated by various processes.

Also, zinc sulfide may be prepared in the laboratory by passing hydrogen sulfide through an aqueous solution of a soluble zinc salt, such as zinc chloride or zinc nitrate. The precipitate is filtered, washed, and dried.

Analysis

Elemental composition: Zn 67.09%, S 32.91%. The compound (or the minerals) may be identified by x-ray methods and from their physical properties. The zinc content may be analyzed by AA or ICP-AES in an acid solution.

ZINC THIOCYANATE

[557-42-6]
Formula Zn $(SCN)_2$; MW 181.56
Synonyms: zinc sulfocyanate; zinc rhodanide

Uses

Zinc thiocyanate is an analytical reagent. Other applications are dyeing of textiles and as a swelling agent for cellulose esters.

Physical Properties

White deliquescent crystals; soluble in water and alcohol; aqueous solution slightly acidic

Preparation

Zinc thiocyante is prepared by the reaction of ammonium thiocyanate with zinc hydroxide

Analysis

The aqueous solution is analyzed for zinc by AA or ICP-AES. Thiocyanate ion can be determined by ion chromatography.

ZIRCONIUM

[7440-67-7]
Symbol Zr; atomic number 40; atomic weight 91.224; a Group IVB (Group 4) element of titanium group; a transition metal; electron configuration $[Kr]4d^25s^2$; valence states, +2, +3, +4; most stable valence +4; atomic radius 1.60Å; ionic radius, Zr^{4+} in crystal 0.84Å for coordination number 8; standard electrode potential, E° for $Zr^{4+} + 4e^- \leftrightarrow Zr$ is –1.45V; five naturally occurring isotopes; Zr-90 (51.45%), Zr-91 (11.22%), Zr-92 (17.15%), Zr-94 (17.38%), Zr-96 (2.80%); twenty-one artificial radioactive isotopes in the mass range 80-89, 93, 95, 97-105; longest-lived radioisotope, is the beta-emitter Zr-93, $t_{1/2}$ 1.5×10^6 years; shortest-lived radioisotope Zr-105, $t_{1/2}$ 1 sec.

History, Occurrence and Uses

Klaproth discovered zirconium oxide in 1789 while investigating a semiprecious gemstone mined in Sri Lanka. The gemstone was a modification of the mineral zircon. Klaproth named the element zirconium from the Arabic word *zargun*, meaning gold color. The element was first prepared in an impure form by Berzelius in 1824 by reduction of potassium zirconium fluoride, K_2ZrF_6 with potassium. Lely and Hamburger in Germany produced high purity zirconium in 1914 by reducing resublimed zirconium tetrachloride, $ZrCl_4$, with highly pure sodium. Very pure metal was produced by van Arkel and de Boer in 1925 by decomposition of zirconium iodide, ZrI_4.

Zirconium is found in small amounts widely spread throughout nature, occurring in many alluvial deposits of lake and stream beds and ocean beaches. The most important mineral is zircon, or zircon orthosilicate, $ZrSiO_4$. Other zirconium minerals are eudialite, $(Na, Ca, Fe)_6ZrSi_6O_{18}(OH, Cl)$, and baddeleyite, ZrO_2. It also occurs in monazite sand. The abundance of zirconium in the earth's crust is estimated as 165 mg/kg.

The most important applications of zirconium involve its alloys, Zircaloy. The alloy offers excellent mechanical and heat-transfer properties and great resistance to corrosion and chemical attack. This, in conjunction with the fact that zirconium has a low neutron absorption cross section, makes this alloy a suitable choice as a construction material for thermal nuclear reactors and nuclear power plants. Other uses are as an ingredient of explosive mixtures, as "getter" in vacuum tubes, and in making flash bulb, flash powder (historical), and lamp filaments, in rayon spinnerets, and in surgical appliances.

Physical Properties

Silvery gray lustrous metal or bluish black amorphous powder; close-packed hexagonal lattice; transforms to a body-centered cubic structure at 865°C; density 6.506 g/cm³; melts at about 1,852°C; vaporizes at 4,377°C; electrical resistivity 38.8 and 42.9 microhm-cm at 0°C and 25°C, respectively; Young's modulus, annealed 11.35×10^6 psi; shear modulus 5.42×10^6 psi; Poisson's ratio 0.33; magnetic susceptibility 1.55×10^{-6} cgs units at 1,000°K; thermal neutron absorption cross section 0.18 barns; insoluble in water; slightly soluble in acids (solubility varies, see under Reactions); soluble in hydrofluoric acid and aqua regia.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	145.5 kcal/mol
$\Delta G_f°$ (cry)	0.0 kcal/mol
$\Delta G_f°$ (gas)	135.4 kcal/mol
S° (cry)	9.32 cal/deg mol
S° (gas)	43.3 cal/deg mol
C_ρ (cry)	6.06 cal/deg mol
C_ρ (gas)	6.37 cal/deg mol
ΔH_{fus}	5.02 kcal/mol
Thermal conductivity(at 27°C)	0.227 W/cm K
Coefficient of linear expansion, at 25°C	5.7×10^{-6}/°C

Recovery

The metal is most often recovered from its principal ore, zircon. The ore is mined, crushed and preliminary segregation is by gravity, electrostatic, and magnetic separation. Separated ore mixed with carbon is charged into an arc furnace and heated to about 3,500°C. This forms zirconium carbide and silicon monoxide, and the monoxide is driven off as vapor. Zirconium carbide is then placed in a chlorinator and heated with chlorine gas at high temperatures. The carbide is converted to zirconium tetrachloride, $ZrCl_4$. Also, small amounts of hafnium that is always associated with zirconium converts to its tetrachloride, $HfCl_4$.

The crude tetrachloride mixture of zirconium and hafnium is dissolved in ammonium thiocyanate solution. The solution is extracted with methyl isobutyl ketone (MIBK). MIBK is passed countercurrent to aqueous mixture of tetrachloride in the extraction column. Hafnium is preferentially extracted into MIBK leaving zirconium in the aqueous phase. Simultaneously, zirconium tetrachloride oxidizes to zirconyl chloride, $ZrOCl_2$. When sulfuric acid is added to aqueous solution of zirconyl chloride, the chloride precipitates as a basic zirconium sulfate. On treatment with ammonia solution the basic sulfate is converted into zirconium hydroxide, $Zr(OH)_4$. Zirconium hydroxide is washed, dried, and calcined to form zirconium oxide, ZrO_2.

Zirconium metal is produced from its tetrachloride by reduction with magnesium by the Kroll process. The oxide obtained above is converted to zirconium tetrachloride by heating with carbon and chlorine. In practice, the oxide is mixed with lampblack, powdered sugar, and a little water, and pelletized. The dried pellet is then heated with chlorine in a chlorinator to produce ziroconium tetrachloride:

$$ZrO_2 + 2C + 2Cl_2 \rightarrow ZrCl_4 + 2CO$$

The Kroll process involves heating molten magnesium and zirconium tetrachloride vapor in a sealed furnace in the absence of air under a helium atmosphere. The reaction forms zirconium sponge and magnesium chloride:

$$ZrCl_4 + 2Mg \rightarrow Zr + 2MgCl_2$$

Magnesium chloride and excess magnesium are removed by distillation at reduced pressure. Pure zirconium may be prepared by several methods that include iodide decomposition process, zone refining, and electron beam melting. Also, Zr metal may be electrorefined in a molten salt bath of potassium zirconium fluoride, K_2ZrF_6

Reactions

Zirconium exhibits quadrivalency in most of its compounds although divalent and trivalent compounds also exist. Zirconium reacts with oxygen to form zirconium oxide, ZrO_2. In powder form, Zr metal ignites spontaneously forming oxide. Solid metal, however, is stable in air at ordinary temperatures, but reacts slowly at 200°C. Reaction is rapid at high temperatures.

Reaction with hydrogen occurs at temperatures of 300 to 1,000°C forming a brittle dihydride, ZrH_2. Zirconium combines with halogens at high temperatures forming tetrahalides. Reactions occur in the range 200 to 400°C. Solid tetrahalides sublime above 300°C.

Zirconium combines with nitrogen at 400°C. The reaction becomes rapid above 800°C. The product is zirconium nitride, ZrN. Some nitrogen also dissolves in the metal forming a solid state solution. Zirconium at elevated temperatures combines with most other nonmetals forming binary compounds, including sulfur, phosphorus, and carbon. Although stable to most acids, the metal is attacked by concentrated hydrochloric and sulfuric acids under boiling conditions, aqua regia, and hydrofluoric acid. The metal is stable in organic acids under all conditions. Also, the metal is stable to caustic alkalies.

The metal reacts rapidly with carbon dioxide above 1,000°C forming zirconium oxide and zirconium carbide:

$$2Zr + CO_2 \rightarrow ZrO_2 + ZrC$$

A similar reaction occurs with carbon monoxide above 800°C forming zirconium oxide and carbide.

Analysis

The metal can be analyzed by several instruments including flame-AA, ICP-AES, ICP-MS, and x-ray fluorescence. Also, it can be detected by neutron activation analysis.

ZIRCONIUM CARBIDE

[12020-14-3]
Formula: ZrC; MW 103.235

Uses

Zirconium carbide is a refractory material. It is used in making incandescent filaments, high temperature electrical conductors, and cutting tool components.

Physical Properties

Gray metallic solid; cubic structure; very hard, hardness > 8.0 Mohs; density 6.73 g/cm^3; melts at 3,532°C; insoluble in water; slightly soluble in concentrated sulfuric acid; soluble in hydrofluoric acid and oxidizing acids, such as nitric and perchloric acids; attacked by oxidizers

Thermochemical Properties

$\Delta H_f°$	–48.5 kcal/mol
$\Delta G_f°$	–47.7 kcal/mol
S°	7.96 cal/deg mol
C_ρ	9.06 cal/deg mol

Preparation

Zirconium carbide is prepared by heating a mixture of zirconium oxide and coke in an arc furnace.

Analysis

Zr carbide is digested with nitric and perchloric acid. The solution is diluted and analyzed for zirconium by AA or ICP-AES. Also, the carbide may be identified by x-ray diffraction.

ZIRCONIUM HYDRIDE

[7704-99-6]
Formula: ZrH_2; MW 93.24

Uses

Zirconium hydride is a “getter” in vacuum tubes. The compound is a powerful reducing agent in acid solution or at high temperatures. Also, it is used as a source of pure hydrogen and a catalyst in hydrogenation reactions. Some other applications are in powder metallurgy; as a moderator in nuclear reactors; and as a metal-foaming agent.

Physical Properties

Grayish-black powder; density 5.60 g/cm^3; stable in water; soluble in dilute hydrofluoric acid; soluble in concentrated acids.

Thermochemical Properties

$\Delta H_f°$	–40.4 kcal/mol
$\Delta G_f°$	–30.8 kcal/mol
S°	8.37 cal/deg mol
C_ρ	7.40 cal/deg mol

Preparation

Zirconium hydride may be prepared by heating zirconium oxide with magnesium in the presence of hydrogen:

$$ZrO_2 + 2Mg + H_2 \rightarrow ZrH_2 + 2MgO$$

Alternatively, hydride may be made by heating zirconium oxide with calcium hydride in the presence of hydrogen.

Hydride also may be obtained by combining zirconium metal with hydrogen at elevated temperature.

Analysis

Elemental composition: Zr 97.84%, H 2.16%. The compound may be dissolved in concentrated hydrochloric acid, diluted, and analyzed for zirconium (See Zirconium).

ZIRCONIUM HYDROXIDE

[14475-63-9]
Formula: $Zr(OH)_4$; MW 159.25

Uses

Zirconium hydroxide is used in glass colorants. The compound also is used to prepare zirconium oxide, sulfate, phosphate, and other salts.

Physical Properties

White, bulky amorphous powder; density 3.25 g/cm^3; decomposes to oxide at about 500°C; very slightly soluble in water, about 200 mg/L at 20°C; soluble in mineral acids

Preparation

Zirconium hydride precipitates on adding sodium hydroxide solution to an aqueous solution of zirconium salt:

$$ZrCl_4\,(aq) + 4NaOH(aq) \rightarrow Zr(OH)_4\,(s) + 4NaCl(aq)$$

Reactions

When heated at 550°C the hydroxide decomposes to oxide:

$$Zr(OH)_4 \rightarrow ZrO_2 + 2H_2O$$

Reacitons with mineral acids followed by crystallization forms corresponding zirconium salts. Thus hydrochloric, sulfuric, and phosphoric acids yield chloride, sulfate and phosphate of zirconium respectively.

Analysis

Elemental composition: Zr 57.28%, H 2.53%, O 40.19%. The compound is dissolved in acid and analyzed for zirconium (See Zirconium). Hydroxide is heated at about 550°C and residual ZrO_2 is measured by gravimetry. Also, the oxide formed may be identified by x-ray diffraction.

ZIRCONIUM NITRATE

[13746-89-9]
Formula: $Zr(NO_3)_4$; MW 339.25; obtained as pentahydrate, $Zr(NO_3)_4 \cdot 5H_2O$, MW 429.32

Uses

Zirconium nitrate is used as a preservative, as an analytical standard for zirconium, and in making zirconium salts

Physical Properties

The pentahydrate is a white crystalline solid; very hygroscopic; refractive index 1.60; very soluble in water; the aqueous solution acidic; soluble in alcohol

Preparation

Zirconium nitrate is prepared by reacting nitric acid with zirconium oxide:

$$ZrO_2 + 4HNO_3 \rightarrow Zr(NO_3)_4 + 2H_2O$$

The compound is crystallized as pentahydrate following evaporation to dryness.

Analysis

Elemental composition (for anhydrous $Zr(NO_3)_4$: Zr 26.89%, N 16.51, O 56.59%. The water of crystallization can be measured by thermogravimetric methods. The nitrate ion can be measured by ion-selective electrode or ion chromatography. Zirconium may be analyzed in an aqueous solution by flame

AA or ICP-AES (See Zirconium).

ZIRCONIUM OXIDE

[1314-23-4]
Formula: ZrO_2; MW 123.22
Synonyms: zirconia; zirconium dioxide; zirconic anhydride

Occurrence and Uses

Zirconium oxide occurs in nature as the mineral baddeleyite. The oxide has many industrial applications. It is used as a refractory material. It is used in making highly reflective glazes for ceramics, glasses, linings of metallurgical furnaces, crucibles, and laboratory equipment. The oxide is used to produce oxyhydrogen and incandescent lights. Other uses are in producing piezoelectric crystals, heat-resistant fibers, and high-frequency induction coils. The hydrous oxide is used in treating dermatitis resulting from poison ivy.

Physical Properties

White, heavy, amorphous powder or monoclinic crystals; refractive index 2.13; density 5.68 g/cm^3; Mohs hardness 6.5; transforms to tetragonal structure above 1,100°C and cubic form above 1,900°C; melts at 2,710°C and vaporizes at about 4,300°C; insoluble in water; soluble in hydrofluoric acid and hot sulfuric, nitric and hydrochloric acids.

Thermochemical Properties

$\Delta H_f°$	–263.0 kcal/mol
$\Delta G_f°$	–249.2 kcal/mol
S°	12.0 cal/deg mol
C_ρ	13.4 cal/deg mol
ΔH_{fus}	20.8 kcal/mol

Production

Zirconium oxide occurs in nature as mineral baddeleyite. Ore is mined from natural deposits and subjected to concentration and purifcation by various processes. The oxide, however, is more commonly obtained as an intermediate in recovering zirconium from zircon, $ZrSiO_4$ (See Zirconium, Recovery).

Also, the oxide may be prepared in the laboratory by thermal decomposition of zirconium hydroxide or zirconium carbonate:

$$Zr(OH)_4 \rightarrow ZrO_2 + 2H_2O$$

$$Zr(CO_3)_2 \rightarrow ZrO_2 + 2CO_2$$

Reactions

Zirconium oxide combines with silica when heated in an arc furnace producing zirconium silicate, $ZrSiO_4$:

$$ZrO_2 + SiO_2 \rightarrow ZrSiO_4$$

Zirconium oxide is reduced by carbon when heated in a arc furnace, forming zirconium carbide

$$ZrO + 2C \rightarrow ZrC + CO$$

Zirconium oxide is reduced to hydride when heated with magnesium in the presence of hydrogen:

$$ZrO + Mg + H_2 \rightarrow ZrH_2 + MgO$$

Reaction with nitric acid forms zirconium nitrate and with hydrochloric acid, zirconyl chloride, $ZrOCl_2$, is produced.

Fusion with caustic soda at high temperatures forms water-soluble sodium zirconate:

$$ZrO_2 + 4NaOH \rightarrow Na_4ZrO_4 + 2H_2O$$

Analysis

Elemental composition: Zr 74.03%, O 25.97%. Oxide may be identified by x-ray diffraction. Zirconium content in the oxide may be measured by analyzing an acid extract by flame AA or ICP-AES.

ZIRCONIUM SILICATE

[10101-52-7]
Formula: $ZrSiO_4$; MW 183.31
Synonyms: zircon; hyacinth; zirconium orthosilicate

Occurrence and Uses

Zirconium silicate occurs in nature as mineral zircon [14940-68-2], the principal source of zirconium. It is used in producing metallic zirconium and its oxide. Other uses are in refractories; glazes; porcelain; enamels; cements; coatings for casting molds; in fritted glass filters; foundry cores; and polishing materials. Also, it is used as a stabilizer for silicon rubbers; and as a catalyst in producing alkyl hydrocarbons. The compound in certain forms is used as gemstone.

Physical Properties

Colorless tetragonal crystals (when pure); presence of impurities forms various colors; density 4.56 g/cm^3; hardness 7.5 Mohs; dissociates to ZrO_2 and SiO_2 above 1,540°C; melts at 2,550°C; insoluble in water, acids, aqua regia, and alkalies; inert in most chemicals

Thermochemical Properties

$\Delta H_f°$	–486.0kcal/mol
$\Delta G_f°$	–458.7kcal/mol
S°	20.1 cal/deg mol
C_ρ	23.58 cal/deg mol

Production

Zirconium silicate occurs in nature as mineral zircon. Ore is mined from natural deposits and concentrated by various techniques (See Zirconium, Recovery). It is separated from sand by electrostatic and electromagnetic methods.

Also, the compound can be made by fusion of SiO_2 and ZrO_2 in an arc furnace, or by reacting a zirconium salt with sodium silicate in aqueous solution.

Analysis

The compound is identified by physical and x-ray diffraction methods.

ZIRCONIUM SULFATE

[14644-61-2]
Formula: $Zr(SO_4)_2$; MW 283.34; forms a stable tetrahydrate, $Zr(SO_4)_2 \cdot 4H_2O$ [7446-31-3], MW 355.41

Uses

Zirconium sulfate is used in tanning white leather, as a catalyst support, to precipitate proteins and amino acids, and as a pigment stabilizer.

Physical Properties

Anhydrous sulfate is a microcrystalline hygroscopic solid; density 3.22 g/cm^3; decomposes at 410°C; soluble in water.

The tetrahydrate, $Zr(SO_4)_2 \cdot 4H_2O$, is a white crystalline solid; orthorhombic crystals; loses three molecules of water between 100 and 150°C; becomes anhydrous at 380°C; soluble in water, 52.5 g/100g solution; the solution deposits a solid on standing; the aqueous solution is strongly acidic, decomposed by bases or on heating.

Thermochemical Properties

$\Delta H_f°$ [$Zr(SO_4)_2$]	–529.9 kcal/mol
$\Delta H_f°$ [$Zr(SO_4)_2 \cdot H_2O$]	–610.4 kcal/mol
$\Delta H_f°$ [$Zr(SO_4)_2 \cdot 4H_2O$]	–825.6 kcal/mol
C_ρ [$Zr(SO_4)_2$]	41 cal/deg mol

Preparation

Zirconium sulfate is prepared by the action of sulfuric acid on zirconium hydroxide:

$$Zr(OH)_4 + 2H_2SO_4 \rightarrow Zr(SO_4)_2 + 4H_2O$$

Also, it is prepared by treating zirconyl chloride with hot concentrated sulfuric acid:

$$ZrOCl_2 + 2H_2SO_4 \rightarrow Zr(SO_4)_2 + H_2O + 2HCl$$

Crystallization forms zirconium tetrahydrate.

Analysis

Water of crystallization may be measured by thermogravimetry. Zirconium may be analyzed in an aqueous solution by flame AA or ICP-AES. Sulfate may be identified in an aqueous solution by ion chromatography or by precipitation with barium chloride.

ZIRCONIUM TETRACHLORIDE

[10026-11-6]
Formula: $ZrCl_4$; MW 233.035
Synonym: zirconium chloride

Uses

Zirconium tetrachloride is used as a Friedel-Crafts catalyst and as a component of Ziegler-type catalysts. It serves as a starting material for producing many zirconium salts and organozirconium compounds. Other uses are in making water-repellent agents for textiles and fibrous materials, tanning agents, and in making zirconium metal.

Physical Properties

White monoclinic crystals; hygroscopic; density 2.80 g/cm^3; sublimes at 331°C; triple point 437°C; vapor pressure 1 torr at 190°C; critical temperature 504.85°C; critical pressure 56.95 atm; critical volume 319 cm^3/mol; decomposed by water; soluble in alcohol, ether, and concentrated hydrochloric acid.

Thermochemical Properties

$\Delta H_f°$	–234.3 kcal/mol
$\Delta G_f°$	–212.7 kcal/mol
S°	43.4 cal/deg mol
C_ρ	28.6 cal/deg mol
ΔH_{fus}	11.95 kcal/mol

Preparation

Zirconium tetrachloride is obtained as an intermediate in recovering zirconium metal from zircon and other minerals (See Zirconium, Recovery). The tetrachloride is obtained by heating a mixture of zirconium hydroxide and carbon with chlorine gas.

Also, tetrachloride can be made by reacting zirconium hydroxide with hydrochloric acid:

$$Zr(OH)_4 + 4HCl \rightarrow ZrCl_4 + 4H_2O$$

Reactions

Zirconium tetrachloride is reduced by heating with sodium, potassium or magnesium at high temperatures. Such reduction of tetrachloride has been the commerical method of producing zirconium metal:

$$ZrCl_4 + 4K \rightarrow Zr + 4KCl$$

Zirconium tetrachloride decomposes in water forming zirconium oxychloride and hydrochloric acid:

$$ZrCl_4 + H_2O \rightarrow ZrOCl_2 + 2HCl$$

Reaction with sodium hydroxide solution forms zirconium hydroxide:

$$ZrCl_4 + 4NaOH \rightarrow Zr(OH)_4 + 4NaCl$$

Reaction with dinitrogen pentoxide yields zirconium nitrate:

$$ZrCl_4 + 4N_2O_5 \rightarrow Zr(NO_3)_4 + 4NO_2Cl$$

Reaction with chlorine oxide forms zirconium oxychloride:

$$ZrCl_4 + Cl_2O \rightarrow ZrOCl_2 + 2Cl_2$$

Reaction with hydrofluoric acid yields zirconium tetrafluoride:

$$ZrCl_4 + 4HF \rightarrow ZrF_4 + 4HCl$$

Analysis

Elemental composition: Zr 39.14%, Cl 60.86%. The compound is decomposed in water to $ZrOCl_2$ and HCl. A portion is analyzed for zirconium (see Zirconium). Another portion is measured for chloride and oxychloride ions by ion chromatography.

ZIRCONYL CHLORIDE

[7699-43-6]
Formula: $ZrOCl_2$; MW 178.13; obtained as octahydrate, $ZrOCl_2$ $8H_2O$[13520-92-8], MW 322.25

Synonyms: zirconium oxychloride; basic zirconium chloride; dichlorooxozirconium

Uses

Zirconyl chloride is used to make pigment toners and improve properties of color lakes of acid and basic dyes. Also, it is used to prepare body deodorants and antiperspirant, water repellant, dye precipitant, catalysts, and many zirconium compounds.

Physical Properties

The octahydrate is a white silky solid; tetragonal crystals consisting of tetramers; effloresces; refractive index 1.552; density 1.91 g/cm^3; loses six water molecules at 150°C; becomes anhydrous at 210°C; decomposes at 400°C; soluble in water; aqueous solution acidic; also soluble in alcohol and ether; slightly soluble in hydrochloric acid

Thermochemical Properties

$\Delta H_f°$ (aq)	–280.3 kcal/mol

Preparation

The compound is prepared by dissolving zirconium tetrachloride, $ZrCl_4$, or sodium zirconate, Na_4ZrO_4, in hydrochloric acid solution followed by evaporation to obtain crystals of octahydrate.

Also, the compound can be prepared by reacting zirconium tetrachloride with chlorine oxide:

$$ZrCl_4 + Cl_2O \rightarrow ZrOCl_2 + 2Cl_2$$

Analysis

Elemental composition (anhydrous $ZrOCl_2$): Zr 51.21%, Cl 39.81%, O 8.98%. The compound is dissolved in water and analyzed for zirconium (See Zirconium). The aqueous solution may be analyzed for oxychloride anion by ion chromatography.

Toxicity

Moderately toxic by ingestion, intraperitoneal and subcutaneous routes.

LD_{50} (intraperitioneal) (rat): 400mg/kg

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Nitrogen monoxide	10024-97-2	664
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Nitrogen pentoxide	10102-03-1	651
Nitrogen peroxide	10102-44-0	648
Nitrogen tetroxide	10544-72-6	652
Nitrogen trichloride	10025-85-1	654
Nitrogen trifluoride	7783-54-2	655
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Nitrosyl fluoride	7789-25-5	659
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Nitroxylsulfuric acid	7782-78-7	661
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Phosphorus pentachloride	10026-13-8	709
Phosphorus pentafluoride	7647-19-0	711
Phosphorus pentaoxide	1314-56-3	713
Phosphorus pentoxide	1314-56-3	713
Phosphorus trichloride	7719-12-2	715
Phosphorus trihydride	7803-51-2	692
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Platinum dichloride	10025-65-7	722
Platinum dioxide	1314-15-4	723
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Platinum tetrachloride	37773-49-2	725
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Potassium acid phthalate	877-24-7	756
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Potassium bichromate	7778-50-9	751
Potassium biphosphate	7778-77-0	772
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Potassium hexacyanoferrate(III)	13746-66-2	752
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Potassium hydride	7693-26-7	756
Potassium hydrogen carbonate	298-14-6	737
Potassium hydrogen phosphate	7758-11-4	772
Potassium hydrogen phthalate	877-24-7	756
Potassium hydrogen sulfide	1310-61-8	738
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Potassium hydroxide	1310-58-3	758
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Potassium metaperiodate	7790-21-8	768
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Potassium nickel hexakis(cyanoferrate(3^{-}))	53295-14-0	422
[potassium nickel hexakis(cyanoferrate(3^{-}))]	53295-14-0	421
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Potassium peroxydicarbonate	589-97-9	766
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Potassium phosphate, monobasic	7778-77-0	772
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Sodium bisulfate	7681-38-1	857
Sodium borohydride	16940-66-2	858
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Sodium hydrogen carbonate	144-55-8	855
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Sodium iodide	7681-82-5	871
Sodium molybdate	7631-95-0	585
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Sodium nitrate	7631-99-4	872
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Sodium orthophosphate, secondary	7558-79-4	874
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Sodium pyroantimonate	10049-22-6	55
Sodium rhodanate	540-72-7	880
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Sodium thiocyanate	540-72-7	880
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Strontium oxide	1314-11-0	888
Strontium sulfate	7759-02-6	889
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Sulfur chloride	10025-67-9	893
Sulfur dioxide	7446-09-5	894
Sulfur hexafluoride	2551-62-4	898
Sulfur hydride	7783-06-4	379
Sulfur monochloride	10025-67-9	893
Sulfur oxychloride	7719-09-7	903
Sulfur subchloride	10025-67-9	893
Sulfur trioxide	7746-11-9	904
Sulfureted hydrogen	7783-06-4	379
Sulfuric acid	7664-93-9	899
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Sulfuric chloride	7791-25-5	906
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[Tetraammonium hexakis(cyanoferrate(4^{-})]	14481-29-9	421
Tetraaquo chromium dichloride	13931-94-7	219
Tetraaquochromium dichloride	13931-94-7	219
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Tetraethyllead	78-00-2	482
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Tetrahydrogen hexakis(cyanoferrate(4^{-}))	17126-47-5	422
[Tetrahydrogen hexakis(cyanoferrate(4^{-})]	17126-47-5	421
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