Manahan, Stanley E. "FUNDAMENTALS OF CHEMISTRY"
Environmental Chemistry
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28 FUNDAMENTALS OF CHEMISTRY

28.1. INTRODUCTION

This chapter is designed to give those readers who have had little exposure to chemistry the basic knowledge needed to understand the material in the rest of the book. Although it is helpful for the reader to have had several courses in chemistry, including organic chemistry and quantitative chemical analysis, most of the material in this book can be understood with less. Indeed, a reader willing to do some independent study on the fundamentals of chemistry can understand much of the material in this book without ever having had any formal chemistry course work.

Chapter 28, “Fundamentals of Chemistry,” can serve two purposes. For the reader who has had no chemistry, it provides the concepts and terms basic to general chemistry. A larger category of reader consists of those who have had at least one chemistry course, but whose chemistry background, for various reasons, is inadequate. By learning the material in this chapter, plus the subject matter of Chapter 29, “Fundamentals of Organic Chemistry,” these readers can comprehend the rest of the material in the book. For a more complete coverage of basic chemistry readers should consult one of a number of basic chemistry books, such as *Fundamentals of Environmental Chemistry*[1] and other supplementary references listed at the end of the chapter.

Chemistry is the science of matter. Therefore, it deals with all of the things that surround humankind, and with all aspects of the environment. Chemical properties and processes are central to environmental science. A vast variety of chemical reactions occur in water, for example, including acid-base reactions, precipitation reactions, and oxidation-reduction reactions largely mediated by microorganisms. Atmospheric chemical phenomena are largely determined by photochemical processes and chain reactions. A large number of organic chemical processes occur in the atmosphere. The geosphere, including soil, is the site of many chemical processes, particularly those that involve solids. The biosphere obviously is where the many biochemical processes crucial to the environment and to the toxic effects of chemicals occur.

This chapter emphasizes several aspects of chemistry. It begins with a discussion of the fundamental subatomic particles that make up all matter, and explains how these are assembled to produce atoms. In turn, atoms join together to make compounds. Chemical reactions and chemical equations that represent them are discussed. Solution chemistry is especially important to aquatic chemistry and is addressed in a separate section. The important, vast discipline of organic chemistry is crucial to all parts of the environment and is addressed in Chapter 29.

28.2. ELEMENTS

All substances are composed of only about a hundred fundamental kinds of matter called **elements**. Elements, themselves, may be of environmental concern. The "heavy metals," including lead, cadmium, and mercury, are well recognized as toxic substances in the environment. Elemental forms of otherwise essential elements may be very toxic or cause environmental damage. Oxygen in the form of ozone, O_3, is the agent most commonly associated with atmospheric smog pollution and is very toxic to plants and animals. Elemental white phosphorus is highly flammable and toxic.

Each element is made up of very small entities called **atoms**; all atoms of the same element behave identically chemically. The study of chemistry, therefore, can logically begin with elements and the atoms of which they are composed. Each element is designated by an **atomic number**, a name, and a **chemical symbol**, such as carbon, C; potassium, K (for its Latin name kalium); or cadmium, Cd. Each element has a characteristic **atomic mass** (atomic weight), which is the average mass of all atoms of the element. Atomic numbers of the elements are integrals ranging from 1 for hydrogen, H, to somewhat more than 100 for some of the transuranic elements (those beyond uranium). Atomic number is a unique, important way of designating each element, and it is equal to the number of protons in the nuclei of each atom of the element (see discussion of subatomic particles and atoms, below).

Subatomic Particles and Atoms

Figure 28.1 represents an atom of deuterium, a form of hydrogen. It is seen that such an atom is made up of even smaller **subatomic particles**—positively charged **protons**, negatively charged **electrons**, and uncharged (neutral) **neutrons**.

Subatomic Particles

The subatomic particles differ in mass and charge. Their masses are expressed by the **atomic mass unit**, **u** (also called the **dalton**), which is also used to express the masses of individual atoms and molecules (aggregates of atoms). The atomic mass unit is defined as a mass equal to exactly 1/12 that of an atom of carbon-12, the isotope of carbon that contains 6 protons and 6 neutrons in its nucleus.

The proton, *p*, has a mass of 1.007277 u and a unit charge of +1. This charge is equal to 1.6022×10^{-19} coulombs, where a coulomb is the amount of electrical charge involved in a flow of electrical current of 1 ampere for 1 second. The neutron, *n*, has no electrical charge and a mass of 1.009665 u. The proton and neu-

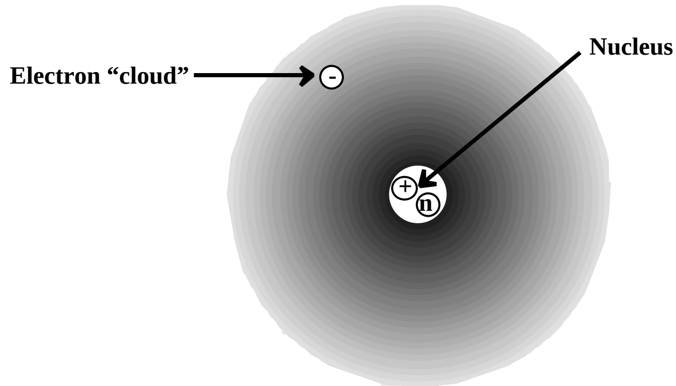


Figure 28.1. Representation of a deuterium atom. The nucleus contains one proton (+) and one neutron (n). The electron (-) is in constant, rapid motion around the nucleus forming a cloud of negative electrical charge, the density of which drops off with increasing distance from the nucleus.

tron each have a mass of essentially 1 u and are said to have a *mass number* of 1. (Mass number is a useful concept expressing the total number of protons and neutrons, as well as the approximate mass, of a nucleus or subatomic particle.) The electron, *e*, has a unit electrical charge of -1. It is very light, however, with a mass of only 0.00054859 u, about 1/1840 that of the proton or neutron. Its mass number is 0. The properties of protons, neutrons, and electrons are summarized in Table 28.1.

Table 28.1. Properties of Protons, Neutrons, and Electrons

Subatomic particle	Symbol	Unit charge	Mass number	Mass in u	Mass in grams
Proton[1]	p	+1	1	1.007277	1.6726×10^{-24}
Neutron[1]	n	0	1	1.008665	1.6749×10^{-24}
Electron[1]	e	-1	0	0.000549	9.1096×10^{-28}

[1] The mass number and charge of each of these kinds of particles may be indicated by a superscipt and subscript, respectively, as in the symbols ${}^{1}_{1}p$, ${}^{1}_{0}n$, and ${}^{0}_{-1}e$.

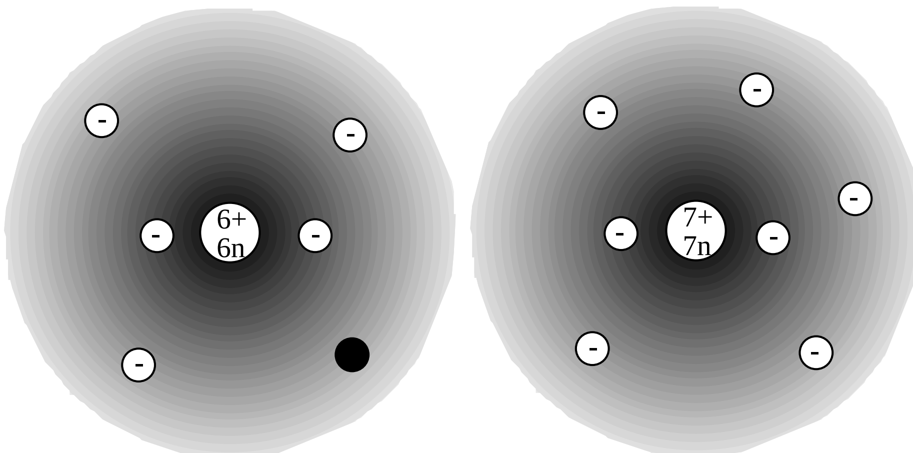
Although it is convenient to think of the proton and neutron as having the same mass, and each is assigned a mass number of 1, it is seen in Table 28.1 that their exact masses differ slightly from each other. Furthermore, the mass of an atom is not exactly equal to the sum of the masses of subatomic particles composing the atom. This is because of the energy relationships involved in holding the subatomic particles together in atoms so that the masses of the atom's constituent subatomic particles do not add up to exactly the mass of the atom.

Atom Nucleus and Electron Cloud

Protons and neutrons, which have relatively high masses compared to electrons, are contained in the positively charged **nucleus** of the atom. The nucleus has essentially all of the mass, but occupies virtually none of the volume, of the atom. An uncharged atom has the same number of electrons as protons. The electrons in an atom are contained in a cloud of negative charge around the nucleus that occupies most of the volume of the atom. These concepts are emphasized in Figure 28.2.

Isotopes

Atoms with the *same* number of protons, but *different* numbers of neutrons in their nuclei are called **isotopes**. They are chemically identical atoms of the same element, but have different masses and may differ in their nuclear properties. Some isotopes are **radioactive isotopes** or **radionuclides**, which have unstable nuclei that give off charged particles and gamma rays in the form of **radioactivity**. Radioactivity may have detrimental, or even fatal, health effects; a number of hazardous substances are radioactive and they can cause major environmental problems. The most striking example of such contamination resulted from a massive explosion and fire at a power reactor in the Ukrainian city of Chernobyl in 1986.



An atom of carbon, symbol C. Each C atom has 6 protons (+) in its nucleus, so the atomic number of C is 6. The atomic mass of C is 12.

An atom of nitrogen, symbol N. Each N atom has 7 protons (+) in its nucleus, so the atomic number of N is 7. The atomic mass of N is 14.

Figure 28.2. Atoms of carbon and nitrogen

Important Elements

An abbreviated list of a few of the most important elements that the reader should learn at this point is given in Table 28.2. A complete list of elements is given on the inside back cover of the book.

The Periodic Table

When elements are considered in order of increasing atomic number, it is observed that their properties are repeated in a periodic manner. For example, ele-

Table 28.2. List of Some of the More Important Common Elements

Element	Symbol	Atomic number	Atomic mass	Significance
Aluminum	Al	13	26.9815	Abundant in Earth's crust
Argon	Ar	18	39.948	Noble gas
Arsenic	As	33	74.9216	Toxic metalloid
Bromine	Br	35	79.904	Toxic halogen
Cadmium	Cd	48	112.40	Toxic heavy metal
Calcium	Ca	20	40.08	Abundant essential element
Carbon	C	6	12.011	"Life element"
Chlorine	Cl	17	35.453	Halogen
Copper	Cu	29	63.54	Useful metal
Fluorine	F	9	18.998	Halogen
Helium	He	2	4.00260	Lightest noble gas
Hydrogen	H	1	1.008	Lightest element
Iodine	I	53	126.904	Halogen
Iron	Fe	26	55.847	Important metal
Lead	Pb	82	207.19	Toxic heavy metal
Magnesium	Mg	12	24.305	Light metal
Mercury	Hg	80	200.59	Toxic heavy metal
Neon	Ne	10	20.179	Noble gas
Nitrogen	N	7	14.0067	Important nonmetal
Oxygen	O	8	15.9994	Abundant, essential nonmetal
Phosphorus	P	15	30.9738	Essential nonmetal
Potassium	K	19	39.0983	Alkali metal
Silicon	Si	14	28.0855	Abundant metalloid
Silver	Ag	47	107.87	Valuable, reaction-resistant metal
Sulfur	S	16	32.064	Essential element, occurs in air pollutant SO_2
Sodium	Na	11	22.9898	Essential, abundant alkali metal
Tin	Sn	50	118.69	Useful metal
Uranium	U	92	238.03	Fissionable metal used for nuclear fuel
Zinc	Zn	30	65.37	Useful metal

ments with atomic numbers 2, 10, and 18 are gases that do not undergo chemical reactions and consist of individual atoms, whereas those with atomic numbers larger by 1—elements with atomic numbers 3, 11, and 19—are unstable, highly reactive metals. An arrangement of the elements in a manner that reflects this recurring behavior is known as the **periodic table** (Figure 28.3). The periodic table is extremely useful in understanding chemistry and predicting chemical behavior. As shown in Figure 28.3, the entry for each element in the periodic table gives the element's atomic number, name, symbol, and atomic mass. More detailed versions of the table include other information as well.

Features of the PeriodicTable

Groups of elements having similar chemical behavior are contained in vertical columns in the periodic table. **Main group** elements may be designated as A groups (1A and 2A on the left, 3A through 8A on the right). **Transition elements** are those between main groups 2A and 3A. **Noble gases** (group 8A), a group of gaseous elements that are virtually chemically unreactive, are in the far right column. The chemical similarities of elements in the same group are especially pronounced for groups 1A, 2A, 7A, and 8A.

Horizontal rows of elements in the periodic table are called **periods**, the first of which consists of only hydrogen (H) and helium (He). The second period begins with atomic number 3 (lithium) and terminates with atomic number 10 (neon), whereas the third goes from atomic number 11 (sodium) through 18 (argon). The fourth period includes the first row of transition elements, whereas lanthanides and actinides are listed separately at the bottom of the table.

Electrons in Atoms

Although a detailed discussion of the placement of electrons in atoms determines how the atoms behave chemically and, therefore, the chemical properties of each element, it is beyond the scope of this chapter to discuss electronic structure in detail. Several key points pertaining to this subject are mentioned here.

Electrons in atoms are present in **orbitals** in which the electrons have different energies, orientations in space, and average distances from the nucleus. Each orbital may contain a maximum of 2 electrons. The placement of electrons in their orbitals determines the chemical behavior of an atom; in this respect the outermost orbitals and the electrons contained in them are the most important. These **outer electrons** are the ones beyond those of the immediately preceding noble gas in the periodic table. They are of particular importance because they become involved in the sharing and transfer of electrons through which chemical bonding occurs that results in the formation of huge numbers of different substances from only a few elements.

Much of environmental chemistry is concerned with electrons in atoms. In Chapters 9 and 13 are discussed examples in which the absorption of electromagnetic radiation promotes electrons to higher energy levels, forming reactive excited species and reactive free radicals with unpaired electrons. Atomic absorption and emission methods of elemental analysis involve transitions of electrons between energy levels.

Active metals | Transition metals | Nonmetals

1A 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8	8B 9	10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
1 **H** 1.0079																	2 **He** 4.00260
3 **Li** 6.941	4 **Be** 9.01218											5 **B** 10.81	6 **C** 12.011	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.998403	10 **Ne** 20.179
11 **Na** 22.98977	12 **Mg** 24.305											13 **Al** 26.98154	14 **Si** 28.0855	15 **P** 30.97376	16 **S** 32.06	17 **Cl** 35.453	18 **Ar** 39.948
19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.9559	22 **Ti** 47.88	23 **V** 50.9415	24 **Cr** 51.996	25 **Mn** 54.9380	26 **Fe** 55.847	27 **Co** 58.9332	28 **Ni** 58.69	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.9059	40 **Zr** 91.22	41 **Nb** 92.9064	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.9055	46 **Pd** 106.42	47 **Ag** 107.8682	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.69	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.9045	54 **Xe** 131.29
55 **Cs** 132.9054	56 **Ba** 137.33	57 ***La** 138.9055	72 **Hf** 178.49	73 **Ta** 180.9479	74 **W** 183.85	75 **Re** 186.207	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.9665	80 **Hg** 200.59	81 **Tl** 204.383	82 **Pb** 207.2	83 **Bi** 208.9804	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.0254	89 **†Ac** 227.0278	104 **Rf** (261)	105 **Ha** (262)	106 **Unh** (263)	107 **Uns** (262)		109 **Une** (266)									

***Lanthanide series**	58 **Ce** 140.12	59 **Pr** 140.9077	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.9254	66 **Dy** 162.50	67 **Ho** 164.9304	68 **Er** 167.26	69 **Tm** 168.9342	70 **Yb** 173.04	71 **Lu** 174.967
†Actinide series	90 **Th** 232.0381	91 **Pa** 231.0359	92 **U** 238.0289	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)

The larger and smaller labels reflect two different numbering schemes in common usage.

Figure 28.3. The periodic table of the elements.

Lewis Structures and Symbols of Atoms

Outer electrons are called **valence electrons** and are represented by dots in **Lewis symbols**, as shown for carbon and argon in Figure 28.4, below:

Lewis symbol of carbon   Lewis symbol of argon

Figure 28.4. Lewis symbols of carbon and argon.

The four electrons shown for the carbon atom are those added beyond the electrons possessed by the noble gas that immediately precedes carbon in the periodic table (helium, atomic number 2). Eight electrons are shown around the symbol of argon. This is an especially stable electron configuration for noble gases known as an **octet**. (Helium is the exception among noble gases in that it has a stable shell of only two electrons.) When atoms interact through the sharing, loss, or gain of electrons to form molecules and chemical compounds (see Section 28.3) many attain an octet of outer shell electrons. This tendency is the basis of the **octet rule** of chemical bonding. (Two or three of the lightest elements, most notably hydrogen, attain stable helium-like electron configurations containing two electrons when they become chemically bonded.)

Metals, Nonmetals, and Metalloids

Elements are divided between metals and nonmetals; a few elements with intermediate character are called metalloids. **Metals** are elements that are generally solid, shiny in appearance, electrically conducting, and malleable—that is, they can be pounded into flat sheets without disintegrating. They tend to have only 1–3 outer electrons, which they may lose in forming chemical compounds. Examples of metals are iron, copper, and silver. Most metallic objects that are commonly encountered are not composed of just one kind of elemental metal, but are alloys consisting of homogeneous mixtures of two or more metals. **Nonmetals** often have a dull appearance, are not at all malleable, and frequently occur as gases or liquids. Colorless oxygen gas, green chlorine gas (transported and stored as a liquid under pressure), and brown bromine liquid are common nonmetals. Nonmetals tend to have close to a full octet of outer-shell electrons, and in forming chemical compounds they gain or share electrons. **Metalloids**, such as silicon or arsenic, are elements with properties intermediate between those of metals and nonmetals. Under some conditions, a metalloid may exhibit properties of metals, and under other conditions, properties of nonmetals.

28.3. CHEMICAL BONDING

Only a few elements, particularly the noble gases, exist as individual atoms; most atoms are joined by chemical bonds to other atoms. For example, elemental hydrogen exists as **molecules**, each consisting of 2 H atoms linked by a **chemical bond** as shown in Figure 28.5. Because hydrogen molecules contain 2 H atoms, they are said to be diatomic and are denoted by the **chemical formula**, H_2. The H atoms in the H_2 molecule are held together by a **covalent bond** made up of 2 electrons, each contributed by one of the H atoms, and shared between the atoms. (Bonds formed by transferring electrons between atoms are described later in this section.) The shared electrons in the covalent bonds holding the H_2 molecule together are represented by two dots between the H atoms in Figure 28.5. By analogy with Lewis symbols defined in the preceding section, such a representation of molecules showing outer-shell and bonding electrons as dots is called a **Lewis formula**.

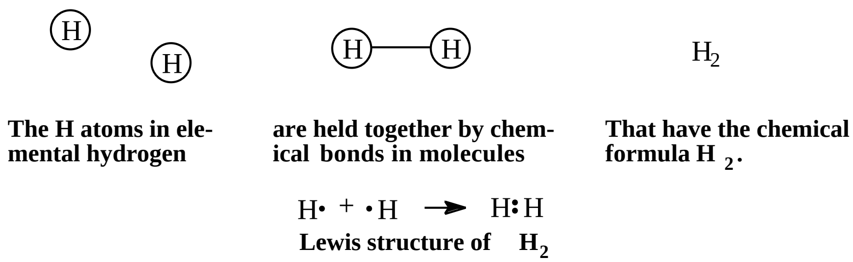


Figure 28.5. Molecule and Lewis formula of H_2.

Chemical Compounds

Most substances consist of two or more elements joined by chemical bonds. As an example consider the chemical combination of hydrogen and oxygen shown in Figure 28.6. Oxygen, chemical symbol O, has an atomic number of 8 and an atomic mass of 16.00, and it exists in the elemental form as diatomic molecules of O_2. Hydrogen atoms combine with oxygen atoms to form molecules in which 2 H atoms are bonded to 1 O atom in a substance with a chemical formula of H_2O (water). A substance such as H_2O that consists of a chemically bonded combination of two or more elements is called a **chemical compound**. In the chemical formula for water the letters H and O are the chemical symbols of the two elements in the compound and the subscript 2 indicates that there are 2 H atoms per O atom. (The absence of a subscript after the O denotes the presence of just 1 O atom in the molecule.).

As shown in Figure 28.6, each of the hydrogen atoms in the water molecule is connected to the oxygen atom by a chemical bond composed of two electrons shared between the hydrogen and oxygen atoms. For each bond one electron is contributed by the hydrogen and one by oxygen.The two dots located between each H and O in the Lewis formula of H_2O represent the two electrons in the covalent bond joining these atoms. Four of the electrons in the octet of electrons surrounding O are involved in H-O bonds and are called bonding electrons. The other four electrons shown around the oxygen that are not shared with H are nonbonding outer electrons.

Molecular Structure

As implied by the representations of the water molecule in Figure 28.6, the atoms and bonds in H_2O form an angle somewhat greater than 90 degrees. The shapes of molecules are referred to as their **molecular geometry**, which is crucial in determining the chemical and toxicological activity of a compound and structure-activity relationships.

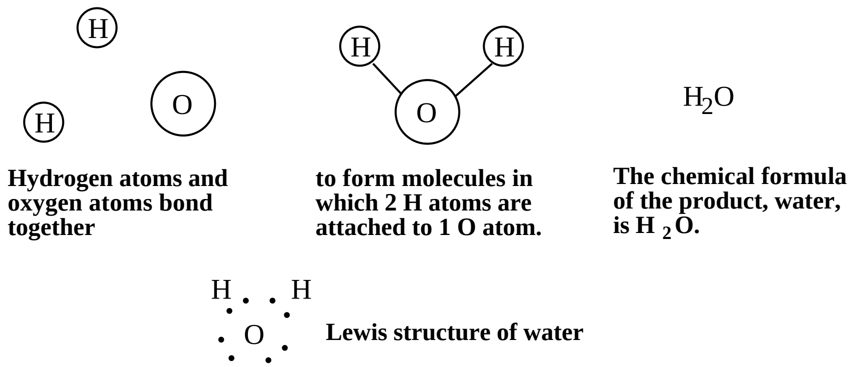


Figure 28.6. Formation and Lewis formula of a chemical compound, water.

Ionic Bonds

As shown in Figure 28.7, the transfer of electrons from one atom to another produces charged species called **ions**. Positively charged ions are called **cations** and negatively charged ions are called **anions**. Ions that make up a solid compound are held together by **ionic bonds** in a **crystalline lattice** consisting of an ordered arrangement of the ions in which each cation is largely surrounded by anions and each anion by cations. The attracting forces of the oppositely charged ions in the crystalline lattice constitute ionic bonds in the compound.

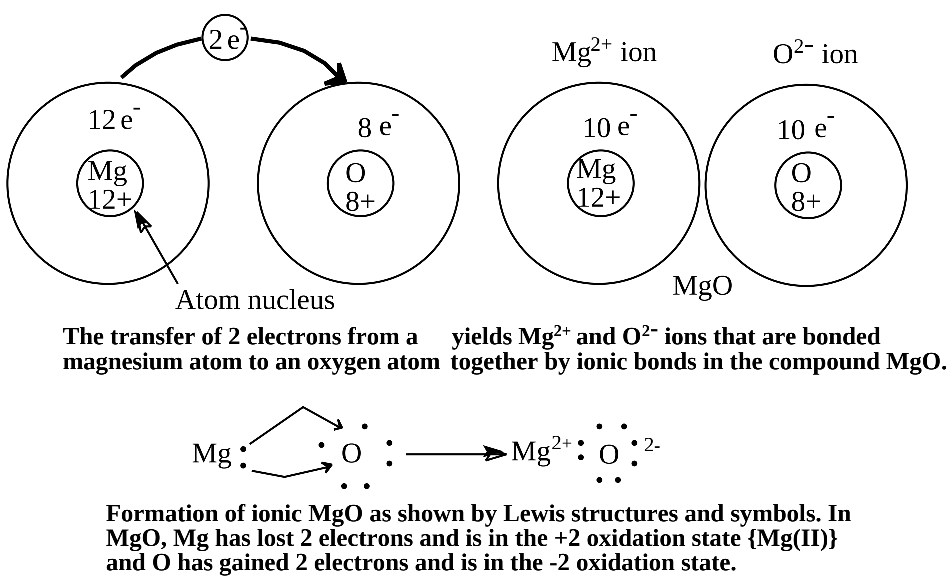


Figure 28.7. Ionic bonds are formed by the transfer of electrons and the mutual attraction of oppositely charged ions in a crystalline lattice.

The formation of magnesium oxide is shown in Figure 28.7. In naming this compound, the cation is simply given the name of the element from which it was formed, magnesium. However, the ending of the name of the anion, ox*ide*, is different from that of the element from which it was formed, ox*ygen.*

Rather than individual atoms that have lost or gained electrons, many ions are groups of atoms bonded together covalently and having a net charge. A common example of such an ion is the ammonium ion, NH_4^+,

$$\left[\begin{array}{ccc} & H & \\ & \cdot\cdot & \\ H\!: & N & :\!H \\ & \cdot\cdot & \\ & H & \end{array}\right]^{+} \quad \text{Lewis formula of the ammonium ion}$$

which consists of 4 hydrogen atoms covalently bonded to a single nitrogen (N) atom and having a net electrical charge of +1 for the whole cation, as shown by its Lewis formula above.

Summary of Chemical Compounds and the Ionic Bond

The preceding several pages have just covered some material on chemical compounds and bonds that are essential to understand chemistry. To summarize, these are the following:

- Atoms of two or more different elements can form *chemical bonds* with each other to yield a product that is entirely different from the elements.
- Such a substance is called a *chemical compound.*
- The *formula* of a chemical compound gives the symbols of the elements and uses subscripts to show the relative numbers of atoms of each element in the compound.
- *Molecules* of some compounds are held together by *covalent bonds* consisting of shared electrons.
- Another kind of compound consists of *ions* composed of electrically charged atoms or groups of atoms held together by *ionic bonds* that exist because of the mutual attraction of oppositely charged ions.

Molecular Mass

The average mass of all molecules of a compound is its **molecular mass** (formerly called molecular weight). The molecular mass of a compound is calculated by multiplying the atomic mass of each element by the relative number of atoms of the element, then adding all the values obtained for each element in the compound. For example, the molecular mass of NH_3 is 14.0 + 3 x 1.0 = 17.0. As another example consider the following calculation of the molecular mass of ethylene, C_2H_4.

1. The chemical formula of the compound is C_2H_4.
2. Each molecule of C_2H_4 consists of 2 C atoms and 4 H atoms.

3. From the periodic table or Table 28.2, the atomic mass of C is 12.0 and that of H is 1.0.

4. Therefore, the molecular mass of C_2H_4 is

$$\underbrace{12.0 + 12.0}_{\text{From 2 C atoms}} + \underbrace{1.0 + 1.0 + 1.0 + 1.0}_{\text{From 4 H atoms}} = 28.0.$$

Oxidation State

The loss of two electrons from the magnesium atom as shown in Figure 28.7 is an example of **oxidation**, and the Mg^{2+} ion product is said to be in the +2 **oxidation state**. (A positive oxidation state or oxidation number is conventionally denoted by a Roman numeral in parentheses following the name or symbol of an element as in magnesium(II) and Mg(II)). In gaining 2 negatively charged electrons in the reaction that produces magnesium oxide, the oxygen atom is **reduced** and is in the -2 oxidation state. (Unlike positive oxidation numbers, negative ones are not conventionally shown by Roman numerals in parentheses.) In chemical terms an **oxidizer** is a species that takes electrons from a reducing agent in a chemical reaction. Many hazardous waste substances are oxidizers or strong reducers and oxidation/reduction is the driving force behind many dangerous chemical reactions. For example, the reducing tendencies of the carbon and hydrogen atoms in propane cause it to burn violently or explode in the presence of oxidizing oxygen in air. The oxidizing ability of concentrated nitric acid, HNO_3, enables it to react destructively with organic matter, such as cellulose or skin.

Covalently bonded atoms that have not actually lost or gained electrons to produce ions are also assigned oxidation states. This can be done because in covalent compounds electrons are not shared equally. Therefore, an atom of an element with a greater tendency to attract electrons is assigned a negative oxidation number compared to the positive oxidation number assigned to an element with a lesser tendency to attract electrons. For example, Cl atoms attract electrons more strongly than do H atoms so that in hydrogen chloride gas, HCl, the Cl atom is in the -1 oxidation state and the H atoms are in the +1 oxidation state. **Electronegativity** values are assigned to elements on the basis of their tendencies to attract electrons.

The oxidation state (oxidation number) of an element in a compound may have a strong influence on the hazards posed by the compound. For example, chromium from which each atom has lost 3 electrons to form a chemical compound, designated as chromium(III) or Cr(III), is not toxic, whereas chromium in the +6 oxidation state (CrO_4^{2-}, chromate) is regarded as a cancer-causing chemical when inhaled.

28.4. CHEMICAL REACTIONS AND EQUATIONS

Chemical reactions occur when substances are changed to other substances through the breaking and formation of chemical bonds. For example, water is produced by the chemical reaction of hydrogen and oxygen:

Hydrogen plus oxygen yields water

Chemical reactions are written as **chemical equations**. The chemical reaction between hydrogen and water is written as the **balanced chemical equation**

$$2H_2 + O_2 \rightarrow 2H_2O \tag{28.4.1}$$

in which the arrow is read as "yields" and separates the hydrogen and oxygen **reactants** from the water **product**. Note that because elemental hydrogen and elemental oxygen occur as *diatomic molecules* of H_2 and O_2, respectively, it is necessary to write the equation in a way that reflects these correct chemical formulas of the elemental form. All correctly written chemical equations are **balanced** in that *the same number of each kind of atom must be shown on both sides of the equation*. The equation above is balanced because of the following:

On the left

- There are 2 H_2 *molecules* each containing 2 H *atoms* for a total of 4 H atoms on the left.
- There is 1 O_2 *molecule* containing 2 O *atoms* for a total of 2 O atoms on the left.

On the right

- There are 2 H_2O *molecules* each containing 2 H *atoms* and 1 O *atom* for a total of 4 H atoms and 2 O atoms on the right.

Reaction Rates

Most chemical reactions give off heat and are classified as exothermic reactions. The rate of a reaction may be calculated by the Arrhenius equation, which contains absolute temperature (K = ˚C + 273) in an exponential term. As a general rule the speed of a reaction doubles for each 10˚C increase in temperature. Reaction rate factors are important factors in fires or explosions involving hazardous chemicals.

28.5. SOLUTIONS

A liquid **solution** is formed when a substance in contact with a liquid becomes dispersed homogeneously throughout the liquid in a molecular form. The substance, called a **solute**, is said to **dissolve**. The liquid is called a **solvent**. There may be no readily visible evidence that a solute is present in the solvent; for example, a deadly poisonous solution of sodium cyanide in water looks like pure water. The solution may have a strong color, as is the case for intensely purple solutions of potassium permanganate, $KMnO_4$. It may have a strong odor, such as that of ammonia, NH_3, dissolved in water. Solutions may consist of solids, liquids, or gases dissolved in a solvent. Technically, it is even possible to have solutions in which a solid is a solvent, although such solutions are not discussed in this book.

Solution Concentration

The quantity of solute relative to that of solvent or solution is called the **solution concentration**. Concentrations are expressed in numerous ways. Very high concentrations are often given as percent by weight. For example, commercial concentrated hydrochloric acid is 36% HCl, meaning that 36% of the weight has come from dissolved HCl and 64% from water solvent. Concentrations of very dilute solutions, such as those of hazardous waste leachate containing low levels of contaminants, are expressed as weight of solute per unit volume of solution. Common units are milligrams per liter (mg/L) or micrograms per liter (μg/L). Since a liter of water weighs essentially 1,000 grams, a concentration of 1 mg/L is equal to 1 part per million (ppm) and a concentration of 1 μg/L is equal to l part per billion (ppb).

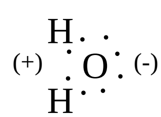
Chemists often express concentrations in moles per liter, or **molarity**, M. Molarity is given by the relationship

$$M = \frac{\text{Number of moles of solute}}{\text{Number of liters of solution}} \tag{28.5.1}$$

The number of moles of a substance is its mass in grams divided by its molar mass. For example, the molecular mass of ammonia, NH_3, is 14 + 1 + 1 +1, so a mole of ammonia has a mass of 17 g. Therefore, 17 g of NH_3 in 1 L of solution has a value of M equal to 1 mole/L.

Water as a Solvent

Most liquid wastes are solutions or suspensions of waste materials in water. Water has some unique properties as a solvent which arise from its molecular structure as represented by the Lewis structure of water below:



The H atoms are not on opposite sides of the O atom and the two H–O bonds form an angle of 105˚. Furthermore, the O atom (-2 oxidation state) is able to attract electrons more strongly than the 2 H atoms (each in the +1 oxidation state) so that the molecule is **polar**, with the O atom having a partial negative charge and the end of the molecule with the 2 H atoms having a partial positive charge. This means that water molecules can cluster around ions with the positive ends of the water molecules attracted to negatively charged anions and the negative end to positively charged cations. This kind of interaction is part of the general phenomenon of **solvation**. It is specifically called **hydration** when water is the solvent and is partially responsible for water’s excellent ability to dissolve ionic compounds including acids, bases, and salts.

Water molecules form a special kind of bond called a **hydrogen bond** with each other and with solute molecules that contain O, N, or S atoms. As its name implies, a hydrogen bond involves a hydrogen atom held between two other atoms of O, N, or S. Hydrogen bonding is partly responsible for water’s ability to solvate and dissolve chemical compounds capable of hydrogen bonding.

As noted above, the water molecule is a polar species, which affects its ability to act as a solvent. Solutes may likewise have polar character. In general, solutes with polar molecules are more soluble in water than nonpolar ones. The polarity of an impurity solute in wastewater is a factor in determining how it may be removed from water. Nonpolar organic solutes are easier to take out of water by an adsorbent species such as activated carbon than are more polar solutes.

Solutions of Acids and Bases

Acid-Base Reactions

The reaction between H^+ ion from an acid and OH^- ion from a base is a **neutralization** reaction. As a specific example consider the reaction of H^+ from a solution of sulfuric acid, H_2SO_4, and OH^- from a solution of calcium hydroxide:

Acid, source of H^+ ion **Water**

$$\underset{}{H_2SO_4} + Ca(OH)_2 \rightarrow 2H_2O + CaSO_4 \qquad (28.5.2)$$

Base, source of OH^- ion **Salt**

In addition to water, which is always the product of a neutralization reaction, the other product is calcium sulfate, $CaSO_4$. This compound is a **salt** composed of Ca^{2+} ions and SO_4^{2-} ions held together by ionic bonds. A salt, consisting of a cation other than H^+ and an anion other than OH^-, is the other product in addition to water produced when an acid and base react. Some salts are hazardous substances and environmental pollutants because of their dangerous or harmful properties. Some examples are the following:

- Ammonium perchlorate, NH_4ClO_4, (reactive oxidant)
- Barium cyanide, $Ba(CN)_2$(toxic)
- Lead acetate, $Pb(C_2H_3O_2)_2$ (toxic)
- Thallium(I) carbonate, Tl_2CO_3 (toxic)

Concentration of H^+ Ion and pH

Acids such as HCl and sulfuric acid (H_2SO_4) produce H^+ ion, whereas bases, such as sodium hydroxide and calcium hydroxide (NaOH and $Ca(OH)_2$, respectively), produce hydroxide ion, OH^-. Molar concentrations of hydrogen ion, $[H^+]$, range over many orders of magnitude and are conveniently expressed by pH defined as

$$pH = -\log [H^+] \qquad (28.5.3)$$

In absolutely pure water at 25˚C, the value of $[H^+]$ is exactly 1×10^{-7} mole/L, the pH is 7.00, and the solution is **neutral** (neither acidic nor basic). **Acidic** solutions have pH values of less than 7, and **basic** solutions have pH values of greater than 7.

Strong acids and strong bases are **corrosive** substances that exhibit extremes of pH. They are destructive to materials and flesh. Strong acids can react with cyanide and sulfide compounds to release highly toxic hydrogen cyanide (HCN) or hydrogen sulfide (H_2S) gases, respectively. Bases liberate noxious ammonia gas (NH_3) from solid ammonium compounds.

Metal Ions Dissolved in Water

Metal ions dissolved in water have some unique characteristics that influence their properties as natural water constituents and heavy metal pollutants, and in biological systems. The formulas of metal ions are usually represented by the symbol for the ion followed by its charge. For example, iron(II) ion (from a compound such as iron(II) sulfate, $FeSO_4$) dissolved in water is represented as Fe^{2+}. Actually, in water solution each iron(II) ion is strongly solvated and bonded to water molecules, so that the formula is more correctly shown as $Fe(H_2O)_6{}^{2+}$. Many metal ions have a tendency to lose hydrogen ions from the solvating water molecules as shown by the following:

$$Fe(H_2O)_6{}^{2+} \rightarrow Fe(OH)(H_2O)_5 + H^+ \tag{28.5.4}$$

Ions of the next higher oxidation state, iron(III), have such a tendency to lose H^+ ion in aqueous solution that, except in rather highly acidic solutions, they precipitate out as solid hydroxides, such as iron(III) hydroxide, $Fe(OH)_3$:

$$Fe(H_2O)_6{}^{3+} \rightarrow Fe(OH)_3(s) + 3H_2O + 3\,H^+ \tag{28.5.5}$$

Complex Ions Dissolved in Water

It was noted above that metal ions are solvated (hydrated) by binding to water molecules in aqueous solution. Some species in solution have a stronger tendency than water to bond to metal ions. An example of such a species is cyanide ion, CN^-, which displaces water molecules from some metal ions in solution as shown below:

$$Ni(H_2O)_4{}^{2+} + 4CN^- \leftarrow\rightarrow Ni(CN)_4{}^{2-} + 4H_2O \tag{28.5.6}$$

The species that bonds to the metal ion, cyanide in this case, is called a **ligand**, and the product of the reaction is a **complex ion** or metal complex. The overall process is called **complexation**.

Colloidal Suspensions

Very small particles on the order of 1 micrometer or less in size, called **colloidal particles**, may stay suspended in a liquid for an indefinite period of time. Such a mixture is a **colloidal suspension** and it behaves in many respects like a solution. Colloidal suspensions are used in many industrial applications. Many waste materials are colloidal and are often emulsions consisting of colloidal liquid droplets suspended in another liquid, usually wastewater. One of the challenges in dealing with colloidal wastes is to remove a relatively small quantity of colloidal material from a large quantity of water by precipitating the colloid. This process is called **coagulation** or **flocculation** and is often brought about by the addition of chemical agents.

Solution Equilibria

Many of the phenomena in aquatic chemistry (Chapters 3–8) and geochemistry (Chapters 15 and 16) involve solution equilibrium. In a general sense, solution equilibrium deals with the extent to which **reversible** acid-base, solubilization (precipitation), complexation, or oxidation-reduction reactions proceed in a forward or backward direction. This is expressed for a generalized equilibrium reaction,

$$aA + bB \rightleftarrows cC + dD \tag{28.5.7}$$

by the following **equilibrium constant expression**:

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = K \tag{28.5.8}$$

where K is the **equilibrium constant**.

A reversible reaction may approach equilibrium from either direction. In the example above, if A were mixed with B, or C were mixed with D, the reaction would proceed in a forward or reverse direction such that the concentrations of species—[A], [B], [C], and [D]—substituted into the equilibrium expression gave a value equal to K.

As expressed by **Le Châtelier's principle**, a stress placed upon a system in equilibrium will shift the equilibrium to relieve the stress. For example, adding product "D" to a system in equilibrium will cause Reaction 28.5.7 to shift to the left, consuming "C" and producing "A" and "B," until the equilibrium constant expression is again satisfied. This **mass action effect** is the driving force behind many environmental chemical phenomena.

In most cases this book uses concentrations and pressures in equilibrium constant expression calculations. When this is done, K is not exactly constant with varying concentrations and pressures; it is an *approximate equilibrium constant* that applies only to limited conditions. **Thermodynamic equilibrium constants** are more exact forms derived from thermodynamic data that make use of *activities* in place of concentrations. At a specified temperature, the value of a thermodynamic equilibrium constant is applicable over a wide concentration range. The activity of a species, commonly denoted as a_X for species "X," expresses how effectively it interacts with its surroundings, such as other solutes or electrodes in solution. (The analogy may be drawn of an environmental chemistry class with a "concentration" of 20 students per classroom. Their "activity" in relating to the subject is likely to be much higher on a cold, rainy day than on a balmy, sunny day in springtime.) Activities approach concentrations at low values of concentration. The thermodynamic equilibrium constant expression for Reaction 28.5.7 is expressed as the following in terms of activities:

$$\frac{a_C{}^c\, a_D{}^d}{a_A{}^a\, a_B{}^b} = K \tag{28.5.9}$$

There are several major kinds of equilibria in aqueous solution. One of these is acid-base equilibrium (see Chapter 3) as exemplified by the ionization of acetic acid, HAc,

$$HAc \rightleftarrows H^+ + Ac^- \tag{28.5.10}$$

for which the acid dissociation constant is

$$\frac{[H^+][Ac^-]}{[HAc]} = K = 1.75 \times 10^{-5} \quad (\text{at } 25^\circ\text{C}) \tag{28.5.11}$$

Very similar expressions are obtained for the formation and dissociation of metal **complexes** or **complex ions** (Chapter 3) formed by the reaction of a metal ion in solution with a **complexing agent** or **ligand**, both of which are capable of independent existence in solution. This can be shown by the reaction of iron(III) ion and thiocyanate ligand

$$Fe^{3+} + SCN^- \rightleftarrows FeSCN^{2+} \tag{28.5.12}$$

for which the **formation constant expression** is:

$$\frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = K_f = 1.07 \times 10^3 \quad (\text{at } 25^\circ\text{C}) \tag{28.5.13}$$

The bright red color of the $FeSCN^{2+}$ complex formed is used to test for the presence of iron(III) in acid mine water (Chapter 7).

An example of an **oxidation-reduction reaction**, which involves the transfer of electrons between species, is

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightleftarrows Mn^{2+} + 5Fe^{3+} + 4H_2O \tag{28.5.14}$$

for which the equilibrium expression is:

$$\frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^-][Fe^{2+}]^5[H^+]^8} = K = 3 \times 10^{62} \quad (\text{at } 25^\circ\text{C}) \tag{28.5.15}$$

The value of K is calculated from the Nernst equation, as explained in Chapter 4.

Distribution between Phases

As discussed in Chapter 5, many important environmental chemical phenomena involve distribution of species between phases. This most commonly involves the equilibria between species in solution and in a solid phase. **Solubility equilibria** (see Chapter 5) deal with reactions such as,

$$AgCl(s) \rightarrow Ag^+ + Cl^- \quad (28.5.16)$$

in which one of the participants is a solid that is slightly soluble (virtually insoluble). For the example shown above, the equilibrium constant is,

$$[Ag^+][Cl^-] = K_{sp} = 1.82 \times 10^{-10} \quad \text{(at 25˚C)} \quad (28.5.17)$$

a **solubility product**. Note that in the equilibrium constant expression there is not a value given for the solid AgCl. This is because the activity of a solid is constant at a specific temperature and is contained in the value of K_{sp}.

An important example of distribution between phases is that of a hazardous waste species partitioned between water and a body of immiscible organic liquid in a hazardous waste site. The equilibrium for such a reaction,

$$X(aq) \leftrightarrows X(org) \quad (28.5.18)$$

is described by the **distribution law** expressed by a **distribution coefficient** or **partition coefficient** in the following form:

$$\frac{[X(org)]}{[X(aq)]} = K_d \quad (28.5.19)$$

LITERATURE CITED

1. Manahan, Stanley E., *Fundamentals of Environmental Chemistry*, CRC Press, Boca Raton, FL, 1993.

SUPPLEMENTARY REFERENCES

Brown, Theodore L., H. Eugene Lemay, and Bruce Edward Bursten, *Chemistry: The Central Science*, 8th ed., Prentice Hall, Upper Saddle River, NJ, 1999.

Burns, Ralph A., *Fundamentals of Chemistry*, 3rd ed., Prentice Hall, Upper Saddle River, NJ, 1999.

Dickson, T. R., *Introduction to Chemistry*, 8th ed, John Wiley & Sons, New York, 1999.

Ebbing, Darrell D. and Steven D. Gammon, *General Chemistry*, 6th ed., Houghton Mifflin, Boston, 1999.

Hein, Morris and Susan Arena, *Foundations of College Chemistry/With Infotrak*, 10th ed, Brooks/Cole Publishing Co., Pacific Grove, CA, 1999.

Hill, John W., and Doris K. Kolb, *Chemistry for Changing Times*, 8th ed., Prentice Hall, Upper Saddle River, NJ, 1998.

Kotz, John C. and Paul Treichel, *Chemistry and Chemical Reactivity*, 4th ed, Saunders College Publishing, Philadelphia, 1998.

McMurry, John and Mary E. Castellion, *Fundamentals of General, Organic and Biological Chemistry*, Prentice Hall, Upper Saddle River, NJ, 1999.

Rosenberg, Jerome L. and Lawrence M. Epstein, *Schaum's Outline of Theory and Problems of College Chemistry*, 8th edition, McGraw-Hill, New York, 1997.

QUESTIONS AND PROBLEMS

1. What distinguishes a radioactive isotope from a “normal” stable isotope?

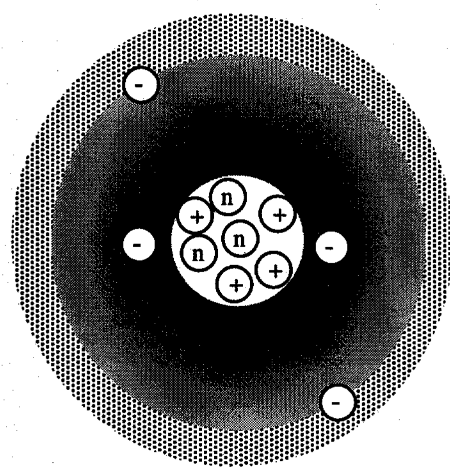
2. Why is the periodic table so named?

3. After examining Figure 28.7, consider what might happen when an atom of sodium (Na), atomic number 11, loses an electron to an atom of fluorine, (F), atomic number 9. What kinds of particles are formed by this transfer of a negatively charged electron? Is a chemical compound formed? If so, what is it called?

4. Match the following:

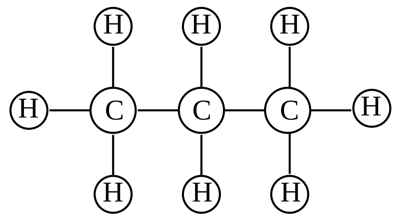
1. O_2	(a) Element consisting of individual atoms
2. NH_3	(b) Element consisting of chemically bonded atoms
3. Ar	(c) Ionic compound
4. NaCl	(d) Covalently bound compound

5. Consider the following atom:



How many electrons, protons, and neutrons does it have? What is its atomic number? Give the name and chemical symbol of the element of which it is composed.

6. Give the chemical formula and molecular mass of the molecule represented below:



7. Calculate the molecular masses of (a) C_2H_2, (b) N_2H_4, (c) Na_2O, (d) O_3 (ozone), (e) PH_3, (f) CO_2.

8. Is the equation, $H_2 + O_2 \rightarrow H_2O$, a balanced chemical equation? Explain. Point out the reactants and products in the equation.

9. Define and distinguish the differences between environmental chemistry, environmental biochemistry, and toxicological chemistry.

10. An uncharged atom has the same number of ____________________ as protons. The electrons in an atom are contained in a cloud of _________________ around the nucleus that occupies most of the __________________ of the atom.

11. Match:

1. Argon	(a) A halogen
2. Hydrogen	(b) Fissionable element
3. Uranium	(c) Noble gas
4. Chlorine	(d) Has an isotope with a mass number of 2
5. Mercury	(e) Toxic heavy metal

12. The entry for each element in the periodic table gives the element's ___________ ____ and the periodic table is arranged horizontally in ___________________ and vertically in ____________.

13. Electrons in atoms occupy ________________________ in which electrons have different ___________________. Each orbital may contain a maximum of ______ electrons.

14. The Lewis symbol of carbon is ________________ in which each dot represents ____________________.

15. Elements that are generally solid, shiny in appearance, electrically conducting, and malleable are _________________ whereas elements that tend to have a dull appearance, are not at all malleable, and frequently occur as gases or liquids are ________________. Elements with intermediate properties are called _________.

16. In the Lewis formula,

$$H:H$$

the two dots represent ____.

17. Explain why H_2 is not a chemical compound whereas H_2O is a chemical compound.

18. Using examples, distinguish between covalent and ionic bonds.

19. In terms of c, h, o, and the appropriate atomic masses, write a formula for the molecular mass of a compound with a general formula of $C_cH_hO_o$.

20. Considering oxidation/reduction phenomena, when Al reacts with O_2 to produce Al_2O_3, which contains the Al^{3+} ion, the Al is said to have been _______________ and is in the ___________ oxidation state.

21. Calculate the concentration in moles per liter of (a) a solution that is 27.0% H_2SO_4 by mass and that has a density of 1,198 g/L, and (b) of a solution that is 1 mg/L H_2SO_4 having a density of 1,000 g/L.

22. Calculate the pH of the second solution described in the preceding problem, keeping in mind that each H_2SO_4 molecule yields two H^+ ions.

23. Write a balanced neutralization reaction between NaOH and H_2SO_4.

24. Distinguish between solutions and colloidal suspensions.

25. What is the nature of the Fe^{3+} ion? Why are solutions containing this ion acidic?

26. What kind of species is $Ni(CN)_4^{2-}$?

27. What is the solubility product expression for lead sulfate, $PbSO_4$, in terms of concentrations of Pb^{2+} ion and SO_4^{2-} ion?