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Ninth Edition

JEROME L. ROSENBERG, Ph.D. LAWRENCE M. EPSTEIN, Ph.D. PETER J. KRIEGER, Ed.D.

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PERIODIC CHART OF THE ELEMENTS

	I 1	II 2	3	4	5	6	7	8	9	10	11	12	III 13	IV 14	V 15	VI 16	VII 17	VIII 18
1	1 — atomic number H — symbol Hydrogen — name 1.00794 — atomic mass																	2 He Helium 4.00260
2	3 Li Lithium 6.941	4 Be Beryllium 9.01218											5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.99840	10 Ne Neon 20.1797
3	11 Na Sodium 22.98977	12 Mg Magnesium 24.3050											13 Al Aluminum 26.98154	14 Si Silicon 28.0855	15 P Phosphorus 30.97376	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
4	19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.95591	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.93805	26 Fe Iron 55.845	27 Co Cobalt 58.93320	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
5	37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29
6	55 Cs Cesium 132.90545	56 Ba Barium 137.327	57-71 See Lanthanides	72 Hf Hafnium 178.49	73 Ta Tantaium 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
7	87 Fr Francium (223)	88 Ra Radium (226)	89-103 See Actinides	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (264)	108 Hs Hassium (265)	109 Mt Meitnerium (268)									

Lanthanides	57 La Lanthanum 138.9055	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
Actinides	89 Ac Actinium (227)	90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

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Theory and Problems of
COLLEGE CHEMISTRY

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PREFACE

This book is designed to help the student of college chemistry by summarizing the chemical principles of each topic and relating the solution of quantitative problems to those fundamentals. Although the book is not intended to replace a textbook, its solved problems, with complete and detailed solutions, do cover most of the subject matter of a first course in college chemistry. The student is referred to one of the many standard General Chemistry textbooks for such matters as full treatment of nomenclature, descriptive chemistry of the elements, and more extensive exposition and illustration of principles. Both the solved and the supplementary problems are arranged to allow a progression in difficulty within each topic.

Several important features have been introduced into the sixth edition, notably the kinetic theory of gases, a more formal treatment of thermochemistry, a modern treatment of atomic properties and chemical bonding, and a chapter on chemical kinetics.

In the seventh edition the early chapters were revised to conform more closely to the methods used in current textbooks to introduce calculational skills to the beginning student. Some changes in notation were made, and the usage of SI units was expanded. An attempt was made to increase the variety of stoichiometry problems, especially in the chapters on gases and solutions, while eliminating some of the very complex problems that arise in gaseous and aqueous equilibria. In the treatment of chemical bonding the subject of molecular orbitals was de-emphasized in favor of VSEPR theory. A new chapter on Organic Chemistry and Biochemistry was added, conforming to the trend in current texts.

In the eighth edition we carefully conformed to the language and style of the currently most-used textbooks, for example, using the term “molar mass” broadly, and eliminating “molecular weight” and the like. At least 15% of the problems in each chapter are new, and some old ones were dropped, so that the problems better reflect the practical situations of the laboratory, industry, and the environment. The use of SI units has been expanded further, but liter and atmosphere are retained where appropriate.

We decided to make this ninth edition meet the needs of today’s students by adopting a simplified approach in the content reviews, and eliminating the technical jargon. The solved problems were revamped to include replacement problems oriented toward real-world situations. We also added one hundred additional practice problems in areas such as forensics and materials science to reinforce students’ learning.

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CHAPTER 1

Quantities and Units

INTRODUCTION

One of the responsibilities of those who work in science is to communicate findings. Communication means that we must generate written or spoken materials that will be understood and, often, must do so by reporting measurements. Measurements must be performed and reported in a standardized procedure or the communications will be misunderstood.

Chemistry and physics measure kinds of *quantities* such as length, velocity, volume, mass, and energy. All measurements are expressed using a number and a unit. The *number* is used to tell us how many of the units are contained in the quantity being measured. The unit tells us the specific nature of the dimension—measuring in feet is different than measuring in liters. *If you are not comfortable with exponents and scientific notation (Examples:* 1×10^4, 3×10^{-9}*, or* 10^6*) and the rules for dealing with significant figures, please refer to Appendices A and B for help.*

SYSTEMS OF MEASUREMENT

Dimensional calculations are simplified if the unit for each kind of measure is expressed in terms of special reference units. The reference dimensions for mechanics are *length*, *mass*, and *time*. Other measurements performed are expressed in terms of these reference dimensions; units associated with speed contain references to length and time—mi/hr or m/s. Some units are simple multiples of the reference unit—area is expressed in terms of length squared (m^2) and volume is length cubed (in^3). Other reference dimensions, such as those used to express electrical and thermal phenomena, will be introduced later.

There are differing systems of measurement in use throughout the world, making the ability to convert values between systems important (convert inches to centimeters, or pounds to kilograms).

INTERNATIONAL SYSTEM (SI) OF UNITS

A system known as SI from the French name, Système International d'Unités, has been adopted by many international bodies, including the International Union of Pure and Applied Chemistry, to institute a standard for measurements. In SI, the reference units for *length*, *mass*, and *time* are meter, kilogram, and second, with the symbols m, kg, and s, respectively.

A multiplier can be used to represent values larger or smaller than the basic unit (gram, liter, meter, etc.). The multipliers are ten raised to a specific power, as listed in Table 1-1. This system avoids the necessity of having different basic units, such as the inch, foot, yard, or ounce, pint, quart, gallon, etc. The multiplier abbreviation precedes the symbol of the base unit with neither a space nor punctuation; an example is *m* in mL,

Table 1-1 Multiples for Units

Prefix	Abbreviation	Multiplier	Prefix	Abbreviation	Multiplier
deci	d	10^{-1}	deka	da	10
centi	c	10^{-2}	hecto	h	10^{2}
milli	m	10^{-3}	kilo	k	10^{3}
micro	μ	10^{-6}	mega	M	10^{6}
nano	n	10^{-9}	giga	G	10^{9}
pico	p	10^{-12}	tera	T	10^{12}
femto	f	10^{-15}	peta	P	10^{15}
atto	a	10^{-18}	exa	E	10^{18}

the milliliter (10^{-3} L). Since, for historical reasons, the SI reference unit for mass, kilogram, already has a prefix, multiples for mass should be derived by applying the multiplier to the unit *gram* rather than *kilogram*—then, 10^{-9} kg is expressed in micrograms (10^{-6} g), abbreviated μg.

Simple units can be combined to produce compound units that can be manipulated algebraically.

EXAMPLE 1 The unit for volume in SI is the cubic meter (m^3), since

$$\text{Volume} = \text{length} \times \text{length} \times \text{length} = \text{m} \times \text{m} \times \text{m} = \text{m}^3$$

EXAMPLE 2 The unit for speed is a unit for length (distance) divided by a unit for time:

$$\text{Speed} = \frac{\text{distance}}{\text{time}} = \frac{\text{m}}{\text{s}}$$

EXAMPLE 3 The unit for density is the unit for mass divided by the unit for volume:

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{\text{kg}}{\text{m}^3}$$

Symbols for compound units may be expressed in the following formats:

1. Multiple of units. Example: *kilogram second.*
   - (*a*) Dot between units $\text{kg} \cdot \text{s}$
   - (*b*) Spacing without dot kg s (*not used in this book*)
2. Division of units. Example: *meter per second.*
   - (*a*) Division sign $\frac{\text{m}}{\text{s}}$ (or m/s)
   - (*b*) Negative power $\text{m} \cdot \text{s}^{-1}$ (or m s^{-1})

The use of *per* in a word definition is equivalent to *divide by* in the mathematical form (refer to 2(*a*) directly above). Also, symbols are not handled as abbreviations; they are not followed by a period unless at the end of a sentence.

There are non-SI units that are widely used. Table 1-2 provides a list of commonly used symbols, both SI and non-SI. The listed symbols are used in this book; however, there are others that will be introduced at appropriate places to aid in solving problems and communicating.

TEMPERATURE

Temperature can be defined as that property of a body which determines the direction of the flow of heat. This means that two bodies at the same temperature placed in contact with each other will not display a transfer

Table 1-2 Some SI and Non-SI Units

Physical Quantity	Unit Name	Unit Symbol	Definition
Length	Angstrom	Å	10^{-10} m
	inch	in	2.54×10^{-10} m
	meter (SI)	m	
Area	square meter (SI)	m^2	
Volume	cubic meter (SI)	m^3	
	liter	L	dm^3, 10^{-3} m^3
	cubic centimeter	cm^3, mL	
Mass	atomic mass unit	u	1.66054×10^{-27} kg
	pound	lb	0.45359237 kg
Density	kilogram per cubic meter (SI)	kg/m^3	
	gram per milliliter, *or* gram per cubic centimeter	g/mL, *or* g/cm^3	
Force	Newton (SI)	N	$kg \cdot m/s^2$
Pressure	pascal (SI)	Pa	N/m^2
	bar	bar	10^5 Pa
	atmosphere	atm	101325 Pa
	torr (millimeters mercury)	torr (mm Hg)	atm/760 *or* 133.32 Pa

of heat. On the other hand, if there are two bodies of differing temperatures in contact, the heat will flow from the hotter to the cooler. The SI unit for temperature is the *kelvin*; 1 kelvin (K) is defined as 1/273.16 times the *triple point* temperature. The *triple point* is the temperature at which liquid water is in equilibrium with ice (solid water) at the pressure exerted by water vapor only. Most people are more familiar with the *normal freezing point* of water (273.15 K), which is just below the triple point of water (0.01 K). The *normal freezing point* of water is the temperature at which water and ice coexist in equilibrium with air at standard atmospheric pressure (1 atm).

The SI unit of temperature is so defined that 0 K is the absolute zero of temperature. The SI or Kelvin scale is often called the *absolute temperature scale*. Although absolute zero does not appear to be attainable, it has been approached to within 10^{-4} K.

OTHER TEMPERATURE SCALES

On the commonly used *Celsius* scale (old name: the *centigrade* scale), a temperature difference of one degree is the same as one degree on the Kelvin scale. The normal boiling point of water is 100°C; the normal freezing point of water is 0°C; and absolute zero is −273.15°C.

A difference of one degree on the *Fahrenheit* scale is exactly 5/9 K. The normal boiling point of water is 212°F; the normal freezing point of water is 32°F; and absolute zero is −459.67°F.

Figure 1-1 illustrates the relationships between the three scales. Converting one scale into another is by the equations below. The equation on the right is a rearrangement of the equation on the left. We suggest you know one equation, substitute values and solve for the unknown, rather than taking the time to memorize two equations for essentially the same calculation.

$$\mathrm{K} = {}^\circ\mathrm{C} + 273.15 \qquad \text{or} \qquad {}^\circ\mathrm{C} = \mathrm{K} - 273.15$$

$$^\circ\mathrm{F} = \frac{9}{5}{}^\circ\mathrm{C} + 32 \qquad \text{or} \qquad {}^\circ\mathrm{C} = \frac{5}{9}({}^\circ\mathrm{F} - 32)$$

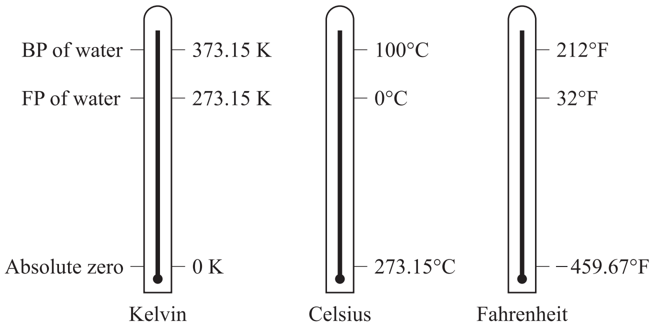


Fig. 1-1

USE AND MISUSE OF UNITS

It is human nature to leave out the units associated with measurements (e.g., cm, kg, g/mL, ft/s); however, leaving out the units is a good way to get into trouble when working problems. Keeping the units in the problem and paying attention to them as the problem progresses will help determine if the answer is correctly presented. When physical quantities are subjected to mathematical operations, the units are carried along with the numbers and undergo the same operations as the numbers. Keep in mind that quantities cannot be added or subtracted directly unless they have not only the same dimensions, but also the same units. Further, units can be canceled during multiplication and/or division operations. The units of the answer must match the nature of the dimension (e.g., length cannot be expressed in grams).

EXAMPLE 4 We cannot add 5 hours (time) to 20 miles/hour (speed) since *time* and *speed* have different physical significance. If we are to add 2 lb (mass) and 4 kg (mass), we must first convert lb to kg or kg to lb. Quantities of various types, however, can be combined in multiplication or division, in which *the units as well as the numbers* obey the algebraic laws of multiplication, squaring, division, and cancellation. Keeping these concepts in mind:

1. $6\,\text{L} + 2\,\text{L} = 8\,\text{L}$
2. $(5\,\text{cm})(2\,\text{cm}^2) = 10\,\text{cm}^3$
3. $(3\,\text{ft}^3)(200\,\text{lb/ft}^3) = 600\,\text{lb}$
4. $(2\,\text{s})(3\,\text{m/s}^2) = 6\,\text{m/s}$
5. $\dfrac{15\,\text{g}}{3\,\text{g/cm}^3} = 5\,\text{cm}^3$

FACTOR-LABEL METHOD

One way of looking at problems is to follow what happens to the units. This technique is referred to in textbooks as the *factor-label method*, the *unit-factor method*, or *dimensional analysis*. In essence, the solution of the problem goes from unit(s) given by the problem to the desired final unit(s) by multiplying by a fraction called a *unit-factor* or just *factor*. The numerator and denominator of the factor must represent the same quantity (mL/mL, ft/ft, *not* mL/L, ft/in).

EXAMPLE 5 Convert 5.00 inches to centimeters.

The appropriate unit-factor is 2.54 cm/1 in. The setup for this problem is achieved by presenting the factor to the problem value of 5.00 inches so that the like dimensions cancel.

$$5.00\,\text{in} \times \frac{2.54\,\text{cm}}{1\,\text{in}} = 12.7\,\text{cm}$$

Notice that the units of inches (in) will cancel and leave only the units of centimeters (cm).

EXAMPLE 6 What is the weight in grams of seven nails from a batch of nails that weighs 0.765 kg per gross?

$$7\text{ nails} \times \frac{1\text{ gross nails}}{144\text{ nails}} \times \frac{0.765\text{ kg}}{1\text{ gross nails}} \times \frac{1000\text{ g}}{1\text{ kg}} = 37.2\text{ g}$$

As with Example 5, following the cancellation of the units will help you see how the problem is solved.

The solution contains a unit-factor of mixed dimensions (0.765 kg/1 gross nails). The unit-factor is not composed of universally equivalent measures because different kinds of nails will weigh differently for each gross of nails. Many similar examples will be encountered during your studies and throughout this book.

ESTIMATION OF NUMERICAL ANSWERS

When we work problems, we assume that the calculator is working properly; the numbers were all put into the calculator; and that we keyed them in correctly. Suppose that one or more of these suppositions is incorrect; will the incorrect answer be accepted? A very important skill is to determine, by visual inspection, an approximate answer. Especially important is the correct order of magnitude, represented by the location of the decimal point (or the power of 10). Sometimes the answer may contain the correct digits, but the decimal point is in the wrong location. A little practice to learn how to estimate answers and a few seconds used to do so when working problems can boost accuracy (and your grades) significantly.

EXAMPLE 7 Consider the multiplication: $122\text{ g} \times 0.0518 = 6.32\text{ g}$. Visual inspection shows that 0.0518 is a little more than 1/20th (0.05); the value of 1/20th of 122 is a little more than 6. This relationship tells us that the answer should be a little more than 6 g, which it is. Suppose that the answer were given as 63.2 g; this answer is not logical because it is much larger than the estimated answer of somewhere around 6 g.

Estimates of the answer only need to supply us with a rough value, often called a *guesstimate*. Actually, these guesstimates may need to be only accurate enough to supply the appropriate place for the decimal point.

EXAMPLE 8 Calculate the power required to raise 639 kg mass 20.74 m in 2.120 minutes. The correct solution is:

$$\frac{639\text{ kg} \times 20.74\text{ m} \times 9.81\text{ m}\cdot\text{s}^{-2}}{2.120\text{ min} \times 60\text{ s/min}} = 1022\text{ J/s} = 1022\text{ watts}$$

Even though you may not be familiar with the concepts and units, you can judge whether or not the answer is logical. A guesstimate can be generated quickly by writing each term in exponential notation, using one significant figure. Then, mentally combine the powers of ten and the multipliers separately to estimate the result like this:

Numerator:	$6 \times 10^2 \times 2 \times 10^1 \times 1 \times 10^1 = 12 \times 10^4$
Denominator	$2 \times 6 \times 10^1 = 12 \times 10^1$
Num/Den	10^3 or 1000 estimated, compared to 1022 calculated

Solved Problems

UNITS BASED ON MASS OR LENGTH

1.1. The following examples illustrate conversions among various units of length, volume, or mass:

$1\text{ inch} = 2.54\text{ cm} = 0.0254\text{ m} = 25.4\text{ mm} = 2.54 \times 10^7\text{ nm}$
$1\text{ foot} = 12\text{ in} = 12\text{ in} \times 2.54\text{ cm/in} = 30.48\text{ cm} = 0.3048\text{ m} = 304.8\text{ mm}$
$1\text{ liter} = 1\text{ dm}^3 = 10^{-3}\text{ m}^3$
$1\text{ mile} = 5280\text{ ft} = 1.609 \times 10^5\text{ cm} = 1.609 \times 10^3\text{ m} = 1.609\text{ km} = 1.609 \times 10^6\text{ mm}$

$1\text{ pound} = 0.4536\,\text{kg} = 453.6\,\text{g} = 4.536 \times 10^5\,\text{mg}$
$1\text{ metric ton} = 1000\,\text{kg} = 10^6\,\text{g}\ (\textit{or}\ 1 \times 10^6\,\text{g})$

1.2. Convert 3.50 yards to (*a*) millimeters, (*b*) meters. According to Table 1-2, the conversion factor used to move between the English and metric system (SI) units is 1 in/2.54 cm (2.54×10^{-2} m).

(*a*)
$$3.50\,\text{yd} \times \frac{36\,\text{in}}{1\,\text{yd}} \times \frac{2.54\,\text{cm}}{1\,\text{in}} \times \frac{10\,\text{mm}}{1\,\text{cm}} = 3.20 \times 10^3\,\text{mm}$$

Note that the use of three successive conversion factors was necessary. The units yd, in, and cm cancel out leaving the required unit, mm.

(*b*)
$$3.20 \times 10^3\,\text{mm} \times \frac{1\,\text{m}}{10^3\,\text{mm}} = 3.20\,\text{m}$$

1.3. Convert (*a*) 14.0 cm and (*b*) 7.00 m to inches.

(*a*)
$$14.0\,\text{cm} = (14\,\text{cm})\left(\frac{1\,\text{in}}{2.54\,\text{cm}}\right) = 5.51\,\text{in} \qquad \text{or} \qquad 14.0\,\text{cm} = \frac{14.0\,\text{cm}}{2.54\,\text{cm/in}} = 5.51\,\text{in}$$

The conversion factor used in the first part, (*a*), is expressed on one line (1 in/254 cm) in part (*b*). The one-line version is much more convenient to type and write for many people.

(*b*)
$$700\,\text{m} = (7.00\,\text{m})(100\,\text{cm}/1\,\text{m})(1\,\text{in}/2.54\,\text{cm}) = 276\,\text{in}$$

Note: The solution directly above contains sets of parentheses that are not truly necessary. The authors take the liberty throughout this book of using parentheses for emphasis, as well as for the proper isolation of data.

1.4. How many square inches are in one square meter?

A square meter has two dimensions—length and width ($A = L \times W$). If we calculate the length of one meter in inches, all we need to do is square that measurement.

$$1\,\text{m} = (1\,\text{m})(100\,\text{cm}/1\,\text{m})(1\,\text{in}/2.54\,\text{cm}) = 39.37\,\text{in}$$

$$1\,\text{m}^2 = 1\,\text{m} \times 1\,\text{m} = 39.37\,\text{in} \times 39.37\,\text{in} = (39.37\,\text{in})^2 = 1550\,\text{in}^2$$

Note that the conversion factor is a ratio; it may be squared without changing the ratio, which leads us to another setup for the solution. Pay particular attention to the way in which the units cancel.

$$1\,\text{m}^2 = (1\,\text{m})^2\left(\frac{100\,\text{cm}}{1\,\text{m}}\right)^2\left(\frac{1\,\text{in}}{2.54\,\text{cm}}\right)^2 = \frac{(100)^2}{(2.54)^2}\,\text{in}^2 = 1550\,\text{in}^2$$

1.5. (*a*) How many cubic centimeters are in one cubic meter? (*b*) How many liters are in one cubic meter? (*c*) How many cubic centimeters are in one liter?

(*a*)
$$1\,\text{m}^3 = (1\,\text{m})^3\left(\frac{100\,\text{cm}}{1\,\text{m}}\right)^3 = (100\,\text{cm})^3 = 1{,}000{,}000\,\text{cm}^3 = 10^6\,\text{cm}^3$$

(*b*)
$$1\,\text{m}^3 = (1\,\text{m})^3\left(\frac{10\,\text{dm}}{1\,\text{m}}\right)^3\left(\frac{1\,\text{L}}{1\,\text{dm}^3}\right) = 10^3\,\text{L}$$

(*c*)
$$1\,\text{L} = 1\,\text{dm}^3 = (1\,\text{dm})^3\left(\frac{10\,\text{cm}}{1\,\text{dm}}\right)^3 = 10^3\,\text{cm}^3$$

The answers can also be written as $1 \times 10^6\,\text{cm}^3$, $1 \times 10^3\,\text{L}$, and $1 \times 10^3\,\text{cm}^3$ respectively.

1.6. Find the capacity in liters of a tank 0.6 m long (L), 10 cm wide (W), and 50 mm deep (D).

Since we are given the dimensions of the tank and $V = L \times W \times D$ (depth = height, the more traditional name for the dimension), all that we really need to do is convert the various expressions to dm ($1\ \text{dm}^3 = 1\ \text{L}$).

$$\text{Volume} = \text{Length} \times \text{Width} \times \text{Depth}$$

$$\text{Volume} = (0.6\ \text{m})\left(\frac{10\ \text{dm}}{1\ \text{m}}\right) \times (10\ \text{cm})\left(\frac{1\ \text{dm}}{10\ \text{cm}}\right) \times (50\ \text{mm})\left(\frac{1\ \text{dm}}{100\ \text{mm}}\right)$$

$$\text{Volume} = (6\ \text{dm}) \times (1\ \text{dm}) \times (0.5\ \text{dm}) = 3\ \text{dm}^3 = 3\ \text{L}$$

1.7. Determine the mass of 66 lb of sulfur in (*a*) kilograms and (*b*) grams. (*c*) Find the mass of 3.4 kg of copper in pounds.

(*a*) $66\ \text{lb} = (66\ \text{lb})(0.4536\ \text{kg/lb}) = 30\ \text{kg}$ or $66\ \text{lb} = (66\ \text{lb})(1\ \text{kg}/2.2\ \text{lb}) = 30\ \text{kg}$

(*b*) $66\ \text{lb} = (66\ \text{lb})(453.6\ \text{g/lb}) = 30{,}000\ \text{g}$ or $3.0 \times 10^4\ \text{g}$

(*c*) $3.4\ \text{kg} = (3.4\ \text{kg})(2.2\ \text{lb/kg}) = 7.5\ \text{lb}$

COMPOUND UNITS

1.8. Fatty acids spread spontaneously on water to form a monomolecular film. A benzene solution containing $0.10\ \text{mm}^3$ of stearic acid is dropped into a tray full of water. The acid is insoluble in water, but spreads on the surface to form a continuous film covering an area of $400\ \text{cm}^2$ after all of the benzene has evaporated. What is the average film thickness in (*a*) nanometers and (*b*) angstroms?

Since $1\ \text{mm}^3 = (10^{-3}\ \text{m})^3 = 10^{-9}\ \text{m}^3$ and $1\ \text{cm}^2 = (10^{-2}\ \text{m})^2 = 10^{-4}\ \text{m}^2$

(*a*)
$$\text{Film thickness} = \frac{\text{volume}}{\text{area}} = \frac{(0.10\ \text{mm}^3)(10^{-9}\ \text{m}^3/\text{mm}^3)}{(400\ \text{cm}^2)(10^{-4}\ \text{m}^2/\text{cm}^2)} = 2.5 \times 10^{-9}\ \text{m} = 2.5\ \text{nm}$$

(*b*)
$$\text{Film thickness} = 2.5 \times 10^{-9}\ \text{m} \times 10^{10}\ \text{Å/m} = 25\ \text{Å}$$

1.9. A pressure of one atmosphere is equal to 101.3 kPa. Express this pressure in pounds force (lbf) per square inch. (The pound force—lbf—is equal to 4.448 newtons, N.)

$$1\ \text{atm} = 101.3\ \text{kPa} = \left(\frac{101.3 \times 10^3\ \text{N}}{1\ \text{m}^2}\right)\left(\frac{1\ \text{lbf}}{4.48\ \text{N}}\right)\left(\frac{2.54 \times 10^{-2}\ \text{m}}{1\ \text{in}}\right)^2 = 14.69\ \text{lbf/in}^2$$

Notice that the conversion factor between meters (m) and inches (in) is squared to give the conversion factor between m^2 and in^2.

1.10. An Olympic-class sprinter can run 100 meters in about 10.0 seconds. Express this speed in (*a*) kilometers per hour and (*b*) miles per hour.

(*a*)
$$\frac{100\ \text{m}}{10.0\ \text{s}} \times \frac{1\ \text{km}}{1000\ \text{m}} \times \frac{60\ \text{s}}{1\ \text{min}} \times \frac{60\ \text{min}}{1\ \text{hr}} = 36.0\ \text{km/hr}$$

(*b*)
$$36.0\ \text{km/hr} \times 1\ \text{mi}/1.609\ \text{km} = 22.4\ \text{mi/hr}$$

Notice that the (*b*) portion of this problem requires the information from the (*a*) part of the problem.

1.11. New York City's 7.9 million people in 1978 had a daily per capita consumption of 656 liters of water. How many metric tons (10^3 kg) of sodium fluoride (45% fluorine by weight) would be required per year to give this water a tooth-strengthening dose of 1 part (by weight) fluorine per million parts water? The density of water is $1.000\ \text{g/cm}^3$, or $1.000\ \text{kg/L}$.

A good start is to calculate the mass of water, in tons, required per year.

$$\left(7.9\times10^6\ \text{persons}\right)\left(\frac{656\,\text{L water}}{\text{person}\cdot\text{day}}\right)\left(\frac{365\ \text{days}}{\text{year}}\right)\left(\frac{1\ \text{kg water}}{1\,\text{L water}}\right)\left(\frac{1\ \text{metric ton}}{1000\,\text{kg}}\right)=1.89\times10^9\ \frac{\text{metric tons water}}{\text{yr}}$$

Note that all units cancel except metric tons water/yr; it is needed for the next step.

Now, set up and calculate the total mass of sodium fluoride, in tons, required each year.

$$1.89\times10^9\left(\frac{\text{(metric) tons water}}{\text{year}}\right)\left(\frac{1\ \text{ton fluorine}}{10^6\ \text{tons water}}\right)\left(\frac{1\ \text{ton sodium fluoride}}{0.45\,\text{ton fluorine}}\right)=4.2\times10^3\ \frac{\text{tons sodium fluoride}}{\text{year}}$$

1.12. In a measurement of air pollution, air was drawn through a filter at the rate of 26.2 liters per minute for 48.0 hours. The filter gained 0.0241 grams in mass because of entrapped solid particles. Express the concentration of solid contaminants in the air in units of micrograms per cubic meter.

$$\frac{(0.0241\ \text{g})(106\,\mu\text{g}/\ 1\ \text{g})}{(48.0\,\text{h})(60\,\text{min/h})(1\,\text{min}/26.2\,\text{L})(1\,\text{L}/1\,\text{dm}^3)(10\,\text{dm}/1\,\text{m})^3}=319\frac{\mu\text{g}}{\text{m}^3}$$

1.13. Calculate the density, in g/cm^3, of a body that weighs 420 g (i.e., has a mass of 420 g) and has a volume of 52 cm^3.

$$\text{Density}=\frac{\text{mass}}{\text{volume}}=\frac{420\ \text{g}}{52\ \text{cm}^3}=8.1\ \text{g/cm}^3$$

1.14. Express the density of the above body in the standard SI unit, kg/m^3.

$$\left(\frac{8.1\,\text{g}}{1\,\text{cm}^3}\right)\left(\frac{1\,\text{kg}}{1000\,\text{g}}\right)\left(\frac{100\,\text{cm}}{1\,\text{m}}\right)^3=8.1\times10^3\,\text{kg/m}^3$$

1.15. What volume will 300 g of mercury occupy? The density of mercury is 13.6 g/cm^3.

$$\text{Volume}=\frac{\text{mass}}{\text{density}}=\frac{300\,\text{g}}{13.6\,\text{g/cm}^3}=22.1\,\text{cm}^3$$

1.16. The density of cast iron is 7200 kg/m^3. Calculate its density in pounds per cubic foot.

$$\text{Density}=\left(7200\,\frac{\text{kg}}{\text{m}^3}\right)\left(\frac{1\,\text{lb}}{0.4536\,\text{kg}}\right)\left(\frac{0.3048\,\text{m}}{1\,\text{ft}}\right)^3=449\,\text{lb/ft}^3$$

The two conversions were borrowed from Problem 1.1.

1.17. A casting of an alloy in the form of a disk weighed 50.0 g. The disk was 0.250 inches thick and had a diameter of 1.380 inches. What is the density of the alloy, in g/cm^3?

$$\text{Volume}=\left(\frac{\pi d^2}{4}\right)h=\left(\frac{\pi(1.380\,\text{in})^2(0.250\,\text{in})}{4}\right)\left(\frac{2.54\,\text{cm}}{1\,\text{in}}\right)^3=6.13\,\text{cm}^3$$

$$\text{Density of the alloy}=\frac{\text{mass}}{\text{volume}}=\frac{50.0\,\text{g}}{6.13\,\text{cm}^3}=8.15\,\text{g/cm}^3$$

1.18. The density of zinc is 455 lb/ft^3. Find the mass in grams of 9.00 cm^3 of zinc.

Let us start the solution by calculating the density in g/cm^3.

$$\left(455\frac{\text{lb}}{\text{ft}^3}\right)\left(\frac{1\,\text{ft}}{30.48\,\text{cm}}\right)^3\left(\frac{453.6\,\text{g}}{1\,\text{lb}}\right)=7.29\ \frac{\text{g}}{\text{cm}^3}$$

Then, we can determine the total mass of the zinc.

$$(9.00\,\text{cm}^3)(7.29\,\text{g/cm}^3)=65.6\,\text{g}$$

1.19. Battery acid has a density of 1.285 g/cm^3 and contains 38% by weight H_2SO_4. How many grams of pure H_2SO_4 are contained in a liter of battery acid?

1 cm^3 of acid has a mass of 1.285 g. Then, 1 L of acid (1000 cm^3) has a mass of 1285 g. Since 38.0% by weight (by mass) of the acid is pure H_2SO_4, the amount of H_2SO_4 in 1 L of battery acid is

$$0.380 \times 1285\,\text{g} = 488\,\text{g}$$

Formally, the above solution can be expressed as follows:

$$\text{Mass of } H_2SO_4 = (1285\,\text{g } H_2SO_4)\left(\frac{38\,\text{g } H_2SO_4}{100\,\text{g } H_2SO_4}\right) = 488\,\text{g } H_2SO_4$$

The information provided in the problem generated the conversion factor utilizing the ratio of pure H_2SO_4 to H_2SO_4 solution.

$$\frac{38\,\text{g } H_2SO_4}{100\,\text{g } H_2SO_4 \text{ solution}}$$

It is extremely important to note that this conversion factor is only good for the conditions of this problem. However, this conversion factor does mean that every 100 g of this particular acid solution contains 38 g H_2SO_4, information that is important in both the logical and the formal explanations above. Liberal use of special conversion factors will be made in subsequent chapters where conversion factors are generated and valid for only particular cases. Of course, universally valid conversions will also be used as indicated.

1.20. (*a*) Calculate the mass of pure of HNO_3 per cm^3 of the concentrated acid which assays 69.8% by weight HNO_3 and has a density of 1.42 g/cm^3. (*b*) Calculate the mass of pure HNO_3 in 60.0 cm^3 of concentrated acid. (*c*) What volume of concentrated acid contains 63.0 g of pure HNO_3?

(*a*) 1 cm^3 of acid has a mass of 1.42 g. Since 69.8% of the total mass of the acid is pure HNO_3, the number of grams of HNO_3 in 1 cm^3 is

$$0.698 \times 1.42\,\text{g} = 0.991\,\text{g}$$

(*b*) The mass of the HNO_3 in 60.0 cm^3 of acid = (60.0 cm^3)(0.991 g/cm^3) = 59.5 g HNO_3

(*c*) 63.0 g HNO_3 is contained in

$$\frac{63.0\,\text{g}}{0.991\,\text{g/cm}^3} = 63.6\,\text{cm}^3 \text{ acid}$$

TEMPERATURE

1.21. Ethyl alcohol (*a*) boils at 78.5°C and (*b*) freezes at −117°C, at one atmosphere of pressure. Convert these temperatures to the Fahrenheit scale.

Use this conversion:

$$^\circ\text{F} = \frac{9}{5}{}^\circ\text{C} + 32$$

(*a*) $$\left(\frac{9}{5} \times 78.5^\circ\text{C}\right) + 32 = 173^\circ\text{F}$$

(*b*) $$\left(\frac{9}{5} \times -117^\circ\text{C}\right) + 32 = -179^\circ\text{F}$$

1.22. Mercury (*a*) boils at 675°F and (*b*) solidifies at −38.0°F, at one atmosphere of pressure. Express these temperatures in degrees Celsius.

Use this conversion:

$$°\mathrm{C} = \frac{5}{9}(°\mathrm{F} - 32)$$

(*a*) $$\frac{5}{9}(675 - 32) = 357°\mathrm{C}$$

(*b*) $$\frac{5}{9}(-38.0 - 32) = -38.9°\mathrm{C}$$

1.23. Change (*a*) 40°C and (*b*) −5°C to the Kelvin scale.

Use this conversion:

$$°\mathrm{C} + 273 = \mathrm{K}$$

(*a*) $$40°\mathrm{C} + 273 = 313\ \mathrm{K}$$

(*b*) $$-5°\mathrm{C} + 273 = 268\ \mathrm{K}$$

1.24. Convert (*a*) 220 K and (*b*) 498 K to the Celsius scale.

Use this conversion:

$$\mathrm{K} - 273 =°\ \mathrm{C}$$

(*a*) $$220\,\mathrm{K} - 273 = -53°\mathrm{C}$$

(*b*) $$498\,\mathrm{K} - 273 = 225°\mathrm{C}$$

1.25. During the course of an experiment, laboratory temperature rose 0.8°C. Express this rise in degrees Fahrenheit.

Temperature *intervals* are converted differently than are temperature *readings*. For intervals, it is seen from Fig. 1-1 that

$$100°\mathrm{C} = 180°\mathrm{F} \quad \text{or} \quad 5°\mathrm{C} = 9°\mathrm{F}$$

therefore

$$\left(\frac{9°\mathrm{F}}{5°\mathrm{C}}\right)(0.8°\mathrm{C}) = 1.4°\mathrm{F}$$

Supplementary Problems

UNITS BASED ON MASS OR LENGTH

1.26. (*a*) Express 3.69 m in kilometers, in centimeters, and in millimeters. (*b*) Express 36.24 mm in centimeters and in meters.

Ans. (*a*) 0.00369 km, 369 cm, 3690 mm; (*b*) 3.624 cm, 0.03624 m

1.27. Determine the number of (*a*) millimeters in 10 in, (*b*) feet in 5 m, (*c*) centimeters in 4 ft 3 in.

Ans. (*a*) 254 mm; (*b*) 16.4 ft; (*c*) 130 cm

1.28. A long shot is in the 300 yard range, but is within the training parameters for a SWAT officer. How far is the target as measured in (*a*) feet, (*b*) meters, and (*c*) kilometers?

Ans. (*a*) 900 ft; (*b*) 274 m; (*c*) 0.27 km

1.29. A recovered bullet is found to be from a 38 special revolver. The bullet measures 0.378 inches in diameter; what must you record in terms of the metric system using cm?

Ans. 1.04 cm

1.30. Express in cm (*a*) 14.0 in, (*b*) 7.00 yd.

Ans. (*a*) 35.6 cm; (*b*) 640 cm

1.31. A roll of the yellow crime scene tape contains 250 yards of tape. An area of a grassy field to be marked off is a rectangle 42 m by 31 m; how many yards of tape will be left?

Ans. 90 yd

1.32. A ¼ mile long suspension bridge is being planned which will require 16 miles of 150 strand (150 wires twisted) cable to be placed. What is the minimum (ignoring length for twisting) length in km of wire the cable manufacturer needs to have to produce the cable?

Ans. 3862 km

1.33. The average man can run at a top speed of 22 mph. Express this speed in (*a*) kilometers per hour and (*b*) meters per second.

Ans. (*a*) 35.4 km/h; (*b*) 9.83 m/s

1.34. Convert the molar volume, 22.4 liters, to cubic centimeters, to cubic meters, and to cubic feet.

Ans. 22,400 cm^3; 0.0224 m^3; 0.791 ft^3

1.35. Express the weight (mass) of 32 g of oxygen in milligrams, in kilograms, and in pounds.

Ans. 32,000 mg; 0.032 kg; 0.0705 lb

1.36. How many grams in 5.00 lb of copper sulfate? How many pounds in 4.00 kg of mercury? How many milligrams in 1 lb 2 oz of sugar?

Ans. 2270 g; 8.82 lb; 510,000 mg

1.37. Convert the weight (mass) of a 2176 lb compact car to (*a*) kilograms; (*b*) metric tons; (*c*) U.S. tons (1 ton = 2000 lb).

Ans. (*a*) 987 kg; (*b*) 0.987 metric ton; (*c*) 1.088 ton (U.S.)

1.38. The steel used in the fabrication of the cable (16 mi, diameter 12 cm; assume solid; $V_{\text{cylinder}} = \pi r^2 h$) for the bridge in Problem 1.32 has the density of 8.65 g/cm^3. The cable can be drawn from a solid block of the metal. What would that block weigh in (*a*) kg? (*b*) in lbs? (*c*) in tons?

Ans. (*a*) 1.01×10^7 kg; (*b*) 2.2×10^7 lb; (*c*) 1110 tons (1.01×10^4 metric tons)

1.39. The color of light depends on its wavelength. The longest visible rays, at the red end of the visible spectrum, are 7.8×10^{-7} m in length. Express this length in micrometers, in nanometers, and in angstroms.

Ans. 0.78 μm; 780 mm; 7800 Å

1.40. An average person should have no more than 60 grams of fat in their daily diet. A package of chocolate chip cookies is labeled “1 portion is 3 cookies” and also “fat: 6 grams per portion.” How many cookies can you eat before exceeding 50% of the recommended maximum fat intake?

Ans. 15 cookies

1.41. In a crystal of platinum, the centers of the atoms are 2.8 Å apart along the direction of the closest packing. How many atoms would lie on a one-centimeter line in this direction?

Ans. 3.5×10^7 atoms

1.42. The blue iridescence of butterfly wings is due to striations that are 0.15 μm apart, as measured by the electron microscope. What is this distance in centimeters? How does this spacing compare with the wavelength of blue light, about 4500 Å?

Ans. 1.5×10^{-5} cm, 1/3 wavelength of blue light

1.43. An average man requires about 2.00 mg of riboflavin (vitamin B_2) per day. How many pounds of cheese would a man have to eat per day if this were his only source of riboflavin and if the cheese were to contain 5.5 μg of riboflavin per gram?

Ans. 0.80 lb/day

1.44. When a sample of blood from a healthy person is diluted to 200 times its initial volume and microscopically examined in a layer 0.10 mm thick, an average of 30 red blood cells are found in each 100 × 100 micrometer square. (*a*) How many red cells are in a cubic millimeter of blood? (*b*) The red blood cells have an average life of 1 month, and the blood volume of a particular patient is about 5 L. How many red blood cells are generated every second in the bone marrow of the patient?

Ans. (*a*) 6×10^6 cells/mm^3; (*b*) 1×10^7 cells/s

1.45. A porous catalyst for chemical reactions has an internal surface area of 800 m^2 per cm^3 of bulk material. Fifty percent of the bulk volume consists of the pores (holes), while the other 50% of the volume is made up of the solid substance. Assume that the pores are all cylindrical tubules of uniform diameter d and length l, and that the measured internal surface area is the total area of the curved surfaces of the tubules. What is the diameter of each pore? (*Hint*: Find the number of tubules per bulk cm^3, n, in terms of l and d, by using the formula for the volume of a cylinder $V = 0.25\,\pi d^2 l$. Then apply the surface-area formula, $S = \pi dl$, to the cylindrical surfaces of n tubules.)

Ans. 25 Å

1.46. Suppose that a rubber tire loses a layer one molecule thick from its surface during each revolution on the pavement. (By "molecule" you should infer one monomer unit.) Assume that the molecules average 7.50 Å in thickness, that the tire tread is 35.6 cm in radius, and 19.0 cm wide. On a 483 km drive from Pittsburgh to Philadelphia (*a*) how much is the radius reduced (in mm), and (*b*) what volume of rubber (in cm^3) is lost from each tire?

Ans. (*a*) 0.162 mm; (*b*) 68.8 cm^3

COMPOUND UNITS

1.47. Refer to Problem 1.46. If the tire has a density of 963 kg/m^3, calculate the mass in grams lost by each tire on the trip.

Ans. 66.3 g

1.48. The density of water is 1.000 g/cm^3 at 4°C. Calculate the density of water in pounds per cubic foot at the same temperature.

Ans. 62.4 lb/ft^3

1.49. There is an estimate that a cube 60 ft by 60 ft by 60 ft would contain all of the gold ever mined and refined. Considering that the density of pure gold is 19.3 g/cm^3, calculate the mass in (*a*) kilograms, (*b*) pounds, and (*c*) tons represented by this estimate.

Ans. (*a*) 1.18×10^8 kg; (*b*) 5.36×10^7 lb; (*c*) 26,800 tons (1.18×10^5 metric tons)

1.50. A difference of no more than 0.0013 grams/cm^3 from the average density (7.700 g/mL) is normal for empty 9 mm shells (the part that held the propellant) from ABC, Inc.. Two fired shells from a 9 mm handgun were found and taken to the lab. The shells were identified as from ABC, were weighed, and the volumes were measured using displacement of water (#1: 3.077 g and 0.399 mL and #2: 3.092 g and 0.402 mL). Could these shells be from the same lot?

Ans. They could be from the same lot. The first shell, #1, had a density 0.012 from the average and the second shell, #2, was 0.008 g/mL from the average. This is only one test of many.

1.51. The silica gel which is used to protect sealed overseas shipments from moisture seepage has a surface area of 6.0×10^2 m^2 per kilogram. What is the surface area in square feet per gram?

Ans. 6.5×10^3 ft^2/g

1.52. There is reason to think that the length of the day, determined from the earth's period of rotation, is increasing uniformly by about 0.0001 s every century. What is this variation in parts per billion (ppb)?

Ans. 3×10^{-4} s per 10^9 s (*or* 3×10^{-4} ppb)

1.53. The average content of bromine in the Atlantic Ocean is 65 parts per million (ppm) by weight. Assuming 100% recovery, how many cubic meters of ocean water must be processed to produce 0.61 kg of bromine? Assume that the density of seawater is 1.0×10^3 kg/m^3.

Ans. 9.4 m^3

1.54. An important physical quantity's value is 8.314 joules or 0.08206 liter · atmosphere. What is the conversion factor from joules to liter · atmospheres?

Ans. 101.3 J/L · atm

1.55. Find the density of ethyl alcohol if 80.0 cm^3 weighs 63.3 g.

Ans. 0.791 g/cm^3

1.56. Find the volume in liters of 40 kg of carbon tetrachloride, CCl_4. (Density = 1.60 g/cm^3.)

Ans. 25 L

1.57. A type of plastic foam has a density of 17.7 kg/m^3. Calculate the mass in pounds of an insulating slab 4.0 ft wide, 8.0 ft long, and 4.0 in thick.

Ans. 11.8 lb

1.58. Air weighs about 8 lb per 100 cubic feet. Find its density in (*a*) grams per cubic foot, (*b*) grams per liter, and (*c*) kilograms per cubic meter.

Ans. (*a*) 36 g/ft^3; (*b*) 1.3 g/L; (*c*) 1.3 kg/m^3

1.59. The estimates for the caloric content of food are: 9.0 Cal/g for fats, and 5.0 Cal/g for carbohydrates and proteins. A breakfast muffin contains 14% by weight of fat, 64% carbohydrate, and 7% protein (the rest is water, which has no calories). Does it meet the criterion of 30% or less calories from fat, which is recommended for the U.S. population?

Ans. Yes, 26% of the calories are from fat.

1.60. A wood block, 10 in × 6.0 in × 2.0 in, has a weight of 3 lb 10 oz. What is the density of the wood in SI units?

Ans. 840 kg/m^3

1.61. An alloy was machined into a flat disk 31.5 mm in diameter and 4.5 mm thick. A hole 7.5 mm in diameter was drilled through the center. The disk weighed 20.2 g. What was the density of the alloy in SI units?

Ans. 6100 kg/m^3

1.62. A glass vessel weighed 20.2376 g when empty and 20.3102 g when filled to an etched mark with water at 4°C. The same vessel was then dried and filled to the same mark with a solution at 4°C. The vessel was then found to weigh 20.3300 g. What is the density of the solution?

Ans. 1.273 g/cm^3

1.63. A sample of lead shot weighing 321 g was added to a graduated cylinder partially filled with isopropyl alcohol (enough to cover the lead completely). As a result the alcohol level rose 28.3 mL. What is the density of the lead in SI units? (The density of isopropyl alcohol is 0.785 g/cm^3.)

Ans. 1.13×10^4 kg/m^3

1.64. A sample of concentrated sulfuric acid is 95.7% H_2SO_4 by weight and its density is 1.84 g/cm^3. (*a*) How many grams of pure H_2SO_4 are contained in one liter of the acid? (*b*) How many cubic centimeters of acid contain 100 g of pure H_2SO_4?

Ans. (*a*) 1760 g; (*b*) 56.8 cm^3

1.65. A quick method of determining density utilizes Archimedes' principle, which states that the buoyant force on an immersed object is equal to the weight of the liquid displaced. A bar of magnesium metal attached to a balance by a fine thread weighed 31.13 g in air and 19.35 g when completely immersed in hexane (D_{hexane} = 0.659 g/cm^3). See Fig. 1-2. Calculate the density of this sample of magnesium in SI units.

Ans. 1741 kg/m^3

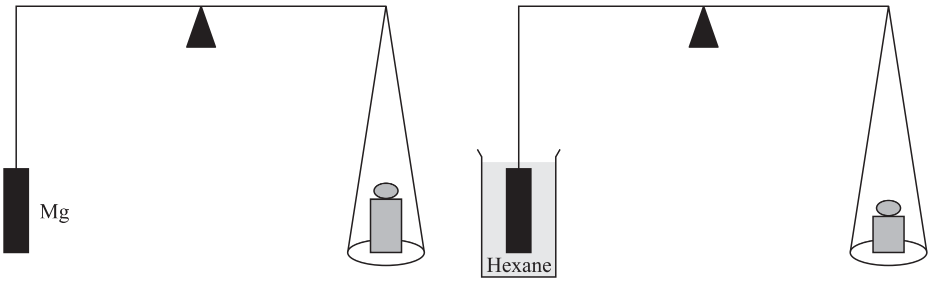


Fig. 1-2

1.66. An electrolytic tin-plating process gives a coating 30 millionths of an inch thick. How many square meters can be coated with one kilogram of tin, density 7300 kg/m^3?

Ans. 180 m^2

1.67. A piece of gold leaf (density 19.3 g/cm^3) weighing 1.93 mg can be beaten further into a transparent film covering an area of 14.5 cm^2. (*a*) What is the volume of 1.93 mg of gold? (*b*) What is the thickness of the transparent film, in angstroms?

Ans. (*a*) 1×10^{-4} cm^{-3}; (*b*) 690 Å

1.68. Calculate the length (km and mi) of the gold leaf mentioned in Problem 1.67 that can be beaten out if the width is 6 inches. *Note:* The moon is 2.4×10^5 mi and the sun is 9.3×10^7 mi (both averages).

Ans. 1.7×10^{11} km, 1×10^6 mi

1.69. A piece of capillary tubing was calibrated in the following manner: A clean sample of the tubing weighed 3.247 g. A thread of mercury, drawn into the tubing, occupied a length of 23.75 mm, as observed under a microscope. The weight of the tubing with the mercury was 3.489 g. The density of mercury is 13.60 g/cm^3. Assuming that the capillary bore is a uniform cylinder, find the diameter of the bore.

Ans. 0.98 mm

1.70. The General Sherman tree, located in Sequoia National Park, is believed to be the most massive of living things. If the overall density of the tree trunk is assumed to be 850 kg/m, calculate the mass of the tree trunk by assuming that it may be approximated by two right conical frusta having lower and upper diameters of 11.2 and 5.6 m, and 5.6 and 3.3 m, respectively, and respective heights of 2.4 and 80.6 m. A frustum is a portion of a cone bounded by two planes, both perpendicular to the axis of the cones. The volume of a frustum is given by

$$\frac{1}{3}\pi h(r_1^2 + r_2^2 + r_1 r_2)$$

where h is the height and r_1 and r_2 are the radii of the circular ends of the frusta.

Ans. 1.20×10^6 kg = 1200 metric tons

TEMPERATURE

1.71. (*a*) Convert 88°F to °C; 16°F to °C; 130°F to °C. (*b*) Convert 35°C to °F; 2°C to °F; −29°C to °F.

Ans. (*a*) 31°C, −9°C, 54°C; (*b*) 95°F, 36°F, −20°F

1.72. Convert the following temperatures: −149.7°C to °F; −396.0°F to °C; 1555°C to °F.

Ans. −237.5°F, −237.8°C, 2831°F

1.73. The temperature of dry ice (sublimation temperature at normal pressure) is −109°F. Is this higher or lower than the temperature of boiling ethane (a component of bottled gas), which is −88°C?

Ans. higher

1.74. An ill person has a temperature of 103°F, about the same temperature as a healthy cat. What is the temperature in (*a*) C and (*b*) kelvins?

Ans. (*a*) 39.4°C; (*b*) 312.6 K

1.75. Gold has been mined and refined for many thousands of years, certainly before electric furnaces and other high-temperature devices were possible. The melting point of gold is 1064°C; express this temperature in terms of the Kelvin and Fahrenheit scales.

Ans. 1303 K and 1947°F

1.76. Metal contracts and expands with temperature changes. A metal bar is being used to build part of the deck of an oil rig for the North Sea and must be able to withstand −45°C. State the temperature in (*a*) °F and (*b*) in the Kelvin scale.

Ans. (*a*) −49°F; (*b*) 228 K

1.77. Gabriel Fahrenheit in 1714 suggested for the zero point on his scale the lowest temperature then obtainable from a mixture of salts and ice, and for his 100° point he suggested the highest known normal animal temperature. Express these "extremes" in Celsius.

Ans. −17.8°C, 37.8°C

1.78. Sodium metal has a very wide liquid range, melting at 98°C and boiling at 892°C. Express the liquid range in degrees Celsius, kelvins, and degrees Fahrenheit.

Ans. 794°C, 794 K, 1429°F

1.79. Convert 298 K, 892 K, and 163 K to degrees Celsius.

Ans. 25°C, 619°C, −110°C

1.80. Express 11 K and 298 K in degrees Fahrenheit.

Ans. −440°F, 77°F

1.81. Convert 23°F to degrees Celsius and kelvins.

Ans. −5°C, 268 K

1.82. An accelerant is suspected when a vehicle fire is so hot that the glass in the windshield melted. The melting point of this car's glass (essentially SiO_2) is 1698°C. Convert that temperature to (*a*) the Kelvin scale and (*b*) the Fahrenheit scale.

Ans. (*a*) 1971 K; (*b*) 3088° F

1.83. At what temperature have the Celsius and Fahrenheit readings the same numerical value?

Ans. −40°

1.84. A water-stabilized electric arc was reported to have reached a temperature of 25,600°F. On the absolute scale, what is the ratio of this temperature to that of an oxyacetylene flame (3500°C)?

Ans. 3.84

1.85. Construct a temperature scale in which the freezing and boiling points of water are 100° and 400°, respectively, and the degree interval is a constant multiple of the Celsius degree interval. What is the absolute zero on this scale, and what is the melting point of sulfur (MP = 444.6°C)?

Ans. −719°, 1433.8°

1.86. Normal body temperature is 98.6°F, but the internal temperature (liver temperature) of a deceased person found in an apartment is at 91.5°F. The expected temperature drop under the conditions in the apartment is 1°C for each hour and 15 minutes after death. (*a*) Express the body temperatures in °C. (*b*) How long ago did this person die? (Only an estimate can be derived from these data and the cooling rate.)

Ans. (*a*) 37°C and 33°C; (*b*) 6 hours, approximately

CHAPTER 2

Atomic and Molecular Mass; Molar Mass

ATOMS

The atomic theory was proposed by John Dalton in 1805. Dalton thought that all atoms of a given element were identical. Chemists in following decades embraced the task of finding the relative masses of atoms of the different elements by precise quantitative chemical analysis. Over a hundred years after Dalton's proposal was made, investigations with radioactive substances showed that not all atoms of a given element were identical. The Periodic Chart (Table) of the Elements recognizes the differing masses of atoms by providing the average atomic mass for each of the elements. An element can exist in several *isotopic* forms in which the number of neutrons is different for each isotope; however, all atoms of the same element have the same number of protons, as is discussed directly below.

NUCLEI

Every atom has a positively charged nucleus which contains over 99.9 percent of the total mass of the atom. There are numerous particles found in the nucleus, but nuclei may be described by considering only two particles. These particles are the *proton* and the *neutron*, collectively known as *nucleons*. These two nucleons have nearly the same mass (1 atomic mass unit, u, although there is an informal use of amu or AMU). Of these two nucleons, only the proton has an electrical charge and the charge is a positive charge. The size of the proton's charge may by considered *the* fundamental unit of charge for atomic and nuclear phenomena, since no smaller charge than this has been discovered in any free particle. The charge of the proton is assigned the value of $+1$ and all other charges are discussed relative to that charge. Since the neutron has no charge, the charge on the nucleus of an atom is solely due to the number of protons.

The atoms of all isotopes of any specific element have the same number of protons. This number is called the *atomic number*, Z, and is a characteristic of the element. The nuclei of different isotopes differ in the number of neutrons providing for a different number of nucleons in the nuclei. One way of referring to specific isotopes is to provide the total number of nucleons, A, which is the *mass number*. Atoms of the different isotopic forms of an element, the *nuclides*, are distinguished by using the mass number as a superscript to the left of the element's symbol. So, the nitrogen isotope containing 8 neutrons will have a mass number of 15 and is represented by ^{15}N (or N-15). Working from the other direction, we can determine the number of neutrons in an isotope by subtracting the atomic number from the mass number $A - Z = 15 - 7 = 8$ neutrons. Further, the charge on the nucleus of a nitrogen atom is $+7$, which is due to the number of protons (atomic number).

RELATIVE ATOMIC MASSES

The masses of individual atoms are very small. Even the heaviest atom discovered has a mass less than 5×10^{-25} kg. Since 1 kg is 2.2 lb, the mass referred to is less than 1.10×10^{-24} lb. It is convenient to define a special unit in which the masses of the atoms are expressed without having to use exponents. This unit is called the *atomic mass unit*, referred to by the symbol u in the literature. It is defined as exactly $\frac{1}{12}$ the mass of a ^{12}C atom. The mass of the ^{12}C atom is taken to be exactly 12 u; the mass of the ^{23}Na atom is 22.9898 u. Table 2-1 lists the masses of some nuclides to which reference will be made in this chapter, as well as others.

Table 2-1 Some Nuclidic Masses (u)

^{1}H	1.00783	^{12}C	12.00000	^{17}O	16.99913	^{35}Cl	34.96885
^{2}H	2.01410	^{13}C	13.00335	^{18}O	17.99916	^{37}Cl	36.96590
^{3}H	3.01605	^{14}C	14.00324	^{18}F	18.00094	^{36}Ar	35.96755
^{4}He	4.00260	^{16}C	16.01470	^{18}Ne	18.00571	^{38}Ar	37.96273
^{6}He	6.01889	^{14}N	14.00307	^{28}Si	27.97693	^{40}Ar	39.96238
^{6}Li	6.01512	^{15}N	15.00011	^{29}Si	28.97649	^{87}Rb	86.90919
^{7}Li	7.01600	^{16}N	16.00610	^{30}Si	29.97377		
^{7}Be	7.01693	^{16}O	15.99491	^{32}S	31.97207		

Most chemical reactions do not discriminate significantly among the various isotopes. For example, the percentages of iron atoms which are ^{54}Fe, ^{56}Fe, ^{57}Fe, and ^{58}Fe are 5.8, 91.8, 2.1, and 0.3, respectively, in all iron ores, meteorites, and iron compounds prepared synthetically. For chemical purposes it is of interest to know the *average mass* of an iron atom in this natural isotopic mixture. These average masses are also tabulated in terms of the unit u and are designated by A_r(E), where E is the symbol for the particular element. The term *atomic mass* will be used in this book to mean the average atomic mass, and *nuclidic mass* will be used when referring to one particular isotope of an element. A_r values, which are listed at the end of this book, form the basis for practically all chemical weight calculations. A_r values used to be determined by precise chemical analysis, but nearly all modern values are the weighted average of the nuclidic masses measured by mass spectroscopy, an extremely accurate process.

MOLE

Any chemical experiment involves the reaction of enormous numbers of atoms or molecules. The term *mole* is used to indicate a collection of a large, fixed number of fundamental chemical entities, comparable to the quantity that might be involved in an actual experiment. In fact, the mole is recognized in SI as the unit for one of the dimensionally independent quantities, the *amount of substance*. The abbreviation for the unit is *mol*. A mole of atoms of any element is defined as that amount of substance containing the same number of atoms as there are carbon atoms in exactly 12 g of pure ^{12}C. This number is called *Avogadro's number* or *Avogadro's constant*, N_A. The value of this quantity may be related to the value of the u, listed in Table 2-1, as follows:

$$\text{Mass of 1 mol of } ^{12}\text{C atoms} = N_A \times (\text{mass of one } ^{12}\text{C atom})$$
$$12\,\text{g/mol} = N_A \times 12\,\text{u}$$

$$N_A = \frac{12\,\text{g/mol}}{12\,\text{u}} = \frac{1\,\text{g/mol}}{1\,\text{u}} = \frac{1\,\text{g/mol}}{(1.66054 \times 10^{-27}\,\text{kg})(10^3\,\text{g/kg})}$$
$$= 6.0221 \times 10^{23}/\text{mol}$$

All units in the expression for N_A canceled except for mol, which remained in the denominator and may be expressed as mol^{-1} ($6.0221 \times 10^{23}\,\text{mol}^{-1}$). The answer may be interpreted as 6.0221×10^{23} things/mol; of course, in chemistry we are usually referring to atoms or molecules.

Let us look at a mole of atoms of some other element of atomic mass A_r. The average mass of an atom of this element is A_r u and the mass of a mole of such atoms is $N_A \times A_r$ u, or simply A_r g/mol. In other words, the mass in grams of a mole of atoms of an element is equal to the atomic mass, and A_r may be considered to have the units of g/mol. Therefore, a "mole of gold" is 197.0 g of gold.

SYMBOLS, FORMULAS, MOLAR MASSES

Each element has a specific symbol that is different from the symbol for any other element. In a chemical formula, the symbol stands for an atom of an element. Molecular substances are composed of two or more atoms that are tightly bound together. The formula for a molecular substance consists of the symbols for the atoms that are found in that molecule. For instance, the formula for carbon dioxide is CO_2. Note the use of the subscript to show that each molecule contains two oxygen atoms in addition to the one carbon atom. Also note that the "1" for the one carbon atom is not written. The molecular mass of CO_2 is the sum of the atomic mass of carbon plus twice the atomic mass of oxygen and is expressed in u. As was discussed directly above, the molar mass of CO_2 is the mass in grams equal to the molecular mass in u. A "mole of carbon dioxide" is $12.0\,\text{u} + 2(16.0\,\text{u}) = 44\,\text{u}$. This result can be expressed as 44 g to indicate one Avogadro's number, N_A, of CO_2 molecules. Recall that N_A is 6.0221×10^{23} things—molecules in this case.

Many common substances are ionic in nature. This means that the atoms are in the form of charged particles, *ions*, and are arranged in a potentially huge spatial array that may have no fixed size. In such cases, the *formula* indicates the relative number of each element present. Table salt is composed of sodium and chloride ions (chlorine ions are called *chloride* ions) in close association. Although the size of a crystal of table salt is not fixed, the ratio of sodium to chloride ions is 1:1; then, the formula for table salt is expressed as NaCl.

P_2O_{10} is the formula for a compound in which 2 atoms of phosphorus are present for every 10 atoms of oxygen. This formula is called the *molecular* formula. If the subscripts are the smallest possible ratio of whole numbers, the formula is called an *empirical formula*—PO_5 is the empirical formula for P_2O_{10}. P_2O_{10} can also refer to the particular amounts of the components of the compound. One mole of P_2O_{10} contains 2 moles of phosphorus atoms and 10 moles of oxygen atoms. We can calculate the mass of one mol of P_2O_{10} by means of adding up the masses of the components—$(2 \times 31.0) + (10 \times 16.0) = 222$ g/mol of P_2O_{10}.

The term "atomic weight" had been widely used rather than "atomic mass," and "molecular weight" rather than "molar mass." (Many writers used "molecular weight" for "molar mass" even for ionic substances.) Because "weight" is a force rather than a mass, such usage is discouraged. The beginning student, however, must be aware of the old terms because they are certainly found in the literature and may still be used. The term "molar mass" is a particularly welcome change because of its universal applicability, referring to Avogadro's number of molecules, ions, formula units, or individual atoms (e.g., the molar mass of gold is 197.0 g/mol; the molar mass of hydroxide ion, OH^-, is 17.0 g/mol).

Solved Problems

ATOMIC MASS

2.1. It has been found by mass spectrometric analysis that in nature the relative abundances of the various isotopic atoms of silicon are 92.23% ^{28}Si, 4.67% ^{29}Si, and 3.10% ^{30}Si. Calculate the atomic mass of silicon from this information and from the nuclidic masses.

The atomic mass is the average of the three nuclides, each weighted according to its own relative abundance. The nuclidic masses are given in Table 2-1.

$$A_r = (0.9223 \times 27.977\,\text{u}) + (0.0467 \times 28.976\,\text{u}) + (0.0301 \times 29.974\,\text{u})$$
$$A_r = 25.803\,\text{u} + 1.353\,\text{u} + 0.929\,\text{u} = 28.085\,\text{u}$$

2.2. Naturally occurring carbon consists of two isotopes, ^{12}C and ^{13}C. What are the percentage abundances of the two isotopes in a sample of carbon whose atomic mass is 12.01112?

Let $$y = \%\text{ abundance of } {}^{13}\text{C};\ \textit{then} 100 - y \text{ is } \%\ {}^{12}\text{C}.$$
$$A_r = 12.01112 = \frac{(12.00000)(100 - y) + (13.00335)y}{100}$$
$$A_r = 12.00000 + \frac{(13.00335 - 12.00000)y}{100} = 12.00000 + 0.0100335y$$

Then,

$$y = \frac{12.01112 - 12.00000}{0.0100335} = \frac{0.01112}{0.0100335} = 1.108\%\ {}^{13}\text{C}$$

and

$$100 - y = 98.892\%\ {}^{12}\text{C}$$

2.3. Before 1961, a physical atomic mass scale was used whose basis was an assignment of the value 16.00000 to ^{16}O. What would have been the physical atomic mass of ^{12}C on the old scale?

We can use the ratio of the two reference points to determine the older value.

$$\frac{\text{New reference}}{\text{Previous reference}} = \frac{A_r \text{ of } {}^{12}\text{C}}{A_r \text{ of } {}^{16}\text{O}} = \frac{12.00000}{15.99491}$$
$$(16.0000)\left(\frac{12.00000}{15.99491}\right) = 12.00382$$

2.4. A 1.5276-g sample of $CdCl_2$ underwent an electrolytic process separating all of the cadmium from the sample. The weight of the metallic cadmium was 0.9367 g. If the atomic mass of chlorine is taken as 35.453, what must be the atomic mass of cadmium from this experiment?

Throughout this book we will specify the amount of a substance in terms of the chemist's unit, the mole. We will use the symbol n(Symbol or formula) to refer to the number of moles of the substance. Since in most laboratory work mass is determined by weighing, the word "weight" (as in the second sentence in the problem) is commonly used where "mass" would be more precise. Unless it leads to an ambiguity, we will follow common usage and not bother to distinguish between "mass" and "weight."

We can approach this problem by first calculating the number of moles of Cl atoms in the weighed sample.

$$\text{Weight of CdCl}_2 = 1.5276\,\text{g}$$
$$\text{Weight of Cd in CdCl}_2 = 0.9367\,\text{g}$$
$$\text{Weight of Cl in CdCl}_2 = 0.5909\,\text{g}$$
$$n(\text{Cl}) = 0.5909\,\text{g} \times \frac{1\,\text{mol}}{35.453\,\text{g}} = 0.016667\,\text{mol}$$

From the formula $CdCl_2$ we see that the number of moles of Cd is exactly half the number of moles of Cl.

$$n(\text{Cd}) = \tfrac{1}{2}n(\text{Cl}) = \tfrac{1}{2}(0.016667) = 0.008333\,\text{mol}$$

The atomic mass is the mass per mole.

$$A_r(\text{Cd}) = \frac{0.9367\,\text{g}}{0.008333\,\text{mol}} = 112.41\,\text{g/mol}$$

2.5. In a chemical determination of the atomic mass of vanadium, 2.8934 g of pure $VOCl_3$ was allowed to undergo a set of reactions as a result of which all the chlorine contained in this compound reacted with silver to produce AgCl. The weight of the AgCl was 7.1801 g. Assuming the atomic masses of Ag and Cl are 107.868 and 35.453, what is the experimental value for the atomic mass of vanadium?

This problem is similar to Problem 2.4, except that $n(\mathrm{Cl})$ must be obtained by way of $n(\mathrm{AgCl})$. The three Cl atoms of $VOCl_3$ are converted to 3 formula units of AgCl, the molar mass of which is 143.321 (the sum of 107.868 and 35.453).

$$n(\mathrm{AgCl}) = 7.1801\ \mathrm{g} \times \frac{1\ \mathrm{mol}}{143.321\ \mathrm{g}} = 0.050098\ \mathrm{mol}$$

From the formula AgCl,

$$n\mathrm{C(l)} = n(\mathrm{AgCl}) = 0.050098\ \mathrm{mol\ Cl}$$

Also, from the formula $VOCl_3$,

$$n(\mathrm{V}) = \tfrac{1}{3}n(\mathrm{Cl}) = \tfrac{1}{3}(0.050098) = 0.016699\ \mathrm{mol\ V}$$

To find the weight of vanadium in the weighed sample of $VOCl_3$, we must subtract the weights of the chlorine and oxygen. If we designate the mass of any substance or chemical constituent X by $m(\mathrm{X})$, then

$$m(\mathrm{X}) = n(\mathrm{X}) \times M(\mathrm{X})$$

where $M(\mathrm{X})$ is the molar mass of X. Note that if X is a single atom, then $M(\mathrm{X})$ is $A_r(\mathrm{X})$. In this problem X is Cl.

$$m(\mathrm{Cl}) = n(\mathrm{Cl}) \times A_r(\mathrm{Cl}) = (0.050098\ \mathrm{mol})(35.453\ \mathrm{g/mol}) = 1.7761\ \mathrm{g\ Cl}$$

The formula $VOCl_3$ tells us that the number of moles of oxygen and vanadium are the same.

$$m(\mathrm{O}) = n(\mathrm{O}) \times A_r(\mathrm{O}) = (0.016699\ \mathrm{mol})(15.999\ \mathrm{g/mol}) = 0.2672\ \mathrm{g\ O}$$

and by difference,

$$m(\mathrm{V}) = m(\mathrm{VOCl_3}) - m(\mathrm{O}) - m(\mathrm{Cl})$$
$$m(\mathrm{V}) = (2.8934 - 0.2672 - 1.7761)\mathrm{g} = 0.8501\ \mathrm{g\ V}$$

and then,

$$A_r(\mathrm{V}) = \frac{m(\mathrm{V})}{n(\mathrm{V})} = \frac{0.8501\ \mathrm{g}}{0.016699\ \mathrm{mol}} = 50.91\ \mathrm{g/mol}$$

Note that this result differs slightly from the accepted value (50.9415 g/mol). The difference can be ascribed to experimental error in this determination.

MOLAR MASS

2.6. Determine the molar mass of (*a*) potassium hexachloroiridate(IV), K_2IrCl_6, and (*b*) the molar mass of trifluorosilane, $SiHF_3$.

Potassium hexachloroiridate(IV) does not exist as discrete molecules represented by the empirical formula, but trifluorosilane does. The term "molar mass" in either case refers to the mass of N_A formula units, which in grams is numerically equal to the sum of all A_r, which appear in the formula (or each element, multiplying its A_r by the number of atoms of that element in the formula).

$$\begin{array}{lrcl}
(a) & 2\,\mathrm{K} = 2(39.098) & = & 78.20 \\
 & 1\,\mathrm{Ir} = 1(192.22) & = & 192.22 \\
 & 6\,\mathrm{Cl} = 6(35.453) & = & \underline{212.72} \\
 & \text{Molar mass} & = & 483.14
\end{array}
\qquad
\begin{array}{lrcl}
(b) & 1\,\mathrm{Si} = 1(28.086) & = & 28.086 \\
 & 1\,\mathrm{H} = 1(1.008) & = & 1.008 \\
 & 3\,\mathrm{F} = 3(18.9984) & = & \underline{56.995} \\
 & \text{Molar mass} & = & 86.089
\end{array}$$

Note that the atomic masses are not all known to the same number of significant figures or to the same number of decimal places in u. In general, the rules for significant figures discussed in Appendix B apply. The value of $A_r(\mathrm{Ir})$ is known to only 0.01 u. Note that in order to express 6 times the atomic mass of Cl to 0.01 u, it was necessary to use the atomic mass to 0.001 u. Similarly, an extra figure was used in the atomic mass for fluorine to give the maximum significance to the last digit in the sum column.

2.7. How many (*a*) grams of H_2S, (*b*) moles of H and of S, (*c*) grams of H and of S, (*d*) molecules of H_2S, (*e*) atoms of H and of S, are contained in 0.400 mol H_2S?

The atomic masses involved are H, 1.008; of S, 32.066. The molecular mass of H_2S is $2(1.008)+32.066 = 34.08$.

Note that it is not necessary to express the molecular mass to 0.001 u, even though the atomic masses are known to this significance. Since the limiting factor in this problem is $n(H_2S)$, known to one part in 400, the value 34.08 (expressed to one part in over 3000) for the molecular mass is more than adequate. This a time-saving device; if you had used the complete atomic masses, your answer would be the same.

(*a*)

$$\text{Number of grams of compound} = (\text{number of moles}) \times (\text{mass of 1 mole})$$

$$\text{Number of grams of } H_2S = (0.400\,\text{mol})(34.08\,\text{g/mol}) = 13.63\,\text{g } H_2S$$

(*b*) One mole of H_2S contains 2 moles of H and 1 mole of S. Then 0.400 mol H_2S contains

$$(0400\,\text{mol } H_2S)\left(\frac{2\,\text{mol H}}{1\,\text{mol } H_2S}\right) = 0.800\,\text{mol H}$$

and 0.400 mol S (half as much as H).

(*c*) Number of grams of element = (number of moles) × (mass of 1 mole)

$$\text{Number of grams of H} = (0.800\,\text{mol})(1.008\,\text{g/mol}) = 0.806\,\text{g H}$$

$$\text{Number of grams of S} = (0.400\,\text{mol})(32.066\,\text{g/mol}) = 12.83\,\text{g S}$$

(*d*) Number of molecules = (number of moles) × (number of molecules in 1 mole)

$$= (0.400\,\text{mol})(6.02 \times 10^{23}\,\text{molecules/mol}) = 2.41 \times 10^{23}\text{molecules}$$

(*e*) Number of atoms of element = (numbers of moles) × (number of atoms per mole)

$$\text{Number of atoms of H} = (0.800\,\text{mol})(6.02 \times 10^{23}\,\text{atoms/mol}) = 4.82 \times 10^{23}\,\text{atoms H}$$

$$\text{Number of atoms of S} = (0.400\,\text{mol})(6.02 \times 10^{23}\,\text{atoms/mol}) = 2.41 \times 10^{23}\,\text{atoms S}$$

2.8. How many moles of atoms are contained in (*a*) 10.02 g calcium, (*b*) 92.91 g phosphorus? (*c*) How many moles of molecular phosphorus are contained in 92.91 g phosphorus if the formula of the molecule is P_4? (*d*) How many atoms are contained in 92.91 g phosphorus? (*e*) How many molecules are contained in 92.91 g phosphorus?

Atomic masses of Ca and P are 40.08 and 30.974; when expressed in grams, we have one mole of each.

(*a*)

$$n(\mathrm{Ca}) = \frac{\text{mass of Ca}}{\text{atomic mass of Ca}} = \frac{10.02\,g}{40.08\,\text{g/mol}} = 0.250\,\text{mol Ca atoms}$$

(*b*)
$$n(\text{P}) = \frac{\text{mass of P}}{\text{atomic mass of P}} = \frac{92.91\,\text{g}}{30.974\,\text{g/mol}} = 3.000\,\text{mol P atoms}$$

(*c*) Molar mass of P_4 is (4)(30.974) = 123.90. Then

$$n(\text{P}_4) = \frac{\text{mass of P}_4}{\text{molar mass of P}_4} = \frac{92.91\,\text{g}}{123.90\,\text{g/mol}} = 0.7500\,\text{mol P}_4\text{ molecules}$$

(*d*)
$$\text{Number of atoms P} = (3.000\,\text{mol})(6.022\times 10^{23}\,\text{atoms/mol}) = 1.807\times 10^{24}\,\text{atoms P}$$

(*e*)
$$\begin{aligned}\text{Number of molecules of P}_4 &= (0.7500\,\text{mol})(6.022\times 10^{23}\,\text{molecules/mol})\\ &= 4.517\times 10^{23}\,\text{molecules P}_4\end{aligned}$$

2.9. How many moles are represented by (*a*) 6.35 g of CO_2, (*b*) 9.11 g of SiO_2, (*c*) 15.02 g of $Ca(NO_3)_2$?

Refer to the periodic table for the appropriate atomic masses. The molecular masses are calculated using the atomic masses.

$$\begin{aligned}\text{Molar mass of CO}_2 &= 1(12.01) + 2(16.00) = 44.01\,\text{g/mol}\\ \text{Molar mass of SiO}_2 &= 1(28.09) + 2(16.00) = 60.09\,\text{g/mol}\\ \text{Molar mass of Ca(NO}_3)_2 &= 1(40.08) + 2[1(14.01) + 3(16.00)] = 164.10\,\text{g/mol}\end{aligned}$$

(*a*) The amount of CO_2 = 6.35 g × (1 mol/44.01 g) = 0.1443 mol CO_2.

(*b*) Amount of SiO_2 = 9.11 g × (1 mol/60.09 g) = 0.1516 mol SiO_2.

(*c*) Amount of $Ca(NO_3)_2$ = 15.02 g × (1 mol/164.10 g) = 0.0915 mol $Ca(NO_3)_2$.

The result (*a*) is a measure of the number of CO_2 molecules (CO_2 is normally a gas in which the CO_2 molecules are separated from each other and have individual physical identities). SiO_2 on the other hand is a complicated crystalline solid (quartz), in which each silicon is surrounded by more than two oxygens and each oxygen by more than one silicon. Because of these factors, there is no physically distinct cluster of one silicon with two oxygens. The result of (*b*) represents a count of the number of SiO_2 formula units. The $Ca(NO_3)_2$ discussed in (*c*) is an ionic crystal of no specific size, the given sample containing 0.0915 moles of calcium ions and twice that number of moles of nitrate ions.

MULTIPLE PROPORTIONS

2.10. Three common gaseous compounds of nitrogen and oxygen of different elementary composition are known, (A) laughing gas containing 63.65% nitrogen, (B) a colorless gas containing 46.68% nitrogen, and (C) a brown, toxic gas containing 30.45% nitrogen. Show how these data illustrate the *law of multiple proportions*.

According to the law of multiple proportions, the relative amounts of an element combining with some fixed amount of a second element in a series of compounds are in ratios of small whole numbers.

Since percent means “parts per hundred” we can assume 100 g. Then, on the basis of 100 g of each compound, we tabulate below the mass of N, the mass of O (obtained by the difference from 100), and the mass of N per gram of O.

	Compound A	**Compound B**	**Compound C**
g of N	63.65	46.68	30.45
g of O	36.35	53.32	69.55
(g of N)/(g of O)	1.7510	0.8755	0.4378

The relative amounts are not affected if all three amounts are set up in the form of a ratio and then divided by the smallest of the relative amounts.

$$1.7510 : 0.8755 : 0.4378 = \frac{1.7510}{0.4378} : \frac{0.8755}{0.4378} : \frac{0.4378}{0.4378} = 4.000 : 2.000 : 1.000$$

The relative amounts are indeed the ratios of small whole numbers—4.000 : 2.000 : 1.000—within the precision of the analyses.

The law of multiple proportions was an important contribution to the credibility of Dalton's atomic theory. It was discovered before relative atomic masses were well known (note that A_r values were not involved in the calculation above). However, it follows logically that all atoms of the same element have the same mass (which is unchangeable) and that compounds contain elements in the relative proportions of simple whole numbers.

Supplementary Problems

ATOMIC MASS

2.11. Naturally occurring argon consists of three isotopes, the atoms of which occur in the following abundances: 0.34% ^{36}Ar, 0.07% ^{38}Ar, and 99.59% ^{40}Ar. Calculate the atomic mass of argon from these data and from data in Table 2-1.

Ans. 39.948

2.12. Naturally occurring boron consists of 80.22% ^{11}B (nuclidic mass = 11.009) and 19.78% of another isotope. To account for the atomic mass, 10.810, what must be the nuclidic mass of the other isotope?

Ans. 10.01

2.13. ^{35}Cl and ^{37}Cl are the only naturally occurring chlorine isotopes. What percentage distribution accounts for the atomic mass, 35.4527?

Ans. 24.23% ^{37}Cl

2.14. Gallium is important, used in high-temperature thermometers, and has two naturally occurring isotopes. ^{69}Ga comprises 60.1% and ^{71}Ga is the other 30.9%. What is the average atomic mass for Ga?

Ans. 69.723

2.15. To account for nitrogen's atomic mass of 14.00674, what must be the ratio of ^{15}N to ^{14}N atoms in natural nitrogen? Ignore the small amount of ^{16}N.

Ans. 0.00369

2.16. At one time there was a chemical atomic mass scale based on the assignment of the value 16.0000 to naturally occurring oxygen. What would have been the atomic mass, on such a table, of silver, if current information had been available? The atomic masses of oxygen and silver on the present table are 15.9994 and 107.8682.

Ans. 107.872

2.17. The nuclidic mass of ^{90}Sr had been determined on the old physical scale (^{16}O $= 16.0000$) as 89.936. Calculate the mass of ^{90}Sr to the atomic mass scale on which ^{16}O is 15.9949.

Ans. 89.907

2.18. In a chemical atomic mass determination, the tin content of 3.7692 g $SnCl_4$ was found to be 1.7170 g. If the atomic mass of chlorine is taken as 35.453, what is the value for the atomic mass of the tin isolated during this experiment?

Ans. 118.65

2.19. A 12.5843-g sample of $ZrBr_4$ was dissolved and, after several chemical steps, all of the combined bromine was precipitated as AgBr. The silver content of the AgBr was found to be 13.2160 g. Assume the atomic masses of silver and bromine to be 107.868 and 79.904. What value was obtained for the atomic mass of Zr from this experiment?

Ans. 91.23

2.20. The atomic mass of sulfur was determined by decomposing 6.2984 g of Na_2CO_3 with sulfuric acid. The weight of Na_2SO_4 formed was 8.4380 g. In this reaction, all sodium in the starting material (Na_2CO_3) appears in the product (Na_2SO_4). Calculate the atomic mass of sulfur from this experiment.

Ans. 32.017

2.21. Although there is only one naturally occurring isotope of iodine, ^{127}I, the atomic mass is given as 126.9045. Explain.

Ans. The atomic masses indicated on the Periodic Table of the Elements are averages, but they are calculated relative to the mass of ^{12}C. The mass number for iodine's naturally occurring isotope is 127, which is a total of the *number* of protons and neutrons, not true masses.

MOLAR MASS

2.22. Determine the molecular mass (or formula unit mass) to 0.01 u for (*a*) LiOH, (*b*) H_2SO_4, (*c*) O_2, (*d*) S_8, (*e*) $Ca_3(PO_4)_2$, (*f*) $Fe_4[Fe(CN)_6]_3$.

Ans. (*a*) 23.95; (*b*) 98.08; (*c*) 32.00; (*d*) 256.53; (*e*) 310.18; (*f*) 859.28

2.23. How many grams of each of the constituent elements are contained in one mole of (*a*) CH_4, (*b*) Fe_2O_3, (*c*) Ca_3P_2? How many atoms of each element are contained in the same amount of compound?

Ans.	(*a*) 12.01 g C, 4.032 g H	6.02×10^{23} atoms C, 2.41×10^{24} atoms H
	(*b*) 111.69 g Fe, 48.00 g O	1.204×10^{24} atoms Fe, 1.81×10^{24} atoms O
	(*c*) 120.23 g Ca, 61.95 g P	1.81×10^{24} atoms Ca, 1.204×10^{24} atoms P

2.24. One of the commercial bullets that can be fired from a 38 special revolver weighs 156 grains (1 lb = 2000 grains). Assuming the bullet is made from only lead, (*a*) how many moles of lead are required for each bullet? (*b*) What number of atoms are present in a bullet?

Ans. (*a*) 0.17 mol Pb; (*b*) 1.03×10^{23} atoms

2.25. A CO_2 cartridge is used to power a rotary tool for smoothing surfaces; it holds 8 g CO_2. (*a*) How many moles of CO_2 are stored in the cartridge? (*b*) How many molecules of CO_2 are there in the cartridge?

Ans. (*a*) 0.18 mol CO_2; (*b*) 1.1×10^{23} molecules CO_2

2.26. Calculate the number of grams in a mole of each of the following common substances: (*a*) calcite, $CaCO_3$; (*b*) quartz, SiO_2; (*c*) cane sugar, $C_{12}H_{22}O_{11}$; (*d*) gypsum, $CaSO_4 \cdot 2H_2O$; (*e*) white lead, $Pb(OH)_2 \cdot 2PbCO_3$.

Ans. (*a*) 100.09 g; (*b*) 60.09 g; (*c*) 342.3 g; (*d*) 172.2 g; (*e*) 775.7 g

2.27. What is the average mass in kilograms of (*a*) a helium atom; (*b*) a fluorine atom; (*c*) a neptunium atom?

Ans. (*a*) 6.65×10^{-27} kg; (*b*) 3.15×10^{-26} kg; (*c*) 3.94×10^{-25} kg

2.28. What is the mass of one molecule of (*a*) CH_3OH; (*b*) $C_{60}H_{122}$; (*c*) $C_{1200}H_{2000}O_{1000}$?

Ans. (*a*) 5.32×10^{-26} kg; (*b*) 1.40×10^{-24} kg; (*c*) 5.38×10^{-23} kg

2.29. How many moles of atoms are contained in (*a*) 32.7 g Zn; (*b*) 7.09 g Cl; (*c*) 95.4 g Cu; (*d*) 4.31 g Fe; (*e*) 0.378 g S?

Ans. (*a*) 0.500 mol; (*b*) 0.200 mol; (*c*) 1.50 mol; (*d*) 0.0772 mol; (*e*) 0.0118 mol

2.30. Two bottles, one labeled *potassium cyanide* and the other *sodium cyanide*, were found hidden behind a water heater. They each contained 125 g substance. (*a*) Which bottle contains more molecules? (*b*) How many moles are present from (*a*)? (*c*) How many more molecules are present in the bottle from (*a*) than the other bottle?

Ans. (*a*) NaCN; (*b*) 2.55 moles NaCN; (*c*) 3.8×10^{23} molecules NaCN

2.31. How many moles are represented by (*a*) 24.5 g H_2SO_4, (*b*) 4.00 g O_2?

Ans. (*a*) 0.250 mol; (*b*) 0.125 mol

2.32. A sample of a metal is composed of 4.25 moles molybdenum and 1.63 moles of titanium. Express the ratio of the two metals in terms of (*a*) atoms and (*b*) masses.

Ans. (*a*) 425 atoms Mo to 163 atoms Ti; (*b*) 407.7 g Mo to 78.04 g Ti

2.33. (*a*) How many moles of Cd and of N are contained in 132.4 g of $Cd(NO_3)_2 \cdot 4H_2O$? (*b*) How many molecules of water of hydration are in this same amount?

Ans. (*a*) 0.429 mol Cd and 0.858 mol N; (*b*) 1.033×10^{24} molecules H_2O

2.34. How many moles of Fe and of S are contained in (*a*) 1 mol of FeS_2 (pyrite); (*b*) 1 kg of FeS_2? (*c*) How many kilograms of S are contained in exactly 1 kg of FeS_2?

Ans. (*a*) 1 mol Fe, 2 mol S; (*b*) 8.33 mol Fe, 16.7 mol S; (*c*) 0.535 kg S

2.35. A certain public water supply contained 0.10 ppb (parts per billion) of chloroform, $CHCl_3$. How many molecules of $CHCl_3$ would be contained in a 0.05-mL drop of this water?

Ans. 2.5×10^{10}

2.36. Iridium has an extremely high density, 22.65 g/cm^3. How many (*a*) grams Ir, (*b*) moles Ir, and (*c*) atoms of Ir are in a cube 2 cm to the side?

Ans. (*a*) 181.2 g Ir; (*b*) 0.94 mol Ir; (*c*) 5.7×10^{23} atoms Ir

2.37. The threshold after which death occurs is 2500 nanograms cyanide per milliliter of blood. Assuming the average blood volume of 5.6 L for an average-sized person, (*a*) what mass in grams potassium cyanide, KCN, will provide the fatal dose? (*b*) The density is 1.5 g/cm^3 KCN; how large would this sample be in cm^3? (*c*) How many moles KCN are there? (*d*) How many molecules are present?

Ans. (*a*) 0.014 g KCN; (*b*) 0.021 cm^3 (a few small crystals); (*c*) 2.6×10^{-4} mol KCN; (*d*) 1.6×10^{20} molecules KCN

2.38. An alloy named 45 Permalloy contains 54.7% Fe, 45% Ni, and 0.3% Mn by mass. (*a*) Express the content of a 0.685-g sample in terms of moles each metal. (*b*) If the source of the information had expressed the percentage composition of Permalloy in moles, rather than mass, would the 45 (percent nickel) in the name still be correct? Explain.

Ans. (*a*) 6.7×10^{-3} mol Fe; 5.3×10^{-3} mol Ni; 3.7×10^{-5} mol Mn; (*b*) No, since the masses and moles are different numbers for each of the components, the percentages would also be different in moles from that given in mass.

2.39. A 0.01-g sample of crude gunpowder was collected from the site of a pipe bomb detonation. Analysis told us the sample was 20% sulfur by mass. The estimate of the amount of gunpowder used was 0.350 kg (less than $\frac{3}{4}$ lb). Calculate (*a*) the mass (g) of sulfur obtained to produce the bomb, (*b*) mol S, and (*c*) number of atoms S.

Ans. (*a*) 70 g S; (*b*) 2.1 mol S; (*c*) 1.3×10^{24} atoms S

MULTIPLE PROPORTIONS

2.40. Verify the law of multiple proportions for an element, X, which forms oxides having percentages of X equal to 77.4%, 63.2%, 69.6%, and 72.0%. If the compound with 77.4% X is XO, what element is X, and what are the other compounds?

Ans. The relative amounts of X combining with the fixed amount of oxygen are 2, 1, $\frac{4}{3}$, and $\frac{3}{2}$. The relative amounts of oxygen combining with the fixed amount of X are 1, 2, $\frac{3}{2}$, and $\frac{4}{3}$. Since $A_r(\text{X}) = 54.8$, X is Mn. The other compounds have the empirical formulas MnO_2, Mn_2O_3, and Mn_3O_4.

2.41. Rust is a variable mixture of a number of iron compounds. A sample of rust has been separated into the various compounds which have been analyzed. There are two sets of data for compounds composed of iron, oxygen, and hydrogen: (1) is 52.12% iron, 45.04% oxygen, and 2.84% hydrogen; (2) is 62.20% iron, 35.73% oxygen, and 2.25% hydrogen. Identify the compounds; how do these data relate to the *law of multiple proportions*?

Ans. (1) is $Fe(OH)_3$ and (2) is $Fe(OH)_2$. The percentages tell us that there are definitely two compounds. The reason the condition exists is that Fe can have two oxidation numbers, +3 and +2, producing two compounds with a small number ratio of the components.

CHAPTER 3

Formulas and Composition Calculations

EMPIRICAL FORMULA FROM COMPOSITION

The *empirical formula* is the formula for a compound that is expressed in the lowest ratio that can be calculated (refer to Chapter 2). Often, a substance must be analyzed to gather information leading to its identity. Various processes can be used to determine the composition of a sample, and an effective way of expressing these data is in the form of weight. Weights can be converted to moles and expressing a formula is the next logical step. The empirical formula is not necessarily the actual molecular formula; however, the empirical formula does contain important information.

Consider a compound that analyzes 17.09 percent magnesium, 37.93 percent aluminum, and 44.98 percent oxygen. (Unless stated to the contrary, percentages are *weight* percentages, i.e., number of grams of element per 100 g of compound.) Table 3-1 gives a systematic scheme for handling provided data.

The numbers in column (4) represent the numbers of moles of atoms of each of the components of the compound found in the 100-g sample. These three numbers state the ratio of the components of the compound—0.703:1.406:2.812. We could write the compound as $Mg_{0.703}Al_{1.406}O_{2.812}$ except, of course, the numbers used must be whole numbers. Suppose we were to divide all three amounts of moles by the smallest number; such a manipulation (5) preserves the ratio since all three are divided by the same number, and the division does result in a whole-number ratio. This final ratio can be used to correctly write the empirical formula, $MgAl_2O_4$.

COMPOSITION FROM FORMULA

The existence of a formula for a compound implies that fixed relationships exist between the weights of any two elements in a specific compound or between the weight of any element and the weight of the compound as a whole. These relationships can best be seen by writing the formula in a vertical form, as illustrated in Table 3-2 for the compound Al_2O_3.

Table 3-1

(1) Element, E	**(2)** Mass of E per Fixed Amount of Compound (in this case, 100 g), $m(\mathrm{E})$	**(3)** Atomic Mass of E, $A_r(\mathrm{E})$	**(4)** Amount of E in Moles of Atoms, $n(\mathrm{E}) = \dfrac{m(\mathrm{E})}{A_r(E)}$	**(5)** $\dfrac{n(\mathrm{E})}{\text{Smallest } n(\mathrm{E})}$
Mg	17.09 g	24.31 g/mol	0.703 mol	1.00
Al	37.93 g	26.98 g/mol	1.406 mol	2.00
O	44.98 g	16.00 g/mol	2.812 mol	4.00

Table 3-2

(1)	**(2)** $n(\mathrm{E})$ per Mole of Compound	**(3)** $A_r(\mathrm{E})$ (atomic mass of element)	**(4)** $m(\mathrm{E})$ per Mole of Compound $= n(\mathrm{E}) \times A_r(\mathrm{E})$	**(5)** $m(\mathrm{E})$ per g of Compound
Al_2	2 mol	27.0 g/mol	54.0 g	$\dfrac{54.0\text{ g Al}}{102.0\text{ g Al}_2\text{O}_3} = 0.529\text{ g Al/g A}_2\text{O}_3$
			48.0 g	$\dfrac{48.0\text{ g O}}{102.0\text{ g Al}_2\text{O}_3} = 0.471\text{ g O/g Al}_2\text{O}_3$
O_3	3 mol	16.0 g/mol	———	———
Al_2O_3	1 mol		Molar mass = 102.0 g	**Check: 1.000**

The sum of the entries in column (4) for the elements equals the molar mass of the compound. The entries in column (5) represent the *fractional* content of the various elements in the compound. These numbers are really dimensionless (g/g cancel out) and are the same in any unit of mass that may be used in similar calculations. This means that we can express the amounts of the elements in 1 ton of the compound in tons of elements, or 1 pound of the compound in terms of pounds of elements.

The *percentage* of aluminum in Al_2O_3 is the number of parts by weight of Al in 100 parts by weight of Al_2O_3. It follows that the percentage is expressed by a number 100 times as great as the fraction. Then, the percentages of aluminum and oxygen are 52.9 percent and 47.1 percent, respectively. The sum of the constituent percentages of any compound must equal 100 percent.

Sometimes it is desirable to state the composition of a substance with respect to a particular element so contained. For example, the aluminum content of glass may be expressed in terms of Al_2O_3, even though there is no aluminum oxide in the glass formulation. Then, a sample of glass that is 1.3 percent Al_2O_3 contains sufficient aluminum so that, if all the aluminum in a 100-g sample of the glass were converted to Al_2O_3, the weight of Al_2O_3 would be 1.3 g. In many cases oxide notations are the result of historical errors in the assignment of chemical structures to complex substances. Whatever the origin, it is a straightforward procedure to convert the data in such a form to direct elementary composition, or vice versa, by the use of a *quantitative factor* such as that found in column (5) of Table 3-2. The ratio of aluminum to aluminum oxide can be expressed as

$$\frac{54\text{ g Al}}{102.0\text{ g Al}_2\text{O}_3} \quad \text{or} \quad \frac{102.0\text{ g Al}_2\text{O}_3}{54.0\text{ g Al}}$$

and is called a quantitative factor. These factors may be used as special conversion factors in numerical problems, such as was found in Chapter 1, Problem 1.19.

NONSTOICHIOMETRIC FACTORS

Stoichiometry is the series of calculations on the basis of formulas and chemical equations and will be covered in Chapter 4. The use of conversion factors is common even when the relative proportions are not fixed by a chemical formula. Consider a silver alloy used for jewelry production. (Alloys are mixtures of metals and, as mixtures, may be produced in differing ratios of the metals.) A particular alloy contains 86 percent silver. Factors based on this composition, such as

$$\frac{0.86\ \text{g Ag}}{1\ \text{g alloy}} \quad \text{or} \quad \frac{100\ \text{g alloy}}{86\ \text{g Ag}}$$

may be used as conversion factors in all problems involving alloys of this particular composition, and are referred to as *nonstoichiometric factors*.

NUCLIDIC MOLECULAR MASSES AND CHEMICAL FORMULAS

The *molecular mass* of a compound is calculated by adding up the atomic masses of the constituent elements. Those masses are the average atomic masses, which are the weighted masses of the various isotopic forms of the elements involved. The *nuclidic molecular mass* may be defined for a molecule made up of particular nuclides by adding nuclidic atomic masses in the same way that the usual molecular mass is computed from the atomic masses.

The *mass spectrometer* is an instrument that is capable of separating particles of different isotopic composition and measuring their individual relative masses. The mass spectrometer also will pull a compound apart one atom at a time, producing fragments that can be detected by their specific masses. The distinction of various fragments and the level of precision in providing masses can supply information from which the exact molecular formula can be deduced without resorting to a quantitative chemical composition analysis.

EXAMPLE 1 Consider the three gases CO, C_2H_4, and N_2. Since ^{12}C, ^{16}O, ^{14}N, and ^{1}H dominate over all other isotopes, the mass spectrometer will reveal the presence of a particle of approximate mass 28 in all three cases. If the measurements are made with great precision, the three gases can easily be distinguished on the basis of their nuclidic masses, which are calculated below.

$$\begin{array}{lrlrlr}
^{12}C^{16}O & 12.0000 & ^{12}C_2{}^{1}H_4 & 2(12.0000) = 24.0000 & ^{14}N_2 & 2(14.00307) = \underline{28.0061} \\
 & \underline{15.9949} & & 4(1.00783) = \underline{\ 4.0313} & & \\
 & 27.9949\,\text{u} & & 28.0313\,\text{u} & & 28.0061\,\text{u}
\end{array}$$

EXAMPLE 2 Find the formula of an organic compound whose dominant nuclidic species was found to have a precise molecular mass of 44.025. It is known that no elements other than C, H, O, and N are present.

The number of carbon atoms in the molecule, $n(\text{C})$, must be at least 1, otherwise the compound would not be organic. $n(\text{C})$ cannot be greater than 3, because 4 carbon atoms would contribute 48 to the total mass number given of the molecule, 44. Similar constraints limit the number of oxygen or nitrogen atoms per molecule. The possible combinations of carbon, oxygen, and nitrogen consistent with the limiting mass are listed in column (1) of Table 3-3.

Column (2) lists the mass numbers of the carbon, nitrogen, oxygen skeletons. Column (3) lists the number of hydrogen atoms needed to bring the mass number of the molecule to 44. Column (4) lists the maximum number of H atoms consistent with rules for molecular structure as discussed in Chapters 9 and 15. One such role is that $n(\text{H, max})$ is equal to twice the number of carbon atoms plus the number of nitrogen atoms plus 2. Column (5) lists the allowed formulas consistent with the total mass number and with all the assumptions and rules. Note that all skeletons for which the number in column (3) (the mass shortage to be made up by hydrogen) exceeds the number in column (4) (the amount of hydrogen allowable for the skeleton by the rules of oxidations numbers) are rejected. Column (6) tabulates the nuclidic molecular masses for the allowed formulas, computed from the nuclidic masses in Table 2-1. When the computed molecular masses are compared with the experimental value, 44.025, it is seen that C_2OH_4 is the only allowable formula that fits the data within the claimed precision; therefore, this must be the formula of the substance.

Table 3-3

(1) (C, O, N) Skeleton	**(2)** Mass Number of Skeleton	**(3)** 44 minus Mass Number of Skeleton	**(4)** n(H, max)	**(5)** Molecular Formula	**(6)** Nuclidic Molar Mass
C	12	32	4		
C_2	24	20	6		
C_3	36	8	8	C_3H_8	44.063
CO	28	16	4		
CO_2	44	0	4	CO_2	43.990
C_2O	40	4	6	C_2OH_4	44.026
CN	26	18	5		
CN_2	40	4	6	CN_2H_4	44.037
C_2N	38	6	7	C_2NH_6	44.050
CON	42	2	5	$CONH_2$	44.014

Solved Problems

CALCULATION OF FORMULAS

3.1. Derive the empirical formula of a hydrocarbon that on analysis gave the following percentage composition: C = 85.63% and H = 14.37%.

The tabular solution, based on 100 g of compound, is as follows:

E	m(E)	A_r(E)	$n(\mathrm{E}) = \dfrac{m(\mathrm{E})}{A_r(\mathrm{E})}$	$\dfrac{n(\mathrm{E})}{7.129\ \mathrm{mol}}$
C	85.63 g	12.011 g/mol	7.129 mol	1.000
H	14.37 g	1.008 g/mol	14.26 mol	2.000

where E = element; m(E) = mass of the element per 100 g of compound; A_r(E) = atomic mass of the element; n(E) = amount of element per 100 g of compound, expressed in moles of atoms.

The procedure of dividing n(E) by n(C) is equivalent to finding the number of atoms of each element for each atom of carbon. The ratio of H to C atoms is 2:1. This means that the empirical formula is CH_2 and that the molecular formula will be a multiple of CH_2; that is, if we had the information to determine the molecular formula, which we don't.

The empirical formula CH_2 is not a stable substance. It is necessary to determine the molar mass to determine the molecular formula. If this hydrocarbon were a gas or an easily volatilized liquid, its molar mass could be determined from the density of the gas, as shown in Chapter 5. Supposing such a determination yields a molar mass of about 55 g/mol, what is the molecular formula?

Since the mass of the empirical formula, CH_2, is 14 u, we can divide the given molar mass to determine the number of empirical formula units we need to achieve the molar mass of 55. EF in the calculation represents the empirical formula.

$$\frac{55\ \dfrac{\mathrm{g}}{\mathrm{mol}}}{14\ \dfrac{\mathrm{g}}{\mathrm{EF}}} = 3.93\ \mathrm{EF/mol}$$

The calculation tells us there are essentially 4 empirical formula units per molecular formula, which then must be C_4H_8. As a verification, butene is a compound with the formula C_4H_8.

3.2. The analysis of a compound indicates a composition that is 26.57% K, 35.36% Cr, and 38.07% O. Derive the empirical formula of the compound.

We can set up the information and solution in the form of the following table:

(1) E	(2) $m(\text{E})$	(3) $A_r(\text{E})$	(4) $n(\text{E}) = \dfrac{m(\text{E})}{A_r(\text{E})}$	(5) $\dfrac{n(\text{E})}{0.6800\,\text{mol}}$	(6) $\dfrac{n(\text{E})}{0.6800\,\text{mol}} \times 2$
K	26.57 g	39.10 g/mol	0.6800 mol	1.000	2
Cr	35.36 g	52.00 g/mol	0.6800 mol	1.000	2
O	38.07 g	16.00 g/mol	2.379 mol	3.499	7

In contrast to the previous example, the numbers in column (5) are not all integers. The ratio of the numbers of atoms of the two elements must be the ratio of small whole numbers, in order to satisfy one of the postulates of Dalton's atomic theory. Allowing for experimental errors and any uncertainty from calculations, we see that the entry of oxygen in column (5), 3.499, is essentially 3.500 when we allow for error. If we round off to 3.5 we can come to a whole number by multiplying by 2 (to get rid of the 0.5). Of course, we must multiply the remaining elements in the ratio to preserve the relationship. When we do so, we arrive at a 2:2:7 ratio shown in column (6), arriving at $K_2Cr_2O_7$ as the formula of the compound.

3.3. A 15.00-g sample of a hydrated salt, $Na_2SO_4 \cdot xH_2O$, was found to contain 7.05 g of water. Determine the empirical formula of the salt.

Hydrates are compounds containing water molecules loosely bound to the other components. H_2O may usually be removed intact by heating and then may be replaced by wetting or possibly by absorbing moisture from the air. The Na_2SO_4 and H_2O groups may be considered as units of which the compound is made and their formula unit masses are used in place of atomic masses. This problem is different from the previous problems because percent compositions were not provided; instead, we are to work with a mass of the hydrated salt and are given the mass of the *anhydrous* (without the water) salt. We can set up the tabular solution using these data.

(1) X	(2) $m(\text{X})$	(3) M(X)	(4) $n(\text{X}) = \dfrac{m(\text{X})}{\text{M(X)}}$	(5) $\dfrac{n(\text{X})}{0.0559\text{ mol}}$
Na_2SO_4	7.95 g	142.1 g/mol	0.0559 mol	1.00
H_2O	7.05 g	18.02 g/mol	0.391 mol	6.99

Column (5) is determined in this problem, as in the previous problem, by dividing both numbers by the smallest (0.0559) which preserves the mole ratio of 0.0559:0.391 and leads to the whole-number ratio required to write a chemical formula. Column (5) contains 6.99, a number that is so close to a whole number that the difference can be taken for experimental error. The mole ratio of Na_2SO_4 to H_2O is 1 to 7, providing us with an empirical formula of $Na_2SO_4 \cdot 7H_2O$.

3.4. A 2.500-g sample of uranium was heated in air. The resulting oxide weighed 2.949 g. Determine the empirical formula of the oxide.

The oxide contains 2.500 g uranium and, by subtraction (2.949 g uranium oxide – 2.500 g uranium), 0.449 g oxygen. Division of the weights of uranium and oxygen by their respective atomic masses tells us that there are 0.01050 mol U and 0.02806 mol O. Dividing both by the smallest number of moles (0.01050) yields the ratio of 1 mol U:2.672 mol O. Rounding off here would be a mistake, as is discussed directly below. Since 2.672 is close to $2\frac{2}{3}$, multiplying by 3 would give us a number that is either a whole number or, hopefully, close to one. The result is nearly a whole-number relationship, 3.00 mol U:8.02 mol O. Considering the possibility of both human error in the analysis and the error involved in calculation, the compound formula is U_3O_8.

Emphasis must be placed on the importance of carrying out the computations to as many significant figures as the analytical precision requires; the information given in the problem is in 4 significant digits. If the numbers in the ratio, 1:2.67, are rounded off at this point, that would result in a ratio of 1:3 and a formula of UO_3. Although this formula is close (notice U_3O_9), it is not correct. Further, if the numbers in the ratio 1:2.67 had been multiplied by 2 to give 2:5.34 and these numbers had been rounded off to 2:5 (U_2O_5), the wrong formula would have also been advanced.

3.5. A 1.367-g sample of an organic compound was combusted in a stream of dry oxygen to yield 3.002 g CO_2 and 1.640 g H_2O. If the original compound contained only carbon, hydrogen, and oxygen, what is its empirical formula?

Since the relationship within a chemical formula is a small whole-number relationship of moles of elements to each other, the first step in the solution is to determine the number of grams of each of the elements. This step must isolate the desired element from the compound produced by the burning, which can be performed by multiplying by the fraction of the compound that is the element.

$$n(\text{C}) = \left(\frac{1\ \text{mol C}}{1\ \text{mol CO}_2}\right)(3.002\ \text{g CO}_2) = \left(\frac{12.01\ \text{g C}}{44.01\ \text{g CO}_2}\right)(3.002\ \text{g CO}_2) = 0.819\ \text{g C}$$

$$n(\text{H}) = \left(\frac{2\ \text{mol H}}{1\ \text{mol H}_2\text{O}}\right)(1.640\ \text{g H}_2\text{O}) = \left(\frac{2(1.008\ \text{g H})}{18.02\ \text{g H}_2\text{O}}\right)(1.640\ \text{g H}_2\text{O}) = 0.184\ \text{g H}$$

The amount of oxygen in the organic compound is obtained by a simple subtraction of the carbon and hydrogen from the sample mass ($1.367 - 0.819 - 0.184 = 0.364$ g O).

Since the numbers of moles are necessary to write the chemical formula, we must perform a set of conversions from grams to moles.

$$\frac{0.819\ \text{g C}}{12.01\ \text{g C/mol C}} = 0.0682\ \text{mol C}$$

$$\frac{1.835\ \text{g H}}{1.008\ \text{g H/mol H}} = 0.1820\ \text{mol H}$$

$$\frac{0.364\ \text{g O}}{16.00\ \text{g O/mol O}} = 0.0228\ \text{mol O}$$

Dividing each of the results by the smallest value (0.0228) lead us to the ratio of 3:8:1 and the chemical formula, C_3H_8O.

COMPOSITION PROBLEMS

3.6. A strip of copper weighing 3.178 g is strongly heated in a stream of oxygen until it is all converted to 3.978 g of the black copper-oxygen compound. What is the percentage composition of copper and oxygen in this compound?

$$\begin{aligned} \text{Total weight of black oxide} &= 3.978\ \text{g} \\ \text{Weight of copper in oxide} &= \underline{3.178\ \text{g}} \\ \text{Weight of oxygen in oxide} &= 0.800\ \text{g} \end{aligned}$$

$$\text{Fraction of copper} = \frac{\text{weight of copper in oxide}}{\text{total weight of oxide}} = \frac{3.178\ \text{g}}{3.978\ \text{g}} = 0.799 = 79.9\%\ \text{Cu}$$

$$\text{Fraction of oxygen} = \frac{\text{weight of oxygen in oxide}}{\text{total weight of oxide}} = \frac{0.800\ \text{g}}{3.978\ \text{g}} = 0.201 = 20.1\%\ \text{O}$$

Note that the total of the two percentages is 100%, which forms a check for the calculations.

3.7. (*a*) Determine the percentages of iron in $FeCO_3$, Fe_2O_3, and Fe_3O_4. (*b*) How many kilograms of iron could be obtained from 2.000 kg of Fe_2O_3?

(*a*) Molar mass of $FeCO_3$ is 115.86; of Fe_2O_3 is 159.69; of Fe_3O_4 is 231.54. The key is to calculate the fraction of iron found in each compound, then convert each fraction to percent composition.

$$\text{Fraction of Fe in FeCO}_3 = \frac{m(1\text{ mol Fe})}{m(1\text{ mol FeCO}_3)} = \frac{55.847\text{ g}}{115.86\text{ g}} = 0.4820 \quad \text{or} \quad 48.20\%$$

$$\text{Fraction of Fe in Fe}_2\text{O}_3 = \frac{m(2\text{ mol Fe})}{m(1\text{ mol Fe}_2\text{O}_3)} = \frac{2(55.847)}{159.69\text{ g}} = 0.6994 \quad \text{or} \quad 69.94\%$$

$$\text{Fraction of Fe in Fe}_3\text{O}_4 = \frac{m(3\text{ mol Fe})}{m(1\text{ mol Fe}_3\text{O}_4)} = \frac{3(55.847)\text{ g}}{231.54\text{ g}} = 0.7236 \quad \text{or} \quad 72.36\%$$

(*b*) From (*a*), the weight of Fe in 2.00 kg Fe_2O_3 is 0.06994×2.000 kg = 1.399 kg Fe.

3.8. Given the formula K_2CO_3, determine the percent composition of each of the elements in potassium carbonate.

$$\begin{aligned} 2\text{ moles K} &= 2(39.0983) = 78.197\text{ g K} \\ 1\text{ mol C} &= 1(12.011) = 12.011\text{ g C} \\ 3\text{ moles O} &= 3(15.9994) = 47.998\text{ g O} \\ \text{Molar mass K}_2\text{CO}_3 &= 138.206\text{ g} \end{aligned}$$

One mole of K_2CO_3 contains

$$\text{Fraction of K in K}_2\text{CO}_3 = \frac{78.197}{138.206} = 0.5658 \quad \text{or} \quad 56.58\%\text{ K}$$

$$\text{Fraction of C in K}_2\text{CO}_3 = \frac{12.011}{138.206} = 0.0869 \quad \text{or} \quad 8.69\%\text{ C}$$

$$\text{Fraction of O in K}_2\text{CO}_3 = \frac{47.998}{138.206} = 0.3473 \quad \text{or} \quad 34.73\%$$

The sum of the percentages is 100%, our check on our work.

3.9. CaO can be isolated from limestone, $CaCO_3$, by means of driving off CO_2 during heating. (*a*) Calculate the percentage of CaO in $CaCO_3$. (*b*) How many pounds of CaO can be obtained from 1 ton of limestone that is 97.0% $CaCO_3$? (1 ton = 2000 lb)

(*a*) There is 1 mole of CaO per mole of $CaCO_3$. We can write a quantitative factor (conversion factor) and apply to determine the fraction, then the percentage composition, of CaO in $CaCO_3$.

$$\text{Fraction of CaO in CaCO}_3 = \frac{\text{molar mass CaO}}{\text{molar mass CaCO}_3} = \frac{56.1}{100.1} = 0.560 \quad \text{or} \quad 56\%\text{ CaO}$$

(*b*) We must first calculate the weight of $CaCO_3$ in one ton of the limestone, then the weight of the CaO.

$$\text{Weight of CaCO}_3\text{ in 1 ton limestone} = 0.970 \times 2000\text{ lb} = 1940\text{ lb CaCO}_3$$

$$\begin{aligned} \text{Weight of CaO} &= (\text{fraction CaO in CaCO}_3)(\text{weight of CaCO}_3) \\ &= (0.560)(1940) = 1090\text{ lb CaO in 1 ton of limestone} \end{aligned}$$

3.10. How much 58.0% sulfuric acid solution is needed to provide 150 g of H_2SO_4?

Let w = mass (weight) of sulfuric acid solution. Also, notice that there are 58.0 grams of pure acid per 100 grams of solution (58.0% H_2SO_4 solution).

$$\left(\frac{58.0\text{ g H}_2\text{SO}_4}{100\text{ g solution}}\right) w = 150\text{ g H}_2\text{SO}_4$$

$$w = 259\text{ g solution}$$

A second solution avoids the algebra in the solution by using the concept of the conversion factor and setting it up so that units cancel properly.

$$\left(150\,\text{g}\ H_2SO_4\right)\left(\frac{100\,\text{g solution}}{58.0\,\text{g}\ H_2SO_4}\right) = 259\,\text{g solution}$$

3.11. How much calcium is in the amount of $Ca(NO_3)_2$ that contains 20.0 g nitrogen?

It is not necessary to find the weight of calcium nitrate containing 20.0 g N. The relationship between the calcium and the nitrogen can be found directly from the formula. There are 2 atoms of nitrogen for each atom of calcium. This relationship can also be expressed in terms of moles: 2 mol N:1 mol Ca.

$$\text{Weight of Ca} = \left(20.0\,\text{g N}\right)\left(\frac{1\,\text{mol Ca}}{2\,\text{mol N}}\right) = \left(20.0\,\text{g N}\right)\left(\frac{40.08\,\text{g Ca}}{2(14.01\,\text{g N})}\right) = 28.6\,\text{g Ca}$$

3.12. (*a*) How much sulfuric acid, H_2SO_4, could be produced from 500 kg of sulfur? (*b*) How many kilograms of Glauber's salt, $Na_2SO_4 \cdot 10H_2O$, could be obtained from 1000 kg of H_2SO_4?

(*a*) The formula of sulfuric acid indicates that 1 mol S (32.07 g S) will give 1 mol H_2SO_4 (98.08 g H_2SO_4). We assume a 100% efficient reaction. Then, since the *ratio* of any two elements involved in the formula can be expressed in a ratio of the mass units (g/mol), we can use a conversion factor containing the information for both the sulfuric acid and the sulfur.

$$\text{Weight of } H_2SO_4 = \left(500\,\text{kg S}\right)\left(\frac{98.08\,\text{kg}\ H_2SO_4}{32.07\,\text{kg S}}\right) = 1529\,\text{kg}\ H_2SO_4$$

(*b*) 1 mol H_2SO_4 (98.08 g/mol) will give 1 mol $Na_2SO_4 \cdot 10H_2O$ (322.2 g/mol), since each substance contains one sulfate (SO_4) group per formula unit. Then

$$\text{Weight of } Na_2SO_4 \cdot 10H_2O = \left(1.000\,\text{kg}\ H_2SO_4\right)\left(\frac{322.2\,\text{kg}\ Na_2SO_4 \cdot 10H_2O)}{98.08\,\text{kg}\ H_2SO_4}\right)$$

$$= 3.285\,\text{kg}\ Na_2SO_4 \cdot 10H_2O$$

3.13. How many tons of $Ca_3(PO_4)_2$ must be treated with carbon and sand in an electric furnace to make 1 ton of phosphorus? Assume complete conversion of the phosphorus.

The formula for calcium phosphate tells us that 2 mol P (2×30.974 g P $= 61.95$ g P) is contained in 1 mol $Ca_3(PO_4)_2$ (310.2 g/mol). Then changing grams to tons in the weight ratio, we obtain

$$\text{Weight } Ca_3(PO_4)_2 = \left(1\,\text{ton P}\right)\left(\frac{310.2\,\text{tons}\ Ca_3(PO_4)_2}{61.95\,\text{tons P}}\right) = 5.01\ \text{tons}\ Ca_3(PO_4)_2$$

3.14. A 5.82-g silver coin is dissolved in nitric acid. When sodium chloride is added to the solution, all the silver is precipitated as AgCl. The AgCl precipitate weighs 7.20 g. Determine the percentage of silver in the coin.

$$\text{Fraction of Ag in AgCl} = \frac{\text{molar mass Ag}}{\text{molar mass AgCl}} = \frac{107.9}{143.3} = 0.753$$

$$\text{Mass of Ag in 7.20 g AgCl} = (0.753)(7.20\,\text{g}) = 5.42\,\text{g Ag}$$

and, since the 5.82-g coin contains 5.42 g Ag,

$$\text{Percentage Ag in coin} = \frac{5.42\,\text{g}}{5.82\,\text{g}} \times 100 = 0.931 \times 100 = 93.1\%$$

3.15. A sample of impure sulfide ore contains 42.34% Zn. Find the percentage of pure ZnS in the sample.

The formula ZnS shows that 1 mole of ZnS contains 1 mole Zn, providing us with the conversion factor

$$\frac{1 \text{ molar mass ZnS}}{1 \text{ molar mass Zn}} = \frac{97.46 \text{ g ZnS}}{65.39 \text{ g Zn}}$$

Consider 100.0 g of sample; it contains 42.34 g Zn. Then, applying the conversion factor,

$$(42.34 \text{ g Zn})\left(\frac{97.46 \text{ g ZnS}}{65.39 \text{ g Zn}}\right) = 63.11 \text{ g ZnS in 100 g of sample, or } 63.11\% \text{ pure ZnS}$$

3.16. Fertilizers are compounds or mixtures usually used to supply potassium, nitrogen, and phosphorus to soil. If a bag of fertilizer consists of almost pure KNO_3 (potassium nitrate), what percentages of those three important elements should appear on the label?

Let us take a look at one mole pure KNO_3, which contains

$$\begin{aligned} \text{1 mole of K} &= 39.10 \text{ g} \\ \text{1 mole N} &= 14.01 \text{ g} \\ \text{3 moles of O} = 3(16.00) &= \underline{48.00 \text{ g}} \\ \text{Molar mass of } KNO_3 &= 101.11 \text{ g} \end{aligned}$$

$$\text{Percent of K} = (39.10 \text{ g K}/101.11 \text{ g compound}) \times 100 = 38.67\%$$

$$\text{Percent of N} = (14.01 \text{ g N}/101.11 \text{ g compound}) \times 100 = 13.86\%$$

$$\text{Percent of P} = 0\%$$

3.17. (*a*) A Pennsylvania bituminous coal is analyzed as follows: Exactly 2.500 g is weighed into a fused silica crucible. After drying for 1 hour at 110°C, the moisture-free residue weighs 2.415 g. The crucible is then covered with a vented lid and strongly heated until no volatile matter remains. The residual coke button weighs 1.528 g. The crucible is further heated, but without the cover, until all specks of carbon have disappeared, resulting in a final ash that weighs 0.245 g. What is the *proximate analysis* of this coal, i.e., the percents of moisture, volatile combustible matter (VCM), fixed carbon (FC), and ash?

$$\begin{aligned} \text{Moisture} &= 2.500 \text{ g} - 2.415 \text{ g} = 0.085 \text{ g} \\ \text{VCM} &= 2.415 \text{ g} - 1.528 \text{ g} = 0.887 \text{ g} \\ \text{FC} &= 1.528 \text{ g} - 0.245 \text{ g} = 1.283 \text{ g} \\ \text{Ash} &= \underline{0.245 \text{ g}} \\ \text{Total} &= 2.500 \text{ g coal} \end{aligned}$$

$$\text{Fraction of moisture} = \frac{0.085 \text{ g}}{2.50 \text{ g}} = 0.034 \qquad \text{and} \qquad 0.034 \times 100 = 3.4\%$$

Similarly, the other percentages are calculated to be 35.5% VCM, 51.3% FR, and 9.8% ash.

(*b*) On the "dry basis" a sample of coal analyzes as follows: VCM is 21.06%; fixed carbon is 71.80%; and ash is 7.14%. If the moisture present in the coal is 2.49%, what is the analysis on the "wet basis"?

If we were to consider a 100-g sample of the coal, then the percents without the water present (100 − 2.49 = 97.5 g of dry sample) can be used and the solution becomes

VCM	(0.2106)(97.5) = 20.5 g out of 100 g wet coal or	20.5%
FC	(0.7180)(97.5) = 70.0 g out of 100 g wet coal or	70.0%
Ash	(0.0714)(97.5) = 7.0 g out of 100 g wet coal or	7.0%

When we add these percentages and include the 2.5% for moisture, the sum is 100%.

3.18. A certain fertilizer, "A," contains 38.7% K, 13.9% N, and no P. Another, "B," contains 12.2% N, 26.9% P, and no K. (*a*) What will be the percentages of K, N, and P in a fertilizer made by blending equal weights of A and B? (*b*) The manufacturer wishes to market a mixture of A and B in which the two elements K and P are present in equal proportions. What proportions of A and B should be used?

(*a*) If we choose to mix 100 g of each, we arrive at the composition of 200 g of the mixture from which we can calculate the percentages requested.

	K	N	P
From A	38.7 g	13.9 g	0 g
From B	0 g	12.2 g	26.9 g
Mixture	38.7 g	26.1 g	26.9 g
Percents (mix/2)	19.4%	13.1%	13.5%

(*b*) We can consider 100 g of the mixture letting $c =$ g of A; then $100 - c =$ g of B. Setting %K = %P in the mixture,

$$0.387c = 0.269(100 - c)$$

Solving this, we find that $c = 41.0$ g of A, and $(100 - c) = 59.0$ g of B.

3.19. When the *Bayer process* is used for recovering aluminum from siliceous ores, some aluminum is always lost because of the formation of an unworkable "mud" having the average formula $3Na_2O \cdot 3Al_2O_3 \cdot 5SiO_2 \cdot 5H_2O$. Since aluminum and sodium ions are always in excess in the solution from which this precipitate is formed, the precipitation of the silicon in the "mud" is complete. A certain ore contained 13% (by weight) kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and 87% gibbsite ($Al_2O_3 \cdot 3H_2O$). What percent of the total aluminum in this ore is recoverable in the Bayer process?

If we were to obtain 100 g of the ore, it would contain 13 g kaolin and 87 g gibbsite. We can determine the amounts of aluminum by the following procedures:

$$\text{Weight of Al in 13 g kaolin} = 13\text{ g kaolin} \times \frac{2\text{ mol Al}}{1\text{ mol kaolin}} = 13 \times \frac{54.0}{258} = 2.7\text{ g Al}$$

$$\text{Weight of Al in 87 g gibbsite} = 87\text{ g gibbsite} \times \frac{2\text{ mol Al}}{1\text{ mol gibbsite}} = 87 \times \frac{54.0}{156} = 30.1\text{ g Al}$$

$$\text{Total weight of Al in 100 g ore} = 2.7\text{ g} + 30.1\text{ g} = 32.8\text{ g Al}$$

Kaolin has equal numbers of Al and Si atoms, and 13 g kaolin contains 2.7 g Al. The mud takes 6 Al atoms for 5 Si atoms or 6 Al atoms lost for every 5 Si atoms in the kaolin. This means that the precipitation of all the Si from 13 g kaolin involves the loss of $\left(\frac{6}{5}\right)(2.7\text{ g}) = 3.2$ g Al.

$$\text{Fraction of Al recoverable} = \frac{\text{recoverable Al}}{\text{total Al}} = \frac{(32.8 - 3.2)\text{ g}}{32.8\text{ g}} = 0.90 \quad \text{or} \quad 90\%$$

3.20. A clay was partially dried and was found to contain 50% silica and 7% water. The original clay contained 12% water. What is the percentage of silica in the original sample?

We have to make the assumption that only water was lost in the drying process. The original and the partially dried clays have the compositions as indicated directly below.

	% Water	% Silica	% Other
Original	12	p	$88 - p$
Dried	7	50	43

The ratio of silica to the other dry constituents must be the same in both clays; then

$$\frac{p}{88 - p} = \frac{50}{43}$$

Solving, $p = 47$. This means that there was 47% silica in the original clay.

3.21. Bronze is an alloy of copper and tin. A 0.6554-g sample of a certain bronze was reacted with nitric acid and the tin removed. After appropriate treatment of the solution, titration with sodium thiosulfate revealed that it contained 8.351 millimoles of copper. Calculate the percentages of copper and tin in this bronze.

$$\%\ \mathrm{Cu} = 100\% \times \frac{8.351 \times 10^{-3}\ \mathrm{mol\ Cu} \times \left(\dfrac{63.55\ \mathrm{g\ Cu}}{\mathrm{mol\ Cu}}\right)}{0.6554\ \mathrm{g\ sample}} = 80.97\%\ \mathrm{Cu}$$

$$\%\ \mathrm{Sn} = 100.00\% - 80.97\% = 19.03\%\ \mathrm{Sn}$$

3.22. A nugget of gold and quartz weighs 100 g and has a density of 6.4 g/cm^3. The density of gold is 19.3 g/cm^3 and that of quartz is 2.65 g/cm^3. Determine the weight of gold in the nugget.

If we let w be the weight of gold in the nugget, the amount of quartz is $100\ \mathrm{g} - w$.

$$\text{Volume of the nugget} = (\text{volume of gold}) + (\text{volume of quartz})$$

$$\frac{100\ \mathrm{g}}{6.4\ \mathrm{g/cm^3}} = \frac{w}{19.3\ \mathrm{g/cm^3}} + \frac{100\ \mathrm{g} - w}{2.65\ \mathrm{g/cm^3}}$$

Solving for w, we find that the nugget contains 68 g of gold.

MOLAR MASSES

3.23. A purified cytochrome protein isolated from a bacterial preparation was found to contain 0.376% iron. What can be deduced about the molar mass of the protein?

The percent iron content is rather small at 0.376 g per 100 g of sample. Further, the information in the problem implies that each molecule must contain a minimum of one atom of iron. If it does contain only one atom of iron (55.8 u), then the molar mass, M, is given by

$$0.00376\ \mathsf{M} = 55.8\ \mathrm{u}$$

$$\mathsf{M} = 14{,}800\ \mathrm{u} \qquad \text{or} \qquad 14{,}800\ \mathrm{g/mol\ cytochrome}$$

This means that, if the protein molecule contained n number of atoms of Fe, the molar mass would be 14,800n u (14,800n g/mol) cytochrome.

This method of calculation is useful for the determination of the *minimum* molar mass of a macromolecular (large molecule) substance when an analysis can be done for only one of the minor components. Frequently, the approximate molar mass can be determined by a physical method, such as osmotic pressure or sedimentation rate.

3.24. A purified pepsin isolated from a bovine preparation was subject to an amino acid analysis of its hydrolytic products. The amino acid present in the smallest amount was lysine, $C_6H_{14}N_2O_2$, and the amount of lysine recovered was found to be 0.43 g per 100 g protein. What is the minimum molar mass of the protein?

Proteins do not contain free amino acids, but they do contain chemically linked forms of amino acids, which on degradative hydrolysis can be reconverted to the free amino acid form. The molar mass lysine is 146, and we let M be the minimum molar mass of the protein. As in Problem 3.23, the protein molecule must be at least heavy enough to contain one lysine residue.

$$\text{Number of moles lysine} = \text{number of moles protein}$$

$$0.43\ \mathrm{g} \times \frac{1\ \mathrm{mol}}{146\ \mathrm{g}} = 100\ \mathrm{g} \times \frac{1\ \mathrm{mol}}{\mathsf{M}\ \mathrm{g}}$$

Solving for M, we find that the pepsin has a molecular mass of 34,000 u.

3.25. Unsaturated polyesters produced from maleic acid ($C_4H_4O_4$) and ethylene glycol ($C_2H_6O_2$) are widely used (with styrene and fiberglass) to make reinforced resin structures. A 5.00-g portion of a batch of polyester was dissolved and treated with 0.00420 moles of sodium hydroxide (NaOH), an amount just sufficient to neutralize all of the acid "end-groups" present. Since there are two end-groups in each molecule, what is the average molar mass of the polyester?

$$2 \times \text{ moles of polyester} = \text{moles of NaOH}$$

$$\text{Moles of polyester} = 0.00420/2 = 0.00210\,\text{moles polyester}$$

$$\mathsf{M} = \text{molar mass} = 5.00\,\text{b}/0.00210\,\text{mol} = 2380\,\text{g/mol}$$

FORMULA FROM PRECISE NUCLIDIC MOLECULAR MASS

3.26. An organic compound was prepared containing at least one and no more than two sulfur atoms per molecule. The compound had no nitrogen, but oxygen could have been present. The mass-spectrometrically determined molecular mass of the predominant nuclidic species was 110.020. (*a*) What are the allowable molecular formulas consistent with the mass number 110 and with the facts about the elementary composition? (*b*) What is the molecular formula of the compound?

(*a*) The skeleton, minus the hydrogen present in the molecule, would be made up of the elements C, O, and S. The number of possible skeletons can be reduced by the following considerations: (i) The maximum number of carbon atoms is 6, since the mass number of carbons plus 1 sulfur would be 116, which is too heavy to conform to the problem. (ii) The maximum number of hydrogen atoms is $2n(\text{C}) + 2 = 14$ by the rules of organic molecular composition. (iii) The skeleton (C, O, S) must contribute between 96 and 110 u to the mass number. A rather short list, Table 3-4, will now suffice.

Table 3-4

(1) (C, O, S) Skeleton	**(2)** Mass number of Skeleton	**(3)** 100 − **(2)**	**(4)** n(H, max)	**(5)** Molecular Formula	**(6)** Nuclidic Molecular Mass
CO_4S	108	2	4	CO_4SH_2	109.967
CO_2S_2	108	2	4	$CO_2S_2H_2$	109.949
C_2O_3S	104	6	6	$C_2O_3SH_6$	110.004
C_2OS_2	104	6	6	$C_2OS_2H_6$	109.986
C_3O_2S	100	10	8		
C_3OS_2	100	10	8		
C_4OS	96	14	10		
C_5OS	108	2	12	C_5OSH_2	109.983
C_6S	104	6	14	C_6SH_6	110.019

(*b*) Of the six formulas consistent with the known mass number, only C_6SH_6 is consistent with the precise molecular mass.

Supplementary Problems

CALCULATION OF FORMULAS

3.27. What are the empirical formulas for the chlorides of vanadium containing 58.0%, 67.8%, and 73.6% chlorine?

Ans. VCl_2, VCl_3, VCl_4

3.28. A compound contains 21.6% sodium, 33.3% chlorine, 45.1% oxygen. Record the empirical formula of the compound (atomic masses: Na = 23.0, Cl = 35.5, and O = 16).

Ans. $NaClO_3$

3.29. When 1.010 g of zinc vapor is burned in air, 1.257 g of the oxide is produced. What is the empirical formula of the oxide?

Ans. ZnO

3.30. A compound has the following percentage composition: H = 2.24%, C = 26.69%, O = 71.07%, and a molar mass of 90. Derive its molecular formula.

Ans. $H_2C_2O_4$

3.31. Determine the simplest formula of a compound that has the following composition: Cr = 26.52%, S = 24.52%, and O = 48.96%.

Ans. $Cr_2S_3O_{12}$ or $Cr_2(SO_4)_3$

3.32. A 3.245-g sample of titanium chloride was reduced with sodium to metallic titanium. After the resultant sodium chloride was washed out, the residual metal was dried and found to weigh 0.819 g. What is the empirical formula of the original compound of titanium?

Ans. $TiCl_4$

3.33. Magnesium can be used to produce strong and light-weight alloys with aluminum. (*a*) Calculate the percent magnesium available from $MgSO_4 \cdot 7H_2O$, Epsom salts, and (*b*) from $Mg_3(PO_4)_2$.

Ans. (*a*) 7.1% Mg; (*b*) 27.7% Mg

3.34. Calculate the formula of the compound, which exists as a hydrate, containing 44.6% ytterbium and 27.5% chlorine.

Ans. $YbCl_3 \cdot 6H_2O$

3.35. An organic compound was found to contain 47.37% carbon and 10.59% hydrogen. The balance was presumed to be oxygen. What is the empirical formula of the compound?

Ans. $C_3H_8O_2$

3.36. Derive the empirical formulas of the minerals that have the following compositions: (*a*) $ZnSO_4$ = 56.14%, H_2O = 43.86%; (*b*) MgO = 27.16%, SiO_2 = 60.70%, H_2O = 12.14%; (*c*) Na = 12.10%, Al = 14.19%, Si = 22.14%; O = 42.09%, H_2O = 9.48%.

Ans. (*a*) $ZnSO_4 \cdot 7H_2O$; (*b*) $2MgO \cdot 3SiO_2 \cdot 2H_2O$; (*c*) $Na_2Al_2Si_3O_{10} \cdot 2H_2O$

3.37. A *borane* (composed of boron and hydrogen) analyzed 88.45% boron. What is the empirical formula?

Ans. B_5H_7

3.38. What is the empirical formula of a catalyst that can be used in the polymerization of butadiene if its composition is 23.3% Co, 25.3% Mo, and 51.4% Cl.

Ans. $Co_3Mo_2Cl_{11}$

3.39. A 1.500-g sample of a compound containing only C, H, and O was burned completely. The only combustion products were 1.738 g CO_2 and 0.711 g H_2O. What is the empirical formula of the compound?

Ans. $C_2H_4O_3$

3.40. Elementary analysis showed that an organic compound contained C, H, N, and O as its only elementary constituents. A 1.279-g sample was burned completely, as a result of which 1.60 g of CO_2 and 0.77 g of H_2O were obtained. A separately weighed 1.625-g sample contained 0.216 g nitrogen. What is the empirical formula of the compound?

Ans. $C_3H_7O_3N$

3.41. Plaster of Paris is supplied as a white powder which can be mixed with water for producing impressions of footprints, tire tracks, and the like. Plaster of Paris is a hydrated calcium sulfate, $CaSO_4$, containing 6.20% H_2O. What is the formula for Plaster of Paris?

Ans. $2CaSO_4 \cdot H_2O$ or $CaSO_4 \cdot \frac{1}{2}H_2O$

3.42. A hydrocarbon containing 92.3% C and 7.74% H was found to have a molar mass of approximately 79. What is the molecular formula?

Ans. C_6H_6

3.43. An alloy with a low melting point is produced from 10.6 lb bismuth, 6.4 lb lead, and 3.0 lb tin. (*a*) What is the percentage composition of the alloy? (*b*) How much of each metal is required to make 70.0 g of alloy? (*c*) What weight of the alloy can be made from 4.2 lb tin?

Ans. (*a*) 53% Bi, 32% Pb, 15% Sn; (*b*) 37.1g Bi, 22.4 g Pb, 10.5 g Sn; (*c*) 28 lb

3.44. Some golden flakes were collected from a fatal puncture wound. The sample of 0.0022 g was collected and turned out to be 0.0019 g copper and the remainder zinc. A brass letter opener was found nearby and was 87% copper and 13% zinc. Are the flakes likely to be from the letter opener?

Ans. The percentage of copper, 86%, is close and appears to be within the intrinsic error of measurement and calculation, but may not be conclusive.

3.45. Calculate the percentage of copper in each of the following minerals: (*a*) cuprite, Cu_2O; copper pyrite, $CuFeS_2$; malachite, $CuCO_3 \cdot Cu(OH)_2$. (*b*) How many grams of cuprite will give 500 kg of copper?

Ans. (*a*) 88.82%, 34.63%, 57.48%; (*b*) 563 kg

3.46. Titanium is used for its strength and light weight; some alloys are 50% the weight of steel with no sacrifice of strength. Titanium is isolated from rutile, TiO_2, and other ores. If the rutile ore is 11.48% titanium(IV) oxide by weight, how much ore must be processed to obtain 900 kg (a little less than a metric ton) of metallic titanium (assume pure)?

Ans. 13,000 kg ore (13 metric tons)

3.47. What is the nitrogen content (fertilizer rating, usually expressed in the percentage composition of nitrogen) of NH_4NO_3? of $(NH_4)_2SO_4$? of NH_3?

Ans. 35.0% N, 21.2% N, 82.3% N

3.48. Determine the percentage composition of (*a*) silver chromate, Ag_2CrO_4; (*b*) calcium pyrophosphate, $Ca_2P_2O_7$.

Ans. (*a*) 65.03% Ag, 15.67% Cr, 19.29% O; (*b*) 31.54% Ca, 24.38% P, 44.08% O

3.49. Find the percentage of arsenic in a polymer having the empirical formula C_2H_8AsB.

Ans. 63.6% As

3.50. A famous case of poisoning occurred in the orange-growing region of Florida (1988, soft drink tampering). The analysis of 5.000 g suspected toxin revealed the chemical composition of 4.049 g thallium, 0.318 g sulfur, and 0.639 g oxygen. Provide the chemical formula and name.

Ans. Tl_2SO_4, thallium(I) sulfate (Use: rat and ant poison; banned in 1975)

3.51. The lethal dose of thallium can be as little as 14 mg Tl/kg body weight; thallium accumulates in the body. (*a*) What mass (g) of the thallium compound in Problem 3.50 would be a single fatal dose for a 220 lb (100 kg) man? (*b*) If the compound were to be introduced into the meals of this man at the rate of 50 mg/day total over three meals/day, how long would it take (days) to build up the fatal dose of thallium assuming no excretion of the metal?

Ans. (*a*) 1.73 g Tl_2SO_4; (*b*) 35 days

3.52. Determine the compound that contains more arsenic: Na_3AsO_4, As_2O_3, or As_2S_3.

Ans. Approximate percents As: 36% in Na_3AsO_4, 75% in As_2O_3, and 70% in As_2S_3

3.53. The specifications for a transistor material called for one boron atom in 10^{10} silicon atoms. What would be the boron content of 1 kg of this material?

Ans. 4×10^{-11} kg B

3.54. The purest form of carbon is prepared by decomposing pure sugar, $C_{12}H_{22}O_{11}$ (driving off the contained H_2O from the carbohydrate). What is the maximum number of grams of carbon that could be obtained from 500 g sugar?

Ans. 211 g C

3.55. The empirical formula for vinyl plastic (a polymer of vinyl chloride, PVC) used in pipe that can be used for building sprinkler systems is CH_2CHCl. (*a*) What is the percentage of chlorine in this plastic, and, as a contrast, (*b*) calculate the percentage of chlorine in table salt, NaCl?

Ans. (*a*) 56.7%; (*b*) Table salt is 60.7% chlorine.

3.56. A compound is known to be composed of 40.002% carbon, 8.063% hydrogen, and 53.285% oxygen. The mass spectrophotometer indicates a molecular mass about 121 u. (*a*) What is the empirical formula? (*b*) What is the likely molecular formula?

Ans. (*a*) CH_2O; (*b*) $C_4H_8O_4$, a carbohydrate, as is glucose, $C_6H_{12}O_6$

3.57. What weight of CuO will be required to furnish 200 kg of copper?

Ans. 250 kg CuO

3.58. Ordinary table salt, NaCl, can be electrolyzed in the molten state to produce sodium and chlorine. Electrolysis of an aqueous solution produces sodium hydroxide (NaOH), hydrogen, and chlorine. The latter two products may be combined to form hydrogen chloride (HCl). How many pounds of metallic sodium and of liquid chlorine can be obtained from 1 ton of salt? Alternately, how many pounds of NaOH and how many pounds of hydrogen chlorine can be obtained from that sample?

Ans. 787 lb Na, 1213 lb liquid Cl_2, 1370 lb NaOH, 1248 lb HCl

3.59. Compute the amount of zinc in a metric ton of ore containing 60.0% zincite, ZnO.

Ans. 482 kg Zn

3.60. How much phosphorus is contained in 5.00 g of the compound $CaCO_3 \cdot 3Ca_3(PO_4)_2$? How much P_2O_5?

Ans. 0.902 g P, 2.07 g P_2O_5

3.61. A 10.00-g sample of crude ore contains 2.80 g HgS. What is the percentage of mercury in the ore?

Ans. 24.1% Hg

3.62. A procedure for analyzing oxalic acid content of a solution involves the formation of the insoluble complex $Mo_4O_3(C_2O_4)_3 \cdot 12H_2O$. (*a*) How many grams of this complex would form per gram of oxalic acid, $H_2C_2O_4$, if 1 mol of the complex results from the reaction with 3 mol of oxalic acid? (*b*) How many grams of molybdenum are contained in the complex formed by the reaction of 1 g of oxalic acid?

Ans. (*a*) 3.38 g complex; (*b*) 1.42 g Mo

3.63. An agricultural insecticide contains 18% arsenic. Express this as the percentage As_2O_5.

Ans. 28% As_2O_5

3.64. During autopsy, a small amount of a white powder was found inside the victim's mouth. The analysis indicates that the molecule mass is in the range of 210 u and that the composition is 33.18% sodium, 74.92% arsenic, and the remainder oxygen. What are the formula and name of the compound?

Ans. Na_3AsO_4, sodium arsenate

3.65. Express the potassium content of a fertilizer in percent potassium if it is 6.8% K_2O.

Ans. 5.6% potassium

3.66. A typical analysis of Pyrex™ glass showed 12.9% B_2O_3, 2.2% Al_2O_3, 3.8% Na_2O, 0.4% K_2O, and the balance was SiO_2. What is the ratio of silicon to boron atoms in the glass?

Ans. 3.6

3.67. A piece of plumber's solder weighing 3.00 g was dissolved in dilute nitric acid, then treated with dilute sulfuric acid. This precipitated the lead as $PbSO_4$, which after washing and drying weighed 2.93 g. The solution was then neutralized to precipitate stannic acid, which was decomposed by heating, yielding 1.27 g SnO_2. What is the analysis of the solder as percent lead and percent tin?

Ans. 66.7% Pb, 33.3% Sn

3.68. Two sources for copper can be purchased in pure form—$CuSO_4$ and $Cu(NO_3)_2$. Suppose you can purchase either at \$28/kg. (*a*) Which is the better deal when considered as a source for copper? (*b*) Suppose you had to purchase for 10,000 kg (22 tons) copper, but purchased the wrong copper source. How much money did you overspend?

Ans. (*a*) $Cu(NO_3)_2$; (*b*) \$88,340 overspent (Does this come out of your pay?)

3.69. Determine the weight of sulfur required to make 1 metric ton of H_2SO_4, sulfuric acid.

Ans. 327 kg S

3.70. A sample of impure cuprite, Cu_2O, contains 66.6% copper. What is the percentage of pure Cu_2O in the sample?

Ans. 75.0% Cu_2O

3.71. A cold cream sample weighing 8.41 g lost 5.83 g of moisture on heating to 110°C. The residue on extracting with water and drying lost 1.27 g of water-soluble glycerol (glycerin). The balance was oil. Calculate the composition of this cream.

Ans. 69.3% moisture, 15.1% glycerol, 15.6% oil

3.72. A household cement gave the following analytical data: A 28.5-g sample, on dilution with acetone, yielded a residue of 4.6 g aluminum powder. The filtrate, on evaporation of the acetone and solvent, yielded 3.2 g of plasticized nitrocellulose, which contained 0.8 g of benzene-soluble plasticizer. Determine the composition of this cement.

Ans. 16.2% Al, 72.6% solvent, 2.8% plasticizer, 8.4% nitrocellulose

3.73. A sample of coal contains 2.4% water. After drying, the moisture-free residue contains 71.0% carbon. Determine the percent carbon on the "wet basis."

Ans. 69.3%

3.74. A certain breakfast food contains 0.637% salt (NaCl). Express this as milligrams of sodium per 60.0 gram serving.

Ans. 150 mg sodium

3.75. A liter flask contains a mixture of two liquids (A and B) of *specific gravity* 1.4. The specific gravity is the density of the sample relative to that of water. The specific gravity of liquid A is 0.8 and that of liquid B is 1.8. What volume of each must have been put into the flask? Assume the volumes are additive with no volume changes on mixing.

Ans. 400 mL of A and 600 mL of B

3.76. When a zinc sulfide ore, ZnS, is roasted, all the sulfur is released to the atmosphere as SO_2. If a maximum of 0.060 mg of SO_2 is permitted per cubic meter of air, (*a*) how many cubic meters of air will be needed for safe disposal of the effluent from the roasting of 1.00 metric tons of zinc sulfide, and (*b*) how large an area would be covered by such a volume of air if it were 1.00 km high?

Ans. (*a*) $1.10 \times 10^{10}\ \mathrm{m}^3$; (*b*) $1.10 \times 10^{7}\ \mathrm{m}^2$ (about 4.2 square miles!)

3.77. A taconite ore consisted of 35.0% Fe_3O_4 and the balance siliceous impurities. How many tons of the ore must be processed in order to recover a ton of metallic iron (*a*) if there is 100% recovery, and (*b*) if there is only 75% recovery?

Ans. (*a*) 3.94 tons; (*b*) 5.25 tons

3.78. A typical formulation for a cationic asphalt emulsion calls for 0.5% tallow amine emulsifier and 70% asphalt, the rest consisting of water and water-soluble ingredients. How much asphalt can be emulsified per pound of emulsifier?

Ans. 140 lb

3.79. Uranium hexafluoride, UF_6, is used in the gaseous diffusion process for separating uranium isotopes since not all uranium isotopes can be undergo chain reaction, a requirement for use in reactors and nuclear weapons. How many kilograms of elementary uranium can be converted to UF_6 per kilogram of combined fluorine?

Ans. 2.09 kg

MOLAR MASSES

3.80. One of the earliest methods for determining the molar mass of proteins was based on chemical analysis. A hemoglobin preparation produced from red blood cells separated from the blood by the use of a centrifuge was found to contain 0.335% iron. (*a*) If the hemoglobin molecule contains 1 atom of iron, what is its molar mass? (*b*) If it contains 4 atoms of iron, what is its molar mass?

Ans. (*a*) 16,700 u; (*b*) 66,700 u

3.81. A polymeric substance, tetrafluoroethylene, can be represented by the formula $(C_2F_4)_n$, where n is a large number. The material was prepared by polymerizing C_2F_4 in the presence of a sulfur-bearing catalyst that served as a nucleus upon which the polymer grew. The final product was found to contain 0.012% S. What is the value of n if each polymeric molecule contains (*a*) 1 sulfur atom, (*b*) 2 sulfur atoms? In either case, assume that the catalyst contributes a negligible amount to the total mass of the polymer.

Ans. (*a*) 2700, (*b*) 5300

3.82. A peroxidase enzyme isolated from human red blood cells was found to contain 0.29% selenium. What is the minimum molecular mass of the enzyme?

Ans. 27,000 u

3.83. Nitroglycerin is an explosive and is also used to produce other explosives, such as dynamite. “Nitro” is 18.5% nitrogen. Calculate the molecular mass of nitro.

Ans. 227.1 u

3.84. A sample of polystyrene prepared by heating styrene with tribromobenzoyl peroxide in the absence of air has the formula $Br_3C_6H_3(C_8H_8)_n$. The number n varies with the conditions of preparation. One sample of polystyrene prepared in this manner was found to contain 10.46% bromine. What is the value of n?

Ans. 19

FORMULA FROM PRECISE NUCLIDIC MOLECULAR MASS

In all the following problems the nuclidic molecular mass reported is that of the species containing the most prevalent nuclide of each of its elements.

3.85. An alkaloid was extracted from the seed of a plant and purified. The molecule was known to contain 1 atom of nitrogen, no more than 4 atoms of oxygen, and no other elements besides carbon and hydrogen. The mass-spectrometrically determined nuclidic molecular mass was found to be 297.138. (*a*) How many molecular formulas are consistent with mass number 297 and with the other known facts except the precise molecular weight? (*b*) What is the probable molecular formula?

Ans. (*a*) 17; (*b*) $C_{18}O_3NH_{19}$

3.86. An organic ester (an organic salt) was decomposed inside a mass spectrometer. An ionic decomposition product had the nuclidic molecular mass 117.090. What is the molecular formula of this product if it is known in advance that the only possible constituent elements are C, O, and H, and that no more than 4 oxygen atoms are present in the molecule?

Ans. $C_6O_2H_{13}$

3.87. An intermediate in the synthesis of a naturally occurring alkaloid had a mass-spectrometrically determined nuclidic molecular mass of 205.147. The compound is known to have no more than 1 nitrogen atom and no more than 2 oxygen atoms per molecule. (*a*) What is the most probable molecular formula of the compound? (*b*) What must the precision of the measurement be to exclude the next most probable formula?

Ans. (*a*) $C_{13}ONH_{19}$ (nuclidic molecular mass is 205.147). (*b*) The next closest molecular mass is 205.159 for $C_{14}OH_{21}$. The range of uncertainty in the experimental value should not exceed half the difference between 205.147 and 205.159, i.e., it should be less than 0.006, or about 1 part in 35,000.

CHAPTER 4

Calculations from Chemical Equations

INTRODUCTION

A ***critical*** skill you must have is the ability to write and balance equations. So much of the heart of chemistry is based on the balanced equation that the study of chemistry is impossible without this skill. The ability to balance an equation is a great deal easier than the skills needed to balance the family checkbook, but the skills required are the same. You can't create money, nor can you ignore it, when you are balancing a checkbook. The chemistry version is the law of conservation of matter: *matter can neither be created nor destroyed by ordinary chemical means*. Just as a bank is required to keep track of the movement of money with no gain or loss of money, the chemist must account for all matter originally present, the reagents, and where that matter goes, the products, with no gain or loss of matter. The chemist's actions produce a *balanced equation*, coefficients specifying the number of molecules (or formula units) of each species involved. The *coefficient* is the number in front of the participants in a chemical reaction that tells us how much of the substance is present. The resulting balanced equation is an expression of the total mass of the reagents being equal to the total mass of the products.

MOLECULAR RELATIONS FROM EQUATIONS

The *relative number of reacting and resulting molecules* are indicated by the coefficients associated with the molecules. For example, the combustion of ammonia in oxygen is described by the balanced chemical equation

$$\underset{\text{(4 molecules)}}{4NH_3} + \underset{\text{(3 molecules)}}{3O_2} \rightarrow \underset{\text{(2 molecules)}}{2N_2} + \underset{\text{(6 molecules)}}{6H_2O}$$

which can be read like a sentence as *four molecules of ammonia react with three molecules of oxygen to yield/produce/form two molecules of nitrogen and six molecules of water*. If we think of an equation being a recipe, then the coefficients tell us how much of the ingredients (the reagents or reactants) we need and the amount of the products that will be produced. Further, the arrow (yields sign) implies that the reaction may go to completion (all the way to the right) if the amount of the reactants conforms to the 4:3 ratio of molecules stated. Incidentally, the ratio provided in molecules in this discussion could just as easily have been presented in moles, could it not?

Some reactions between chemical substances occur almost instantaneously on mixing; some go to completion after sufficient time has elapsed; and some reactions go to only a partial extent even after a lot of time has gone by.

Just about the only way to determine the nature of the reaction is to perform it *empirically* (in the laboratory). Even without running the reaction, we can interpret the balanced equation by stating that, if a large number of ammonia and oxygen molecules are mixed, a certain number of nitrogen and water molecules will be formed. At a given instant it is not necessary that the NH_3 or O_2 is all consumed, but whatever reaction does occur takes place in the molecular (or mole) ratio prescribed by the equation.

In the above *balanced* reaction, the atoms in seven indicated molecules on the left rearrange to form eight molecules on the right. There is no algebraic rule governing these numbers of molecules, but *the number of **atoms** on each side of the equation must balance for each element*, since the reaction obeys the law of conservation of matter, as mentioned above. The number of atoms of any element occurring in a given substance is found by multiplying the subscript of that element in the formula by the coefficient of the formula. The addition of specific atoms in the equation tells us that there are 4 nitrogen atoms both left and right ($4NH_3 \rightarrow 2N_2$), 12 hydrogen atoms on both sides ($4NH_3 \rightarrow 6H_2O$), and, likewise, 6 oxygen atoms ($3O_2 \rightarrow 6H_2O$).

MASS RELATIONS FROM EQUATIONS

Because one mole of any substance is a specific number of molecules (1 mol things $= 6.02 \times 10^{23}$ things from Chapter 2), *the relative numbers of moles undergoing reaction are the same as the relative numbers of molecules*. Because of the relationship of molecules to moles, the equation above can be interpreted in terms of masses calculated directly from the Periodic Table (H = 1, O = 16, N = 24, all in g/mol).

$$\underset{\text{4 moles = 68 g}}{4NH_3} \quad + \quad \underset{\text{3 moles = 96 g}}{3O_2} \quad \rightarrow \quad \underset{\text{2 moles = 56 g}}{2N_2} \quad + \quad \underset{\text{6 moles = 108 g}}{6H_2O}$$

The equation shows that 4 mol NH_3 (4 mol × 17 g/mol) reacts with 3 mol O_2 (3 mol × 32 g/mol) to form 2 mol N_2 (2 mol × 14 g/mol) and 6 mol H_2O (6 mol × 18 g/mol). More generally, the equation shows that the masses are in the ratio of 68:96:56:108 (or 17:24:14:27 with all common factors removed). The mass ratio is the same regardless of which mass unit is used (g, kg, lb, ton, etc.).

The equation with which we have been working is an example of what happens in all cases: The law of conservation of mass requires that the sum of the reactant masses ($68 + 96 = 164$ units) be equal to the sum of the resultant product masses ($56 + 108 = 164$ units).

The importance of mass relations when dealing with chemical equations may be summarized as follows:

1. Mass relations are as exacting as the law of conversation of mass (matter).
2. Mass relations do not require any knowledge about the variable conditions; for example, whether the H_2O is in the liquid form or is steam.
3. Mass relationships do not require any knowledge of the true molecular formulas. In the above example the masses or the number of atoms would be unchanged if the oxygen were assumed to be ozone ($2O_3$, instead of $3O_2$). In either case, the equation would be balanced with 6 oxygen atoms on each side. Similarly, if the water molecules were polymerized, mass relations would be the same whether the equation contained $6H_2O$, $3H_4O_2$, or $2H_6O_3$. This principle is very important in cases where the true molecular formulas are not known. Mass relations are valid for the many equations involving molecules that may dissociate (S_8, P_4, H_6F_6, N_2O_4, I_2, and many others) or those that associate to form complex polymers, such as the many industrially important derivatives of formaldehyde, starch, cellulose, nylon, synthetic rubbers, silicones, etc., regardless of whether empirical or molecular formulas are used.

LIMITING REACTANT

When we are provided with the mass of one of the reactants, we normally assume that the other reactants are in sufficient supply to react or are in excess. What happens if we are given amounts of more than one reactant? We are then responsible for determining if there is a shortage of one or more reactants because the reaction stops when that reactant has been used up. The reactant in the least supply is referred to as the *limiting reactant* and calculations producing the expected amount of products are performed on the basis of the limiting reactant. All reactants in this situation that are not the limiting reactant are the *excess reactants*. See Problems 4.7 and 4.8 for examples of limiting reactant problems.

TYPES OF CHEMICAL REACTIONS

Skill in balancing equations will increase very quickly with practice, especially as you learn to recognize the various types of chemical reactions. Once you have recognized the types of chemical reactions, you will be able to predict the products if you are given just the reactants. A few examples of the more predictable types of reactions are listed below.

1. *Combustion reactions.* Oxygen in excess (usually from the air) combines with organic compounds, those composed of carbon, hydrogen, oxygen, and possibly other elements. Because of the presence of carbon and usually hydrogen, carbon dioxide and water are expected to be products, as the burning of nonane (C_9H_{20}) shows.

$$C_9H_{20} + 14O_2 \rightarrow 9CO_2 + 10H_2O$$

2. *Replacement (displacement) reactions.* A more active element can replace a less active one in a compound.

$$2Na + ZnI_2 \rightarrow 2NaI + Zn$$
$$CaI_2 + F_2 \rightarrow CaF_2 + I_2$$

3. *Double displacement (metathesis) reactions.* This reaction commonly occurs in solution when the reactants produce ionic solution with an exchange of ions if one combination produces a compound that precipitates an insoluble salt.

$$AgNO_3 + NaCl \rightarrow NaNO_3 + AgCl \text{ (insoluble salt)}$$
$$Ba(NO_3)_2 + K_2SO_4 \rightarrow 2KNO_3 + BaSO_4 \text{ (insoluble salt)}$$

4. *Acid-metal reactions.* An acid, such as HCl, HF, H_2CO_3, and a metal more active chemically than the acid's hydrogen can react to form a salt and hydrogen gas.

$$2HCl + 2Na \rightarrow 2NaCl + H_2$$
$$2HNO_3 + Mg \rightarrow Mg(NO_3)_2 + H_2$$

5. *Acid-base reactions (neutralization).* An acid, which contributes H^+ (H_3O^+) ions, and a base, which contributes OH^- ions, undergo metathesis to produce water (HOH or H_2O) and a salt. Isn't this a special case of a double displacement reaction?

$$HCl + NaOH \rightarrow NaCl + HOH$$
$$2HNO_3 + Mg(OH)_2 \rightarrow Mg(NO_3)_2 + 2HOH$$

   With reference to our use of HOH: Balancing the water in these reactions can be a problem since the hydrogen found in the water comes from different sources, hydrogen and hydroxide ions. Balancing the hydrogen ion (hydrondium ion) against the hydrogen in water and the hydroxide on the left against the hydroxide on the right simplifies the balancing process. Try balancing the reaction of nitric acid and magnesium hydroxide using H_2O on the right and this problem will become clear.

6. *Combination reactions.* Elements and/or compounds combine into one product.

$$2SO_2 + O_2 \rightarrow 2SO_3$$
$$P_4 + 6Cl_2 \rightarrow 4PCl_3 \qquad \text{or} \qquad P_4 + 10Cl_2 \rightarrow 4PCl_5$$

The reaction involving P_4 and Cl_2 depends on the ratio of the reactants, temperature, and pressure.

7. *Decomposition reactions.* A single reactant is transformed by heat or electricity into two or more products.

$$2H_2O \xrightarrow{\text{electricity}} 2H_2 + O_2$$

$$2HgO \xrightarrow{\text{heat}} 2Hg + O_2 \qquad \text{or} \qquad 4HgO \xrightarrow{\text{heat}} 2Hg_2O + O_2$$

The reaction involving HgO depends on temperature and oxygen pressure.

Solved Problems

4.1. Balance the following equations:

(*a*) $Li + ZnCl_2 \rightarrow Zn + LiCl$

(*b*) $FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2$

(*c*) $C_7H_6O_2 + O_2 \rightarrow CO_2 + H_2O$

(*a*) There are no fixed rules for balancing equations. Often, a trial-and-error procedure is used (try a coefficient and replace if incorrect). The term *trial-and-error* doesn't mean that there isn't any order or pattern. If you choose a plan of action and follow it consistently, the balancing of equations becomes straightforward, if not easy. A most logical starting place is to look at the left side of the equation and choose an element to balance against the right side.

$$Li + ZnCl_2 \rightarrow Zn + LiCl$$

Let us start with the element furthest on the left, lithium. Since there is one atom on the left and also on the right, we can consider lithium balanced—this might change. The next element is zinc, with one atom on both the left and the right. Chlorine, though, is not in balance because there are two atoms on the left, but only one on the right. Doubling the chlorine on the right will balance the chlorine.

$$Li + ZnCl_2 \rightarrow Zn + \boldsymbol{2}LiCl$$

We now have an error which will be recognized when we go through the balancing procedure again. There is one lithium on the left, but there are two on the right. Doubling the lithium on the left will balance the lithium.

$$\boldsymbol{2}Li + ZnCl_2 \rightarrow Zn + 2LiCl$$

Checking further using the left-to-right pattern as above, we find that the zinc and the chlorine are in balance; therefore, the equation is balanced. It wouldn't hurt to go through the check process one more time just to make certain.

One of the common misconceptions is that we are "putting a 2 in front of the LiCl" in the first step and "putting a 2 in front of the Li" in the second step. This is incorrect; we are multiplying by the coefficient in each case, not just putting it there. This may sound picky, but it is important since the balancing process can become confusing with the more complex chemical reactions. Understanding the process is important, not just going through the motions.

(*b*) This equation is a little more complex because the oxygen appears in one place on the left and is found in two places on the right. Even so, we can use the same pattern just discussed by starting with the left-most element.

There is one iron on the left, but there are two on the right. Let's double the iron on the left.

$$\boldsymbol{2}FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2$$

The next element is sulfur with 4 on the left and only 1 on the right. If we multiply the SO_2 by 4, we will have balanced the sulfur. Notice that the 4 sulfurs on the left are counted because there are two FeS_2 molecules providing 2 × 2 = 4 sulfur atoms on the left of the equation.

$$2FeS_2 + O_2 \rightarrow Fe_2O_3 + \boldsymbol{4}SO_2$$

The last element to be balanced is the oxygen. The oxygen on the left can be multiplied by a coefficient; however, the amount of the oxygen on the right has been established by balancing the iron and sulfur. There are eleven ($4 \times 2 + 3 = 11$) oxygen atoms on the right. Multiplying the oxygen on the left by $5\frac{1}{2}$ will balance the oxygen.

$$2FeS_2 + \boldsymbol{5\frac{1}{2}}O_2 \rightarrow Fe_2O_3 + 4SO_2$$

A final check of the elements tells us that the equation is now balanced. There is a potential problem with this equation as balanced. Most often, equations are balanced without the use of fractions. We can eliminate the fraction $\left(\frac{1}{2}\right)$ by multiplying the participants in the reaction by 2.

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

The equation is still balanced because the ratio of participants in the reaction has been preserved since we multiplied all participants by the same number, 2.

(*c*) Carbon is the left-most element in the equation.

$$C_7H_6O_2 + O_2 \rightarrow CO_2 + H_2O$$

Let us multiply the carbon in carbon dioxide by 7. Since we can't change the ratio within the compound, we multiply the entire molecule, CO_2, by 7.

$$C_7H_6O_2 + O_2 \rightarrow \boldsymbol{7}CO_2 + H_2O$$

The next element is hydrogen. Multiplying the water by 3 will provide us with the 6 hydrogen atoms we need to balance the equation to this point.

$$C_7H_6O_2 + O_2 \rightarrow 7CO_2 + \boldsymbol{3}H_2O$$

There are 2 oxygen atoms on the left in $C_7H_6O_2$, but the amount of oxygen in O_2 just to the left of the yields sign (arrow) is not fixed because we can multiply the molecule as needed. On the right side of the equation, we have set 17 oxygen atoms ($7 \times 2 + 3 = 17$). If we subtract the 2 oxygens in $C_7H_6O_2$ on the left from 17, we must account for 15 more oxygens on the left to balance against the right side of the equation. Multiplying O_2 by $7\frac{1}{2}$ will do the job.

$$C_7H_6O_2 + \boldsymbol{7\frac{1}{2}}O_2 \rightarrow 7CO_2 + 3H_2O$$

And, if we were to double the coefficients in the equation, we will have balanced the equation using whole numbers, as is traditional.

$$2C_7H_6O_2 + 15O_2 \rightarrow 14CO_2 + 6H_2O$$

4.2. Complete and balance the following equations that occur in *aqueous solution* (water is the solvent). [*Note*: Barium phosphate, $Ba_3(PO_4)_2$, is very insoluble; tin is a more active metal than silver.]

(*a*) $Ba(NO_3)_2 + Na_3PO_4 \rightarrow$ (*b*) $Sn + AgNO_3 \rightarrow$ (*c*) $HC_2H_3O_2 + Ba(OH)_2 \rightarrow$

(*a*) Writing the products of the reaction requires the recognition of a metathesis (double displacement) reaction. The reason why this reaction progresses to the right is that the barium phosphate is insoluble and the sodium salts are soluble in water. The precipitation of barium phosphate essentially removes it from the reaction environment.

$$Ba(NO_3)_2 + Na_3PO_4 \rightarrow Ba_3(PO_4)_2 + NaNO_3$$

Once we have established the products and start checking atoms from the left of the equation, we notice that the barium is out of balance. Tripling the barium nitrate on the left will fix that issue.

$$\boldsymbol{3}Ba(NO_3)_2 + Na_3PO_4 \rightarrow Ba_3(PO_4)_2 + NaNO_3$$

Notice that the nitrogen in nitrate, NO_3^-, does not appear twice on either side of the equation. This means that the nitrate ion does not come apart; we can balance nitrogen by balancing nitrate. This balancing act requires that we multiply the nitrate in sodium nitrate on the right by six.

$$3Ba(NO_3)_2 + Na_3PO_4 \rightarrow Ba_3(PO_4)_2 + \boldsymbol{6}NaNO_3$$

The next unit to balance is the sodium. There are 3 on the left and there are 6 on the right. If we were to double the sodium on the left ($2 \times 1Na_3PO_4$), we will have balanced the sodium.

$$Ba(NO_3)_2 + \boldsymbol{2}Na_3PO_4 \rightarrow Ba_3(PO_4)_2 + 6NaNO_3$$

Lastly, we look at the phosphate ion, PO_4^{3-}, and note that phosphate is already balanced.

We should always run through the equation one more time to make certain of the balancing and, when we do so for this reaction, we find that it is balanced.

(*b*) Since we have been informed that tin is a more active element than is silver, we can expect tin to replace the silver in silver nitrate in a single replacement reaction.

$$Sn + AgNO_3 \rightarrow Sn(NO_3)_2 + Ag$$

Working from the left, we find that the tin is currently in balance; then we note that the silver is also. However, the nitrate ion is definitely not balanced. Let's double the silver nitrate on the left.

$$Sn + \boldsymbol{2}AgNO_3 \rightarrow Sn(NO_3)_2 + Ag$$

We double check our work and find that although the tin is OK, the silver is not. There are now 2 silver atoms on the left and only 1 on the right. If we double the silver on the right, it will be balanced.

$$Sn + 2AgNO_3 \rightarrow Sn(NO_3)_2 + \boldsymbol{2}Ag$$

Another check of the equation tells us that the tin is balanced with 1 on each side, the silver is balanced with 2 each side, and the nitrate is also balanced with 2 on each side. The equation is balanced.

We had to go through this equation 3 times to balance and check. A hint that there might be a problem in balancing using the trial-and-error system is having to change the numbers when you are going through a balancing/checking procedure for the third time. If this happens, look to make certain that all of the participants are written correctly as there are ways of incorrectly writing formulas that will make balancing the equation impossible. Unfortunately, some equations can be balanced with incorrectly written formulas.

(*c*) Recognizing that $HC_2H_3O_2 + Ba(OH)_2$ is an acid-base reaction, you can predict the products by recalling that acid-base reactions produce water and the remaining ions form a salt. The acid-base reactions proceed because water does not ionize, which drives the reactions to the right.

$$HC_2H_3O_2 + Ba(OH)_2 \rightarrow Ba(C_2H_3O_2)_2 + HOH$$

First, notice that water has been written as HOH, rather than H_2O, because the hydrogen is coming from the acetic acid and also from the barium hydroxide as part of the hydroxide ion, OH^-. Another factor to note is that acetic acid can be written as CH_3COOH; however, we choose to write the acid in the form matching the other acids (inorganic acids) with the hydrogen that is giving the acid its character on the left (HCl, HNO_3, H_2SO_4, etc.). The last observation to be made is that the hydrogen on the left in $HC_2H_3O_2$ will be balanced with the left-hand hydrogen in ***H***OH; similarly, the OH in $Ba(OH)_2$ is the only source of hydrogen and oxygen balanced with the OH in H***OH***.

Starting with the hydrogen in the acid, we notice that it is in balance with the hydrogen in the water. However, the acetate ion, $C_2H_3O_2^-$, on the left is not in balance with the acetate on the right. Doubling the acetate on the left will balance the ion.

$$2HC_2H_3O_2 + Ba(OH)_2 \rightarrow Ba(C_2H_3O_2)_2 + HOH$$

Continuing, the barium is in balance; the OH is not. Doubling the water balances the hydroxide.

$$2HC_2H_3O_2 + Ba(OH)_2 \rightarrow Ba(C_2H_3O_2)_2 + 2HOH$$

A check of the balancing show us that the equation is in balance.

4.3. Caustic soda, NaOH, is often prepared commercially by the reaction of sodium carbonate, Na_2CO_3, with slaked lime, $Ca(OH)_2$. How many grams of NaOH can be obtained by treating 1 kg of Na_2CO_3 with $Ca(OH)_2$?

Most of the time that you can write an equation to describe what is happening, it is a good idea to do so. The equation is essentially a set of instructions telling us how to perform a process. Further, the equation tells us how much of each of the reactants to use and how much to expect of the products. These factors are provided by the coefficients and can be considered in moles of substances. If we have moles of substances, we can easily convert to grams of substances using the atomic masses of the atoms involved provided by the Periodic Table of the Elements. The equation for this reaction is

$$\underset{\substack{\text{1 mol } Na_2CO_3\\ \text{1 mol} = 106.0\,\text{g}}}{Na_2CO_3} + Ca(OH)_2 \rightarrow \underset{\substack{\text{produces 1 mol NaOH}\\ \text{2 mol} = 2(40.0) = 80.0\,\text{g}}}{2NaOH} + CaCO_3$$

We are only interested in the Na_2CO_3 and NaOH and no longer need to concern ourselves with the $Ca(OH)_2$ and $CaCO_3$ due to the way in which the problem is worded. However, we could not have arrived at the mole ratio of 1:2, nor the mass ratio, 106.0/80.0, without the balanced equation. Depending on how we work the problem, one or both of the relationships is critical to arriving at the correct answer.

Mole Method: As in Chapter 2, the symbol $n(\text{X})$ will be used to refer to the number of moles of substance whose formula is X and $m(\text{X})$ will denote the mass of substance X. Let's consider 1000 g Na_2CO_3.

$$n(Na_2CO_3) = \frac{1000\,\text{g}}{106.0\,\text{g/mol}} = 9.434\,\text{mol } Na_2CO_3$$

From the coefficients in the balanced equation, $n(\text{NaOH}) = 2m(Na_2CO_3) = 2(9.434) = 18.87$ mol NaOH.

$$m(\text{NaOH}) = (18.87\ \text{mol NaOH})(40.0\,\text{g NaOH/mol NaOH}) = 755\,\text{g NaOH}$$

Proportion Method: This method applies the information established by the balanced equation directly. The best part of this method is that the information is presented in a logical manner that practically solves the problem for you. The trick is to write the information given by the balanced equation (Eq. Info.) above the equation and the information provided by the problem (Prob. Info.) below the equation. Write the information above and below the participant identified in the equation by the problem, ignoring those participants not required for the solution of the problem. Place a symbol representing the unknown value as needed in Prob. Info. (*W* reminds us that the answer should come out in weight—grams.)

$$\begin{array}{lcccccccc}
\text{Eq. Info.} & \text{1 mol} & & & & \text{2 mol} & & \\
 & Na_2CO_3 & + & Ca(OH)_2 & \rightarrow & 2NaOH & + & CaCO_3 \\
\text{Prob. Info.} & \text{1 kg} & & & & W & &
\end{array}$$

We next must consider that the units are different and, regardless of what we are to do, the units should be the same—mol and kg must become either moles or kilograms. The units of grams are the desired answer so that we could convert from kilograms as requested by the problem (1 kg = 1000 g).

$$\begin{array}{llcl}
\text{Eq. Info.} & 1\text{ mol} \times 106.0\text{ g/mol} = 106.0\text{ g} & & 2\text{ mol} \times 40.0\text{ g/mol} = 80.0\text{ g} \\
 & Na_2CO_3 + Ca(OH)_2 & \rightarrow & 2NaOH + CaCO_3 \\
\text{Prob. Info.} & 1000\text{ g} & & W
\end{array}$$

We are now ready to set up a ratio and proportion (2 fractions equal to each other) and solve for W.

$$\frac{106.0\text{ g }Na_2CO_3}{1000\text{ g }Na_2CO_3} = \frac{80.0\text{ g NaOH}}{W}$$

Rearrangement solves for W and the weight of the NaOH produced.

$$W = \frac{1000\text{ g }Na_2CO_3 \times 80.0\text{ g NaOH}}{106.0\text{ g }Na_2CO_3} = 755\text{ g NaOH}$$

Had we noticed that the g Na_2CO_3 would cancel out just above, we could have done so before the rearrangement and saved a little writing. Either way, it is important to note that the solution tells us that the units on the answer are to be in grams NaOH, just as was required by the problem.

4.4. The equation for the preparation of phosphorus in an electric furnace is

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSiO_3 + 10CO + P_4$$

Determine

(*a*) the number of moles of phosphorus formed for each mole of $Ca_3(PO_4)_2$ used;

(*b*) the number of grams of phosphorus formed for each mole of $Ca_3(PO_4)_2$ used;

(*c*) the number of grams of phosphorus formed for each gram of $Ca_3(PO_4)_2$ used;

(*d*) the number of pounds of phosphorus formed for each pound of $Ca_3(PO_4)_2$ used;

(*e*) the number of tons of phosphorus formed for each ton of $Ca_3(PO_4)_2$ used;

(*f*) the number of moles each of SiO_2 and C required for each mole of $Ca_3(PO_4)_2$ used.

(*a*) From the equation, 1 mol P_4 is obtained for 2 mol $Ca_3(PO_4)_2$ used, or, $\frac{1}{2}$ mol P_4 per mole of $Ca_3(PO_4)_2$.

(*b*) The molar mass of P_4 is 124. Then $\frac{1}{2}$ mol $P_4 = \frac{1}{2} \times 124 = 62\text{ g}P_4$.

(*c*) One mole $Ca_3(PO_4)_2$ (319 g/mol) yields $\frac{1}{2}$ mol P_4 (62 g). The 1 g $Ca_3(PO_4)_2$ gives $62/310 = 0.20$ g P_4.

(*d*) 0.20 lb; the relative amounts are the same as (*c*) regardless of the units.

(*e*) 0.20 ton (as above).

(*f*) From the coefficients in the balanced equation, 1 mol $Ca_3(PO_4)_2$ required 3 mol SiO_2 and 5 mol C.

4.5. Hydrochloric acid was once prepared commercially by heating NaCl with concentrated H_2SO_4. How much sulfuric acid containing 90.0% H_2SO_4 by weight is needed for the production of 1000 kg of concentrated hydrochloric acid containing 42.0% HCl by weight?

(1) Amount of pure HCl in 1000 kg of 42.0% acid is $0.420 \times 1000\text{ kg} = 420\text{ kg}$.

(2) We need the balanced equation and the molecular masses to determine the answer.

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$$

The relationship from the balanced equation is 1 mol H_2SO_4 ($1 \times 98.1 = 98.1$ g) is required to produce 2 mol HCl ($2 \times 36.46 = 72.92$ g). Therefore,

$$\begin{array}{lll} 72.92\ \text{g HCl} & \text{require} & 98.1\ \text{g}\ H_2SO_4 \\ 1\ \text{g HCl} & \text{requires} & \dfrac{98.1}{72.92}\ \text{g}\ H_2SO_4 \\ 1\ \text{kg HCl} & \text{requires} & \dfrac{98.1}{72.92}\ \text{kg}\ H_2SO_4 \\ 420\ \text{kg HCl} & \text{require} & (420)\left(\dfrac{98.1}{72.92}\ \text{kg}\right) = 565\ \text{kg}\ H_2SO_4 \end{array}$$

(3) Finally, we determine the amount of sulfuric acid solution containing 90.0% H_2SO_4 that contains 565 kg of pure H_2SO_4. We now know that 0.900 kg of pure H_2SO_4 makes 1 kg of 90.0% solution. Then

$$565\ \text{kg of}\ H_2SO_4 \times \frac{1\ \text{kg solution}}{0.900\ \text{kg}\ H_2SO_4} = 628\ \text{kg solution}$$

Factor-Label Method: This method has the advantage of allowing you to write down the solution as one step. There is also the added advantage of having the calculation laid out ready to be put through your calculator. As you read this setup from left to right, cross out the units that cancel and notice that the units on the answer are those that are to be on the final answer.

$$\begin{aligned} \text{Amt. of 90.0\%}\ H_2SO_4 &= (1000\ \text{kg 42.0\% HCl})\left(\frac{42.0\ \text{kg HCl}}{100\ \text{kg 42.0\% HCl}}\right)\left(\frac{1000\ \text{g}}{1\ \text{kg}}\right)\left(\frac{1\ \text{mol HCl}}{36.46\ \text{g HCl}}\right) \\ &\times \left(\frac{1\ \text{mol}\ H_2SO_4}{2\ \text{mol HCl}}\right)\left(\frac{98.1\ \text{g}\ H_2SO_4}{1\ \text{mol}\ H_2SO_4}\right)\left(\frac{100\ \text{g 90.0\%}\ H_2SO_4}{90.0\ \text{g}\ H_2SO_4}\right)\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right) \\ &= 628\ \text{kg 90.0\%}\ H_2SO_4 \end{aligned}$$

4.6. Before the public became serious about pollution, it was common to improve the performance of gasoline by the addition of lead compounds. A 100-octane aviation gasoline used 1.00 cm^3 of tetraethyl lead, $(C_2H_5)_4Pb$, of density 1.66 g/cm^3, per liter of product. How many grams of ethyl chloride, C_2H_5Cl, are needed to make enough tetraethyl lead for 1.00 L gasoline? Tetraethyl lead production is by

$$4C_2H_5Cl + 4NaPb \rightarrow (C_2H_5)_4Pb + 4NaCl + 3Pb$$

The mass of 1.00 cm^3 $(C_2H_5)_4Pb$ is $(1.00\ \text{cm}^3)(1.66\ \text{g/cm}^3) = 1.66$ g required per liter. In terms of moles tetraethyl lead needed per liter:

$$\text{Moles}\ (C_2H_5)_4Pb\ \text{needed} = \frac{1.66\ \text{g}}{323\ \text{g/mol}} = 0.00514\ \text{mol}\ (C_2H_5)_4Pb$$

The chemical equation tells us that 1 mol $(C_2H_5)_4Pb$ requires 4 mol C_2H_5Cl. Using this information, we find that $4(0.00514) = 0.0206$ mol C_2H_5Cl is needed. And,

$$m(C_2H_5Cl) = 0.0206\ \text{mol} \times 64.5\ \text{g/mol} = 1.33\ \text{g}\ C_2H_5Cl$$

Factor-Label Method: Let us use the nonstandard abbreviation TEPb for tetraethyl lead as a convenience.

$$\begin{aligned} \text{Amt. of}\ C_2H_5Cl &= (1.00\ \text{L gasoline})\left(\frac{1.00\ \text{cm}^3\text{TEPb}}{1.00\ \text{L gasoline}}\right)\left(\frac{1.66\ \text{g}}{1.00\ \text{cm}^3}\right)\left(\frac{1\ \text{mol TEPb}}{323\ \text{g TEPb}}\right) \\ &\times \left(\frac{4\ \text{mol}\ C_2H_5Cl}{1\ \text{mol TEPb}}\right)\left(\frac{64.5\ \text{g}\ C_2H_5Cl}{1\ \text{mol}\ C_2H_5Cl}\right) = 1.33\ \text{g}\ C_2H_5Cl\ \text{required} \end{aligned}$$

4.7. A solution containing 2.00 g $Hg(NO_3)_2$ was added to a solution containing 2.00 g Na_2S. Calculate the mass of the insoluble HgS formed according to the reaction, $Hg(NO_3)_2 + Na_2S \rightarrow HgS + 2NaNO_3$.

This problem gives us the amounts of both the reactants; this is a hint that we might be dealing with a limiting reactant problem. In other words, one of the reactants might be used up before the other and that will stop the progression of the reaction. Further, since the mass of both reactants is 2.00 g, the presence of a limiting reactant is nearly guaranteed.

We can use the *proportion method* to set up the problem and *test* to determine which of the reactants, if any, is in short supply. Let's use *t* as the symbol to represent the test amount of a reagent. As has been mentioned, a consistent pattern of approach is a good way to avoid confusion; we test the second reactant to hold to pattern. Instead of using the 2.00 g of Na_2S given in the problem, let *t* represent the amount of Na_2S needed to just react the 2.00 g $Hg(NO_3)_2$ and see if we were given enough. Additionally, let's do the calculation in grams as given in the problem. In order to do so, we must express the Eq. Info. in terms of grams.

$$\begin{array}{llll} \text{Eq. Info.} & 1\text{ mol}\times 324.6\text{ g/mol} & 1\text{ mol}\times 78.00\text{ g/mol} & \\ & \quad\text{Hg(NO}_3)_2 \quad + & \quad\quad \text{Na}_2\text{S} & \rightarrow \text{HgS} + 2\text{NaNO}_3 \\ \text{Prob. Info} & \quad\quad 2.00\text{ g} & \quad\quad\quad t & \end{array}$$

Once we have the values, we set up the ratio and proportion, then solve for *t*. This time, we decided to cancel out like units as we brought them down from the equation to the ratio and proportion (shortcut).

$$\frac{324.6}{2.00} = \frac{78.00\,\text{g}\,\text{Na}_2\text{S}}{t} \qquad t = \frac{2.00 \times 78.00\,\text{g}\,\text{Na}_2\text{S}}{324.6} = 0.48\,\text{g Na}_2\text{S}$$

The interpretation is pretty straightforward because we just found out that we need 0.48 g Na_2S (the value of *t*) to use up the 2.00 g $Hg(NO_3)_2$ given in the problem. We have a good deal more of the Na_2S than we need, approximately one and a half grams too much to use up the other reactant. The limiting reactant is the mercury(II) nitrate, $Hg(NO_3)_2$. We must go back to the relationship of the mercury(II) nitrate to the desired product, mercury(II) sulfide. Once the equation has been balanced, we can ignore the $NaNO_3$ since the problem requested no information about it. *A* is being used as the symbol to represent the amount of HgS that will be produced.

$$\begin{array}{lll} \text{Eq. Info.} & 1\text{ mol}\times 324.6\text{ g/mol} & \quad 1\text{ mol}\times 232.6\text{ g/mol} \\ & \quad\text{Hg(NO}_3)_2 & + \text{Na}_2\text{S} \rightarrow \text{HgS} + 2\text{NaNO}_3 \\ \text{Prob. Info} & \quad\quad 2.00\text{ g} & \quad\quad\quad\quad A \end{array}$$

We use the information associated with the balanced equation to set up the ratio and proportion. Again, we need to watch to see if the desired unit appears in the solution.

$$\frac{324.6}{2.00} = \frac{232.6\,\text{g HgS}}{A} \qquad \text{becomes} \qquad A = \frac{2.00 \times 232.6\,\text{g HgS}}{324.6} = 1.43\,\text{g HgS}$$

In summary, the original 4.00 g of reagents has been transformed to 1.43 g HgS product and there is an excess of 1.52 g Na_2S (2.00 g − 0.48 g from the test).

4.8. How many grams of $Ca_3(PO_4)_2$ can be made by mixing a solution containing 5.00 g calcium chloride with another containing 8.00 g potassium phosphate? The reaction is

$$3CaCl_2 + 2K_3PO_4 \rightarrow Ca_3(PO_4)_2 + 5KCl$$

Using the same procedure as in Problem 4.7, the first action is to run the test to see if there is a limiting reactant. We set up the balanced equation with the information we were given and test to see if there is sufficient K_3PO_4 to use up all of the $CaCl_2$.

$$\begin{array}{llll} \text{Eq. Info.} & 3\text{ mol}\times 111.1\text{ g/mol} & 2\text{ mol}\times 212.3\text{ g/mol} & \\ & \quad\quad 3\text{CaCl}_2 \quad\quad + & \quad\quad 2\text{K}_3\text{PO}_4 & \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 6\text{KCl} \\ \text{Prob. Info.} & \quad\quad 5.00\text{ g} & \quad\quad\quad t & \end{array}$$

Canceling similar units as the values are brought from the equation to the ratio and proportion gives us

$$\frac{333.3}{5.00} = \frac{424.6\,\text{g K}_3\text{PO}_4}{t} \qquad \text{becomes} \qquad t = \frac{5.00 \times 424.6\,\text{K}_3\text{PO}_4}{333.3} = 6.37\,\text{g K}_3\text{PO}_4$$

Since 6.37 g K_3PO_4 are required to use up all of the calcium chloride and we were given 8.00 g K_3PO_4, the limiting reactant is the $CaCl_2$. We are now able to set up the balanced equation with the equation information and the problem information. Since we know that the limiting reactant is the $CaCl_2$, that we have been directed to calculate the amount of $Ca_3(PO_4)_2$, and that the ratio of $CaCl_2$ to $Ca_3(PO_4)_2$ is 3:1, we can set up the ratio and proportion and solve for the answer to this problem.

$$\begin{array}{llllll}
\text{Eq. Info.} & 3\,\text{mol} \times 111.3\,\text{g/mole} & & 1\,\text{mol} \times 310.2\,\text{g/mol} & \\
& 3CaCl_2 + & 2K_3PO_4 \rightarrow & Ca_3(PO_4)_2 & + 5KCl \\
\text{Prob. Info.} & 5.00\,\text{g} & & Z &
\end{array}$$

$$\frac{333.3}{5.00} = \frac{310.2\text{g } Ca_3(PO_4)_2}{Z}$$

$$Z = \frac{5.00 \times 310.2\,\text{g } Ca_3(PO_4)_2}{333.3} = 4.65\,\text{g } Ca_3(PO_4)_2$$

Notes: (1) If there had been no limiting reactant, it would not matter which of the reactants were used for the final calculations. (2) It does not matter which of the reactants you chose for the test (t) so long as you are able to correctly interpret the results.

4.9. In one process for waterproofing, a fabric is exposed to $(CH_3)_2SiCl_2$ vapor. The vapor reacts with hydroxyl groups on the surface of the fabric or with traces of water to form the waterproofing film $[(CH_3)_2SiO]_n$ by the reaction

$$n(CH_3)_2SiCl_2 + 2nOH^- \rightarrow 2nCl^- + nH_2O + [(CH_3)_2SiO]_n$$

where n stands for a large integer. The waterproofing film is deposited on the fabric building up layer on layer. Each layer is 6 Å thick, the thickness of the $(CH_3)_2SiO$ group. How much $(CH_3)_2SiCl_2$ is needed to waterproof one side of a piece of fabric that is 1 m by 2 m with a film of 300 layers thick? The density of the film is $1.0\,\text{g/m}^3$.

$$\begin{aligned}
\text{Mass of film} &= (\text{volume of film})(\text{density of film}) \\
&= (\text{area of film})(\text{thickness of film})(\text{density of film}) \\
&= (100\,\text{cm} \times 200\,\text{cm})(300 \times 6\text{Å} \times 10^{-8}\,\text{cm/Å})(1.0\,\text{g/cm}^3) = 0.36\,\text{g}
\end{aligned}$$

$$\begin{aligned}
\text{Amt. of } (CH_3)_2SiCl_2 &= \{0.36\,\text{g}[(CH_3)_2SiO]_n\}\left\{\frac{1\,\text{mol}[CH_3)_2SiO]_n}{74n\,\text{g}[(CH_3)_2SiO]_n}\right\} \\
&= \left\{\frac{n\,\text{mol}(CH_3)_2SiCl_2}{1\,\text{mol}[(CH_3)_2SiO)]_n}\right\}\left[\frac{129\,\text{g}(CH_3)_2SiCl_2}{1\,\text{mol}(CH_3)_2SiCl_2}\right] \\
&= 0.63\,\text{g } (CH_3)_2SiCl_2
\end{aligned}$$

Note: The unknown integer n canceled in the *factor-label* calculation along with all units except grams.

4.10. What is the percent free SO_3 in an oleum (considered as a solution of SO_3 in H_2SO_4) that is labeled "109% H_2SO_4"? Such a designation refers to the total weight of pure H_2SO_4, 109 g, that would be present after adding sufficient water to 100 g of the oleum to convert it to pure H_2SO_4.

Nine g H_2O will combine with all the free SO_3 in 100 g oleum to give a total of 109 g H_2SO_4. The equation $H_2O + SO_3 \rightarrow H_2SO_4$ indicates that 1 mol of H_2O (18 g) combines with 1 mol SO_3 (80 g). Then

$$(9\,\text{g } H_2O)\left(\frac{80\,\text{g } SO_3}{18\,\text{g } H_2O}\right) = 40\,\text{g } SO_3$$

Therefore, 100 g of the oleum contains 40 g SO_3, or the percent free SO_3 in the oleum is 40%

4.11. $KClO_4$ may be made by a series of sequential reactions. How much Cl_2 is needed to prepare 100 g $KClO_4$ by the sequence?

$$Cl_2 + 2KOH \rightarrow KCl + KClO + H_2O$$
$$3KClO \rightarrow 2KCl + KClO_3$$
$$4KClO_3 \rightarrow 3KClO_4 + KCl$$

The mole method and the factor-label method are the simplest routes to the solution of this problem. In neither case is it necessary to find the masses of the intermediate products.

Mole Method

$$n(KClO) = n(Cl_2)$$
$$n(KClO_3) = \left(\frac{1}{3}\right) n(KClO) = \left(\frac{1}{3}\right) n(Cl_2)$$
$$n(KClO_4) = \left(\frac{3}{4}\right) n(KClO_3) = \left(\frac{3}{4}\right)\left(\frac{1}{3}\right) n(Cl_2) = \left(\frac{3}{12}\right) n(Cl_2) = \left(\frac{1}{4}\right) n(Cl_2)$$
$$n(KClO_4) = \frac{100\,\text{g KClO}_4}{138.6\,\text{gKClO}_4/\text{mol KClO}_4} = 0.7215\,\text{mol KClO}_4$$
$$n(Cl_2) = 4(0.7215) = 2.886\,\text{mol Cl}_2$$
$$m(Cl_2) = (2.886\,\text{mol Cl}_2)(70.9\,\text{g Cl}_2/\text{mol Cl}_2) = 205\,\text{g Cl}_2$$

Factor-Label Method

$$\text{Amt. of Cl}_2 = (100\,\text{g KClO}_4)\left(\frac{1\,\text{mol KClO}_4}{138.6\,\text{g KClO}_4}\right)\left(\frac{4\,\text{mol KClO}_3}{3\,\text{mol KClO}_4}\right)\left(\frac{3\,\text{mol KClO}}{1\,\text{mol KClO}_3}\right)$$
$$\times\left(\frac{1\,\text{mol Cl}_2}{1\,\text{mol KClO}}\right)\left[\frac{70.9\,\text{g Cl}_2}{1\,\text{mol Cl}_2}\right] = 205\,\text{g Cl}_2$$

4.12. A 1.2048-g sample of Na_2CO_3 is suspected of being impure. It is dissolved and allowed to react with $CaCl_2$. The resulting $CaCO_3$, after precipitation, filtration, and drying, was found to weigh 1.0262 grams. Assuming that the impurities do not contribute to the weight of the precipitate, calculate the percentage purity of the Na_2CO_3.

One way of working this problem is to calculate the amount of sodium carbonate that was used in the reaction, then compare that weight to the weight of the sample. Since the problem tells us that there has been a reaction, an equation is written to start us on the way to solving the problem. We may also write the information provided by the problem and by the equation itself to find out just how much Na_2CO_3 was in the sample (S weight of Na_2CO_3). This setup also provides us with the weights we need to calculate the percent composition Na_2CO_3.

Eq. Info.	1 mol × 105.99 g/mol		1 mol × 100.09 g/mol	
	Na_2CO_3	$+CaCl_2 \rightarrow$	$CaCO_3$	$+ 2NaCl$
Prob. Info.	Y		1.0262 g	

$$\frac{105.99\,\text{g Na}_2\text{CO}_3}{Y} = \frac{100.09}{1.0262} \quad \text{becomes} \quad Y = \frac{1.0262 \times 105.99\,\text{g Na}_2\text{CO}_3}{100.09} = 1.0867\,\text{g Na}_2\text{CO}_3\ \text{reacted}$$

Since the sample weight was 1.2048 g and the actual amount of Na_2CO_3 present is 1.0867 g, the calculation is as

$$\frac{1.0867\,\text{g Na}_2\text{CO}_3\ \text{in sample}}{1.2048\,\text{g sample}} \times 100 = 90.20\%\ \text{Na}_2\text{CO}_3$$

4.13. A mixture of NaCl and KCl weighed 5.4892 g. The sample was dissolved in water and silver nitrate was added to the solution. A white precipitate was formed, AgCl. The weight of the dry AgCl was 12.7052 g. What was the percentage NaCl in the mixture?

Silver ions react with chloride ions and those chloride ions are supplied by both of the salts.

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3 \qquad \text{and} \qquad KCl + AgNO_3 \rightarrow AgCl + KNO_3$$

By the *law of conservation of matter*, we must account for all of the chlorine atoms; there are two sources of chlorine. Therefore, the total amount of chlorine formed is the *sum* of that formed in the two equations. Since the chlorine in both reactions is tied up as AgCl and there is one mole of chlorine per mole of AgCl,

$$n(AgCl) = \frac{12.7052\text{ g AgCl}}{143.321\text{ g AgCl/mol}} = 0.088649\text{ mol} = n(NaCl) + n(KCl)$$

Let y = mass of NaCl and z = mass of KCl. Then

$$\frac{y}{58.443\text{ g/mol}} + \frac{z}{74.551\text{ g/mol}} = 0.088649\text{ mol} \tag{1}$$

A second equation for the unknown masses is provided by the data:

$$y + z = 5.4892\text{ g} \tag{2}$$

Eliminating z between (*1*) and (*2*), and solving for y, we obtain $y = m(NaCl) = 4.0624$ g. Then,

$$\%\ NaCl = \frac{4.0624\text{ g}}{5.4892\text{ g}} \times 100 = 74.01\%\ NaCl$$

Supplementary Problems

BALANCING EQUATIONS

Balance the following equations:

4.14. $C_2H_4(OH)_2 + O_2 \rightarrow CO_2 + H_2O$

Ans. $2C_2H_4(OH)_2 + 5O_2 \rightarrow 4CO_2 + 6H_2O$

4.15. $Li + H_2O \rightarrow LiOH + H_2$

Ans. $2Li + 2H_2O \rightarrow 2LiOH + H_2$

4.16. $Sn + SnCl_4 \rightarrow SnCl_2$

Ans. $Sn + SnCl_4 \rightarrow 2SnCl_2$

4.17. $Ba(OH)_2 + AlCl_3 \rightarrow Al(OH)_3 + BaCl_2$

Ans. $3Ba(OH)_2 + 2AlCl_3 \rightarrow 2Al(OH)_3 + 3BaCl_2$

4.18. $KHC_8H_4O_4 + KOH \rightarrow K_2C_8H_4O_4 + H_2O$

Ans. $KHC_8H_4O_4 + KOH \rightarrow K_2C_8H_4O_4 + H_2O$

4.19. $C_2H_2Cl_4 + Ca(OH)_2 \rightarrow C_2HCl_3 + CaCl_2 + H_2O$

Ans. $2C_2H_2Cl_4 + Ca(OH)_2 \rightarrow 2C_2HCl_3 + CaCl_2 + 2H_2O$

4.20. $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + H_2O$

Ans. $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$

4.21. $Zn_3Sb_2 + H_2O \rightarrow Zn(OH)_2 + SbH_3$

Ans. $Zn_3Sb_2 + 6H_2O \rightarrow 3Zn(OH)_2 + 2SbH_3$

4.22. $HClO_4 + P_4O_{10} \rightarrow H_3PO_4 + Cl_2O_7$

Ans. $12HClO_4 + P_4O_{10} \rightarrow 4H_3PO_4 + 6Cl_2O_7$

4.23. $C_6H_5Cl + SiCl_4 + Na \rightarrow (C_6H_5)_4Si + NaCl$

Ans. $C_6H_5Cl + SiCl_4 + 5Na \rightarrow (C_6H_5)_4Si + 5NaCl$

4.24. $Sb_2S_3 + HCl \rightarrow H_3SbCl_6 + H_2S$

Ans. $Sb_2S_3 + 12HCl \rightarrow 2H_3SbCl_6 + 3H_2S$

4.25. $IBr + NH_3 \rightarrow NI_3 + NH_4Br$

Ans. $3IBr + 4NH_3 \rightarrow NI_3 + 3NH_4Br$

4.26. $SF_4 + H_2O \rightarrow SO_2 + HF$

Ans. $SF_4 + 2H_2O \rightarrow SO_2 + 4HF$

4.27. $Na_2CO_3 + C + N_2 \rightarrow NaCN + CO$

Ans. $Na_2CO_3 + 4C + N_2 \rightarrow 2NaCN + 3CO$

4.28. $K_4Fe(CN)_6 + H_2SO_4 + H_2O \rightarrow K_2SO_4 + FeSO_4 + (NH_4)_2SO_4 + CO$

Ans. $K_4Fe(CN)_6 + 6H_2SO_4 + 4H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

4.29. $Fe(CO)_5 + NaOH \rightarrow Na_2Fe(CO)_4 + Na_2CO_3 + H_2O$

Ans. $Fe(CO)_5 + 4NaOH \rightarrow Na_2Fe(CO)_4 + Na_2CO_3 + 2H_2O$

4.30. $H_3PO_4 + (NH_4)2MoO_4 + HNO_3 \rightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + NH_4NO_3 + H_2O$

Ans. $H_3PO_4 + 12(NH_4)2MoO_4 + 21HNO_3 \rightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 12H_2O$

4.31. Identify the type of chemical reaction, write the products, and balance the equations.

(*a*) $HCl + Mg(OH)_2 \rightarrow$

(*b*) $PbCl_2 + K_2SO_4 \rightarrow$

(*c*) $CH_3CH_2OH + O_2$ (excess) $\rightarrow$

(*d*) $NaOH + H_2C_6H_6O_6 \rightarrow$

(*e*) $Fe + AgNO_3 \rightarrow$

Partial answers:

(*a*) acid-base (neutralization), products are H_2O and $MgCl_2$;

(*b*) double displacement (metathesis), products are KCl and $PbSO_4$;

(*c*) combustion, products are CO_2 and H_2O;

(*d*) acid-base (neutralization), products are $Na_2C_6H_6O_6$ and H_2O;

(*e*) replacement (displacement), products are $Fe(NO_3)_2$ and Ag.

MASS RELATIONS

4.32. Consider the combustion of amyl alcohol:

$$2C_5H_{11}OH + 15O_2 \rightarrow 10CO_2 + 12H_2O$$

(*a*) How many moles of O_2 are required for the complete combustion of 1 mole of amyl alcohol? (*b*) How many moles of H_2O are formed for each mole of O_2 consumed? (*c*) How many grams of CO_2 are produced for each mol of amyl alcohol burned? (*d*) How many grams of CO_2 are produced per gram of amyl alcohol burned? (*e*) How many tons of CO_2 are produced per ton of amyl alcohol burned?

Ans. (*a*) 7.5 mol O_2; (*b*) 0.80 mol H_2O; (*c*) 220 g CO_2; (*d*) 2.49 g CO_2; (*e*) 2.49 tons CO_2

4.33. A portable hydrogen generator utilizes the reaction $CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + H_2$. How many grams of H_2 can be produced by a 50-g cartridge of CaH_2?

Ans. 4.8 g H_2

4.34. Iodine can be made by the reaction $2NaIO_3 + 5NaHSO_4 \rightarrow 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2$. (*a*) What mass of $NaIO_3$ must be used for each kilogram of iodine produced (*b*) What mass of $NaHSO_3$/kg I_2 is used?

Ans. (*a*) 1.56 kg $NaIO_3$; (*b*) 2.05 kg $NaHSO_3$

4.35. Nonane, a component in gasoline, was found to be present at a fire that was suspected to be arson. (*a*) Write the balance equation for the burning of nonane, C_9H_{20}, in air. (*b*) How many grams of oxygen, O_2, are required to burn 500 g nonane? (*c*) If 32 g O_2 occupy 22.4 L at 0°C and 1 atm, what volume of oxygen under these conditions is required to burn the nonane?

Ans. (*a*) $C_9H_{20} + 14O_2 \rightarrow 9CO_2 + 10H_2O$; (*b*) 1750 g O_2; (*c*) 1220 L O_2

4.36. The noble gas (Group VIIIA) compound XeF_2 can be safely destroyed by treatment with NaOH:

$$4NaOH + 2XeF_2 \rightarrow 2Xe + O_2 + 4NaF + 2H_2O$$

Calculate the mass of oxygen resulting from the reaction of 85.0 g XeO_2 with excess NaOH solution.

Ans. 8.03 g O_2

4.37. Carbon monoxide, a poisonous gas, is released when nonane burns if there is insufficient oxygen present to produce CO_2. (*a*) Write the balance equation for the burning of nonane producing CO. (*b*) What mass of CO is released by the burning of 500 g nonane?

Ans. (*a*) $2C_9H_{20} + 19O_2 \rightarrow 18CO + 20H_2O$; (*b*) 938 g CO

4.38. How much iron(III) oxide can be produced from 6.76 g of $FeCl_3 \cdot 6H_2O$ by the reaction

$$FeCl_3 \cdot 6H_2O + 3NH_3 \rightarrow Fe(OH)_3 + 3NH_4Cl$$
$$2Fe(OH)_2 \rightarrow Fe_2O_3 + 3H_2O$$

Ans. 2.00 g Fe_2O_3

4.39. Zinc blende, ZnS, reacts when strongly when heated in air ($2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$). (*a*) How many pounds of ZnO will be formed when 1 lb zinc blende reacts as above? (*b*) How many tons of ZnO will be formed from 1 ton ZnS? (*c*) How many kilograms of ZnO will be formed from 1 kg ZnS?

Ans. (*a*) 0.835 lb; (*b*) 0.835 ton; (*c*) 0.835 kg

4.40. Hydrogen cyanide gas was used as a method of administering the death penalty. Potassium cyanide pellets dropped into an HCl solution yield HCN. (*a*) Write the balanced reaction producing HCN in this manner. (*b*) What mass of KCN produces 4 moles HCN gas?

Ans. (*a*) $KCN(aq) + HCl(aq) \rightarrow HCN(g) + KCl(aq)$; (*b*) 260 g KCN

4.41. What mass of HCN can be produced when a 50-g KCN tablet is placed 1 L of solution that contains 6 moles HCl? (*Hint*: refer to Problem 4.40.)

Ans. 21 g HCN, HCl in a large excess

4.42. During the refining process, silver is to be separated from silver sulfide (argentite) and zinc can be used in the process. Suppose the silver could be liberated directly from the argentite, how many metric tons of zinc would be required to treat 100,000 metric tons of argentite?

Ans. 26,500 metric tons Zn

4.43. Hydrazine, N_2H_4, can be used as a rocket fuel; the amount of fuel is to be 250,000 kg for a particular space shot. Assuming the products of the reaction with liquid oxygen (LOX) are N_2O_3 and H_2O, what is the mass of N_2O_3 released during this trip?

Ans. 593,000 kg N_2O_3

4.44. In a rocket motor fueled with butane, C_4H_{10}, how many kilograms of liquid oxygen should be provided with each kilogram of butane to ensure complete combustion?

$$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$$

Ans. 3.58 kg liquid oxygen

4.45. Chloropicrin, CCl_3NO_2, can be made cheaply for use as an insecticide by the reaction

$$CH_3NO_2 + 3Cl_2 \rightarrow CCl_3NO_2 + 3HCl$$

How much nitromethane, CH_3NO_2, is needed to form 500 g of chloropicrin?

Ans. 186 g nitromethane

4.46. Carbide lamps were used as a source of light for miners, but they tended to explode if not carefully maintained. Calcium carbide reacts with water to produce acetylene. (*a*) Write the balanced equation for the reaction. (*b*) What number of grams C_2H_2 can be produced from 75.0 g Ca_2C?

Ans. (*a*) $Ca_2C + 2HCl \rightarrow C_2H_2 + CaCl_2$; (*b*) 30.5 g C_2H_2

4.47. (*a*) $CaCO_3$ is available as an antacid tablet used to neutralize stomach acid, HCl, and knowing that one of the products is CO_2, write the balanced equation. (*b*) How much HCl can be neutralized by a 500-mg tablet available under many market names?

Ans. (*a*) $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$; (*b*) 374 mg HCl neutralized

4.48. (*a*) $CaO + CO_2 \rightarrow CaCO_3$ is a reaction that provides very pure $CaCO_3$. What mass of $CaCO_3$ can be produced by 1 ton of CaO? (*b*) What mass of CO_2 would be used up?

Ans. (*a*) 1.8 metric tons $CaCO_3$; (*b*) 0.78 metric tons CO_2

4.49. What mass of the industrial solvent benzene can be produced by the union of 3 acetylene molecules if 100 moles acetylene were to react by $3C_2H_6 \rightarrow C_6H_6$?

Ans. 2600 g

4.50. As part of the copper refining process, copper(I) sulfide is oxidized to the reaction $Cu_2S + O_2 \rightarrow Cu + SO_2$. SO_2 is an environmental problem and cannot be allowed to enter the atmosphere. How many tons of SO_2 are released by the reaction of 6 tons Cu_2S?

Ans. 2.4 tons SO_2

4.51. One of the sources of iron is magnetite, Fe_3O_4 (FeO and Fe_2O_3 mixed), which reacts with coke (carbon) to produce iron in the liquid state and carbon monoxide. If we assume that coke is pure carbon, how much is supplied to produce 10,000 metric tons of iron?

Ans. 2075 metric tons coke

4.52. Since CO has been produced in the previous problem and can be used to react with Fe_3O_4, how much additional magnetite can be reacted to release Fe(*l*) and CO_2?

Ans. 1000 additional metric tons

4.53. Ethyl alcohol (C_2H_5OH) is made by the fermentation of glucose ($C_6H_{12}O_6$). How many metric tons of alcohol can be made from 2.00 metric tons of glucose by the following reaction?

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

Ans. 1.02 metric tons C_2H_5OH

4.54. How many kilograms of sulfuric acid can be prepared from 1 kg of cuprite, Cu_2S, if each atom of S in Cu_2S is converted into 1 molecule of H_2SO_4?

Ans. 0.616 kg H_2SO_4

4.55. (*a*) How much bismuth nitrate, $Bi(NO_3)_3 \cdot 5H_2O$, would be formed from a solution of 10.4 g bismuth in nitric acid? The reaction is

$$Bi + 4HNO_3 + 3H_2O \rightarrow Bi(NO_3)_3 \cdot\ 5H_2O + NO$$

(*b*) How much 30.0% nitric acid (containing 30.0% HNO_3 by mass) is required to react with 10.4 g Bi?

Ans. (*a*) 24.1 g; (*b*) 41.8 g

4.56. One of the reactions used in the petroleum industry for improving the octane rating of fuels is

$$C_7H_{14} \rightarrow C_7H_8 + 3H_2$$

The two hydrocarbons appearing in this equation are liquids; the hydrogen formed is a gas. What is the percentage reduction in liquid weight accompanying the completion of the above reaction?

Ans. 6.2%

4.57. In the *Mond process* for purifying nickel, the volatile nickel carbonyl, $Ni(CO)_4$, is produced by the reaction below. How much CO is used up per kilogram of nickel?

$$Ni + 4CO \rightarrow Ni(CO)_4$$

Ans. 1.91 kg CO

4.58. When copper is heated with an excess of sulfur, Cu_2S is formed. How many grams of Cu_2S could be produced if 100 g Cu is heated with 50 g S?

Ans. 125 g Cu_2S

4.59. The "thermite" process is of historical interest as a method of welding iron:

$$2Al + Fe_2O_3 \rightarrow 2Fe + Al_2O_3$$

Calculate the maximum amount of aluminum that can be mixed with 500 g of iron(III) oxide to form a thermite charge that will yield pure iron.

Ans. 169 g Al

4.60. A mixture of 1 ton of CS_2 and 2 tons of Cl_2 is passed through a hot reaction tube. The following takes place:

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$$

(*a*) How much CCl_4, carbon tetrachloride, can be made by complete reaction of the limiting starting material? (*b*) Which starting material is in excess, and how much of it remains unreacted?

Ans. (*a*) 1.45 tons CCl_4; (*b*) 0.28 tons CS_2

4.61. A gram (dry weight) of green algae was able to absorb 4.7×10^{-3} mol CO_2 per hour by photosynthesis. If the fixed carbon atoms were all stored after photosynthesis as starch, $(C_6H_{10}O_5)_n$, how long would it take for the algae to double their own weight? (Neglect the increase in photosynthetic rate due to the increasing amount of living matter.)

Ans. 7.9 hours

4.62. Carbon disulfide, CS_2, can be made from sulfur dioxide, SO_2, a waste product of many industrial processes. How much CS_2 can be produced from 450 kg of SO_2 with excess coke, if the SO_2 conversion is 82% efficient? The overall reaction is

$$5C + 2SO_2 \rightarrow CS_2 + 4CO$$

Ans. 219 kg

4.63. Methane, CH_4, has been proposed as a motor fuel by governmental officials and some popular movies. (*a*) How much water would be produced by the complete burning of 3500 g CH_4 by $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$? (*b*) Actually, there is a loss of horsepower when using methane as a fuel for internal combustion engines—propose an explanation.

Ans. (*a*) 3900 g H_2O; (*b*) Methane has only one carbon (4 hydrogens), but gasoline is a mixture of hydrogen-carbon compounds containing much more carbon (4–12 carbons and lots of hydrogen) per mole. The carbon and hydrogen are oxidized and give off the heat necessary for the functioning of internal combustion engines. Gasoline simply provides more heat per mole.

4.64. Ethanol, C_2H_5OH, is the component in alcoholic beverages that produces the neurological disturbances associated with over-use. Ethanol is metabolized to CO_2 and H_2O over time (approximately 20 g/h) by reaction with O_2. (*a*) Write the balanced equation for the metabolism of ethanol. (*b*) How much oxygen is required to metabolize one hour's consumption? (*c*) The equation is the same one for the burning of alcohol as a fuel when mixed with gasoline (gasohol). How much oxygen is needed to burn 1 L of alcohol (density: 0.789 g/mL)?

Ans. (*a*) $2C_2H_5OH + 7O_2 \rightarrow 4CO_2 + 6H_2O$; (*b*) 489 oz O_2 (1380 g); (*c*) 1920 g O_2

4.65. Silicate ores can be solubilized by fusion with sodium carbonate. A simplified equation for what occurs is

$$2Na_2CO_3 + SiO_2 \rightarrow Na_4SiO_4 + 2CO_2$$

Calculate the minimum weight of Na_2CO_3 required to dissolve a 0.500-g sample of an ore which analyzes 19.1% silica (SiO_2).

Ans. 0.337 g (*Note*: A large excess is normally used—about 3 g.)

4.66. The chemical formula of the chelating agent Versene is $C_2H_4N_2(C_2H_2O_2Na)_4$. If each mole of this compound could bind 1 mole of Ca^{2+}, what would be the rating of pure Versene, expressed as mg $CaCO_3$ bound per gram of chelating agent? Here, the Ca^{2+} is expressed in terms of the amount of $CaCO_3$ it could form.

Ans. 264 mg $CaCO_3$ per g

4.67. When calcium carbide, CaC_2, is made in an electric furnace by the reaction below, the crude product is typically 85% CaC_2 and 15% unreacted CaO. How much CaO is to be added to the furnace charge for each 50 tons (*a*) of CaC_2 produced? (*b*) of crude product?

$$CaO + 3C \rightarrow CaC_2 + CO$$

Ans. (*a*) 53 tons CaO; (*b*) 45 tons CaO

4.68. The plastics industry uses large amounts of phthalic anhydride, $C_8H_4O_3$, made by the controlled oxidation of naphthalene:

$$2C_{10}H_8 + 9O_2 \rightarrow 2C_8H_4O_3 + 4CO_2 + 4H_2O$$

Since some of the naphthalene is oxidized to other products, only 70% of the maximum yield predicted by the above equation is actually obtained. How much phthalic anhydride would be produced in practice by the oxidation of 100 lb $C_{10}H_8$?

Ans. 81 lb

4.69. The empirical formula of a commercial ion-exchange resin is $C_8H_7SO_3Na$. The resin can be used to soften water according to the reaction provided. Expressed in moles Ca^{2+} taken up per gram resin used, what would be the maximum uptake of Ca^{2+}?

$$Ca^{2+} + 2C_8H_7SO_3Na \rightarrow (C_8H_7SO_3)_2Ca + 2Na^+$$

Ans. 0.0024 mol Ca^{2+}/g resin

4.70. The insecticide Chlordane is made by a two-step process:

$$C_5Cl_6 \text{ (hexachlorocyclopentadiene)} + C_5H_6 \text{ (cyclopentadiene)} \rightarrow C_{10}H_6Cl_6$$
$$C_{10}H_6Cl_6 + Cl_2 \rightarrow C_{10}H_6Cl_8 \text{ (Chlordane)}$$

(*a*) Calculate how much Chlordane can be made from 500 g of C_5Cl_6. (*b*) What is the percentage of chlorine in Chlordane?

Ans. (*a*) 751 g; (*b*) 69.2%

4.71. Commercial sodium "hydrosulfite" is 90% pure $Na_2S_2O_4$. How much commercial product could be made using 100 tons of zinc with a sufficient supply of the other reactants? The reactions are

$$Zn + 2SO_2 \rightarrow ZnS_2O_4$$
$$ZnS_2O_4 + Na_2CO_3 \rightarrow ZnCO_3 + Na_2S_2O_4$$

Ans. 296 tons

4.72. Fluorocarbon polymers can be made by fluorinating polyethylene according to the reaction

$$(CH_2)_n + 4nCoF_3 \rightarrow (CF_2)_n + 2nHF + 4nCoF_2$$

where n is a large integer. The CoF_3 can be regenerated by the reaction

$$2CoF_2 + F_2 \rightarrow 2CoF_3$$

(*a*) If the HF formed in the first reaction cannot be reused, how many kilograms of fluorine are consumed per kilogram of fluorocarbon produced, $(CF)_n$? (*b*) If the HF can be recovered and electrolyzed to hydrogen and fluorine, and if this fluorine is used for regenerating CoF_3, what is the net consumption of fluorine per kilogram of fluorocarbon?

Ans. (*a*) 1.52 kg; (*b*) 0.76 kg

4.73. A process designed to remove organic sulfur from coal prior to combustion involves the following reactions:

$$Y{-}S{-}Y + 2NaOH \rightarrow X{-}O{-}Y + Na_2S + H_2O$$
$$CaCO_3 \rightarrow CaO + CO_2$$
$$Na_2S + CO_2 + H_2O \rightarrow Na_2CO_3 + H_2S$$
$$CaO + H_2O \rightarrow Ca(OH)_2$$
$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2NaOH$$

In the processing of 100 metric tons of coal having a 1.0% sulfur content, how much limestone ($CaCO_3$) must be decomposed to provide enough $Ca(OH)_2$ to regenerate the NaOH used in the original leaching step?

Ans. 3.12 metric tons

4.74. Silver may be removed from solutions of its salts by reaction with metallic zinc:

$$Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$$

A 50-g piece of zinc was thrown into a 100-L vat containing 3.5 g Ag^+/L. (*a*) Which reactant was completely consumed? (*b*) How much of the other substance remained?

Ans. (*a*) zinc; (*b*) 1.9 g Ag^+/L

4.75. The following reaction proceeds until the limiting substance is completely consumed:

$$2Al + 3MnO \rightarrow Al_2O_3 + 3Mn$$

A mixture containing 100 g Al and 200 g MnO was heated to initiate the reaction. Which reactant remained in excess and what was the weight of that substance?

Ans. Al, 49 g

4.76. A mixture of $NaHCO_3$ and Na_2CO_3 weighed 1.0235 g. The dissolved mixture was reacted with excess $Ba(OH)_2$ to form 2.1028 g $BaCO_3$ by the reactions

$$Na_2CO_3 + Ba(OH)_2 \rightarrow BaCO_3 + 2NaOH$$
$$NaHCO_3 + Ba(OH)_2 \rightarrow BaCO_3 + NaOH + H_2O$$

What was the percentage $NaHCO_3$ in the original mixture?

Ans. 39.51% $NaHCO_3$

4.77. A mixture of NaCl and NaBr weighed 3.5084 g. This mixture was dissolved and treated with enough $AgNO_3$ to precipitate all the chloride and bromide as AgCl and AgBr. The washed precipitate was treated with KCN to increase solubility of the silver, then the solution was electrolyzed. The process is

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$$
$$NaBr + AgNO_3 \rightarrow AgBr + NaNO_3$$
$$AgCl + 2KCN \rightarrow KAg(CN)_2 + KCl$$
$$AgBr + 2KCN \rightarrow KAg(CN)_2 + KBr$$
$$4KAg(CN)_2 + 4KOH \rightarrow 4Ag + 8KCN + O_2 + 2H_2O$$

After the final step was completed, 5.5028 g pure silver were collected. What was the composition of the initial mixture?

Ans. 65.23% NaCl, 34.77% NaBr

CHAPTER 5

Measurement of Gases

GAS VOLUMES

Solids and liquids have volumes that tend to remain constant with changes in their environment. In contrast, the volumes of gases vary with changes in the temperature and/or pressure. This chapter addresses the factors that influence the volume of gases.

PRESSURE

The general definition of *pressure* is the force acting on a unit area of surface. Mathematically,

$$\text{Pressure} = \frac{\text{force acting perpendicularly to an area}}{\text{area over which the force is distributed}}$$

More specifically,

$$\text{Pressure (in pascals)} = \frac{\text{force (in newtons)}}{\text{area (in square meters)}}$$

and, by the above, the *pascal* is defined as

$$1\,\text{Pa} = 1\,\text{N/m}^2 = (1\,\text{kg}\cdot\text{m/s}^2)/\text{m}^2 = 1\,\text{kg/m}\cdot\text{s}^2$$

The pressure exerted by a column of fluid is

$$\text{Pressure} = \text{column height} \times \text{fluid density} \times \text{acceleration of gravity}$$

More specifically,

$$\text{Pressure} = \text{height (in m)} \times \text{density (in kg/m}^3) \times 9.81\,\text{m/s}^2$$

STANDARD ATMOSPHERIC PRESSURE

Because air has weight, it exerts a pressure. The composition of the air tends to vary, leading to changes in the weight of the air (changes in atmospheric pressure). *Standard pressure*, also called a *standard atmosphere*, is set at 1 atm pressure. The value of 1 atm is defined as 101,325 Pa. Another definition of the standard atmosphere is the pressure exerted by a column of mercury 760 mm high when at 0°C and at sea level. The mm Hg is also referred to as the *torr* (1 mm Hg = 1 torr) and 1 atm pressure then becomes 760 torr. The *bar* is often used as a measure of pressure (1 bar = 10^5 Pa = 1 atm).

$$1\text{ atm} = 760\text{ mm Hg} = 760\text{ torr} = 101,325\text{ Pa} \qquad \text{and} \qquad 1\text{ bar} = 10^5\text{ Pa (exact)}$$

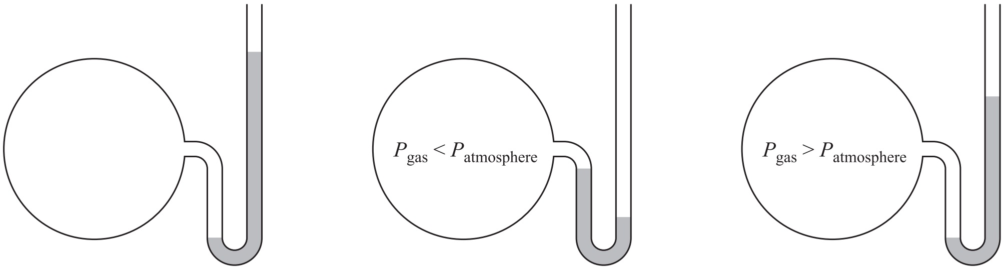
Note that there is a small built-in error when using 1 atm = 1 bar (1325 out of 100,000 or 1.3%).

PRESSURE MEASUREMENT

The pressure of a gas can be measured by attaching a manometer to the vessel containing the gas. A manometer is a tube (U-shaped in our examples) containing a liquid, usually mercury. The height of the liquid is read in mm Hg (i.e torr) pressure units.

The closed-tube manometer, Fig. 5-1(*a*), is originally filled all the way to the closed end so that the difference in mercury levels is the absolute value of the pressure of the gas. An open-tube manometer shows the difference between the pressure of the gas and the barometric pressure—Fig. 5-1(*b*) shows less than barometric pressure and Fig. 5-1(*c*) shows a pressure higher than barometric pressure.

There are mechanical and electronic measuring devices. A familiar one is the tire gauge, which provides a relative reading because the reading is in excess of the existing barometric pressure (a flat tire contains air at the ambient pressure). Gauges that read absolute pressure (starting with 0 pressure, rather than above ambient) are identified as such on the face of the gauge.



(*a*) Closed-tube manometer (*b*) Open-tube manometer (*c*) Open-tube manometer

Fig. 5-1

STANDARD CONDITIONS

The temperature of 273.15 K (0°C) and 1 atm pressure are taken as *standard conditions* (S.T.P.). Unless extreme accuracy is called for, 273.15 K is usually rounded to 273 K. Further, many problems are written using torr rather that atm (1 atm = 760 torr), as many of the measuring devices read in either mm Hg or torr (1 mm Hg = 1 torr).

GAS LAWS

There are three laws to describe the behavior of an unchanging mass of a gas: Boyle's law, Charles' law, and Gay-Lussac's law. These laws detail the effects of volume, temperature, and pressure and the interrelationships of these factors. Each of the three laws holds a single variable (V or P or T) constant with the relationship between the other two addressed. Gases that behave exactly as predicted are referred to as *ideal gases* (*perfect gases*). Most gases do not respond exactly as predicted by the laws because the laws do not account for forces between the molecules of the gases. However, the gas laws are a good starting place for predictions of the behavior of a fixed amount of a gas beginning with the initial conditions and looking to the final conditions after a change in a variable.

BOYLE'S LAW—Constant Temperature

Boyle's law describes the effects of volume and pressure—temperature is constant. The law states that the volume of a gas varies inversely with the pressure at a constant temperature.

$$(PV)_{\text{initial}} = (PV)_{\text{final}} \qquad \text{or} \qquad P_1V_1 = P_2V_2$$

CHARLES' LAW—Constant Pressure

Charles' law describes the effects of volume and temperature—pressure is constant. The law states that the volume of the gas varies directly with the temperature in the Kelvin scale (*absolute temperature*).

$$\left(\frac{V}{T}\right)_{\text{initial}} = \left(\frac{V}{T}\right)_{\text{final}} \qquad \text{or} \qquad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Note: Mathematical relationships involving temperatures most often require the temperatures to be stated in the Kelvin scale. This is because the temperature-dependent phenomena generally conform to neither Celsius nor Fahrenheit relationships. This is true of gas behavior with reference to temperature.

GAY-LUSSAC'S LAW—Constant Volume

Gay-Lussac's law describes the effects of pressure and temperature—volume is constant. The law states that the pressure of the gas varies directly with the absolute temperature.

$$\left(\frac{P}{T}\right)_{\text{initial}} = \left(\frac{P}{T}\right)_{\text{final}} \qquad \text{or} \qquad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

COMBINED GAS LAW

The individual gas laws can be used to derive a law involving all three influencing factors—volume, pressure, and temperature—into one law. Since the three laws deal with a fixed amount of gas (no change in mass), so does the combined gas law.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

DENSITY OF AN IDEAL GAS

The density (D) of a gas varies inversely to the volume, as shown in equation (*a*). We can substitute a rearrangement of the combined gas law from equation (*b*) to provide equation (*c*), which describes changes in density with temperature and pressure.

(*a*) $D_1V_1 = D_2V_2 \qquad \text{or} \qquad D_2 = D_1\dfrac{V_1}{V_2}$

(*b*) $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2} \qquad \text{or} \qquad \dfrac{V_1}{V_2} = \dfrac{P_2T_1}{P_1T_2} = \left(\dfrac{P_2}{P_1}\right)\left(\dfrac{T_1}{T_2}\right)$

(*c*) $D_2 = D_1\dfrac{V_1}{V_2} = D_1\left(\dfrac{P_2}{P_1}\right)\left(\dfrac{T_1}{T_2}\right)$

DALTON'S LAW OF PARTIAL PRESSURES

Dalton's law states that the sum of the pressures of the gases in a mixture is the total pressure exerted—the volume and temperature are constant ($P_{\text{total}} = P_1 + P_2 + P_3 + \cdots$). The pressure of each gas is the *partial pressure* of that gas. As with the other gas laws, this law only holds true when working with ideal gases; however, this law may be applied to the problems in this book for predicting results.

COLLECTING GASES OVER A LIQUID

A gas can be collected by bubbling through a liquid. Since liquids tend to evaporate, the liquid's vapor mixes with the gas being collected contributing to the total pressure (Dalton's law). Gas collection is often over water and the vapor pressure of the water, even though relatively low, must be subtracted from the total to provide the pressure of the gas collected; the result is the pressure of the "dry" gas.

$$P_{\text{gas}} = P_{\text{total}} - P_{\text{water}}$$

If the gas is collected over another volatile liquid, the vapor pressure of that liquid is subtracted from the total pressure. The partial pressures of volatile liquids are constant and dependent on temperature—the partial pressures can be obtained from reference sources.

DEVIATIONS FROM IDEAL BEHAVIOR

The laws discussed above are strictly valid only for ideal gases. The fact that a gas can be liquefied if it is compressed and cooled sufficiently is an indication that the gas is not ideal at high pressures and low temperatures. The predictions made by the application of the laws are most accurate at low pressure and high temperatures, conditions far from those of the change from a gas to a liquid.

Solved Problems

PRESSURE DEFINED

5.1. Calculate the difference in pressure between the top and bottom of a vessel exactly 76 cm deep when filled at 25°C with (*a*) water, then emptied and refilled with (*b*) mercury. The density of water at 25°C is 0.997 g/cm^3 and that of mercury is 13.53 g/cm^3.

Using the equivalent values in SI units for height and density,

(*a*)
$$\text{Pressure} = \text{height} \times \text{density} \times g = (0.76\,\text{m})(997\,\text{kg/m}^3)(9.81\,\text{m/s}^2)$$
$$= 7.43 \times 10^3\,\text{Pa} \qquad \text{or} \qquad 7.43\,\text{kPa}$$

(*b*)
$$\text{Pressure} = (0.76\,\text{m})(13{,}530\,\text{kg/m}^3)(9.81\,\text{m/s}^2)$$
$$= 100.9 \times 10^3\,\text{Pa} \qquad \text{or} \qquad 100.9\,\text{kPa}$$

5.2. How high a column of air would be necessary to cause the barometer to read 76 cm of mercury, if the atmosphere were of uniform density 1.2 kg/m^3? The density of mercury is 13.53×10^3 kg/m^3.

$$\text{Pressure of Hg} = \text{pressure of air}$$

$$\text{Height of Hg} \times \text{density of Hg} \times g = \text{height of air} \times \text{density of air} \times g$$

$$(0.76\,\text{m})(13{,}530\,\text{kg/m}^3) = h(1.2\,\text{kg/m}^3)$$

$$h = \frac{0.76\,\text{m} \times 13{,}530\,\text{kg/m}^3}{1.2\,\text{kg/m}^3} = 8.6\,\text{km}$$

Actually, the density of the air decreases with increasing height so that the atmosphere must extend much beyond 8.6 km. Modern aircraft routinely fly higher than 8.6 km (28,000 ft) and there are modified aircraft that fly in excess of 60,000 feet.

GAS LAWS

5.3. A mass of oxygen occupies 5.00 L under 740 torr pressure. What is the volume of the same mass of gas under the conditions of standard pressure with a constant temperature?

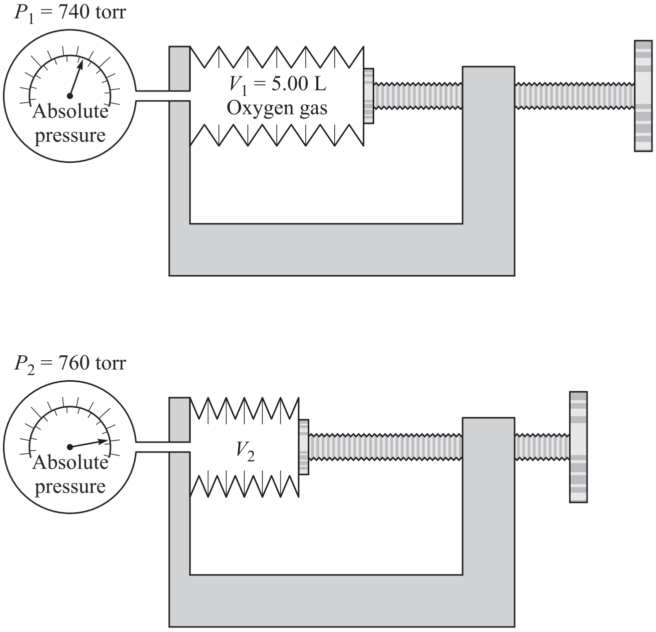


Fig. 5-2

Figure 5-2 provides us with one way the experiment could be performed. We need to know that standard pressure is 760 torr. Boyle's law is applied as follows:

$$P_1V_1 = P_2V_2 \qquad \text{or} \qquad V_2 = \frac{P_1}{P_2}V_1 = \frac{740\,\text{torr}}{760\,\text{torr}}(5.00\,\text{L}) = 4.87\,\text{L}$$

An interesting point about this problem is that any units of volume could have been used (qt, gal, etc.) since the conversions are performed by factors (multiplied by fractions) and would cancel. The same applies to units of pressure.

5.4. A mass of neon occupies 200 cm^3 at 100°C. Find its volume at 0°C under constant pressure.

Figure 5-3 illustrates the change. Applying Charles' law is appropriate for these data and the question.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad \text{or} \qquad V_2 = \frac{T_2}{T_1}V_1 = \frac{(0+273)\,\text{K}}{(100+273)\,\text{K}}(200\,\text{cm}^3) = 146\,\text{cm}^3$$

Absolute temperatures, the Kelvin scale, must be used when performing gas law calculations.

5.5. A steel tank contains carbon dioxide at 27°C and 12.0 atm. Determine the internal gas pressure when the tank and contents are heated to 100°C. The volume of the tank does not change.

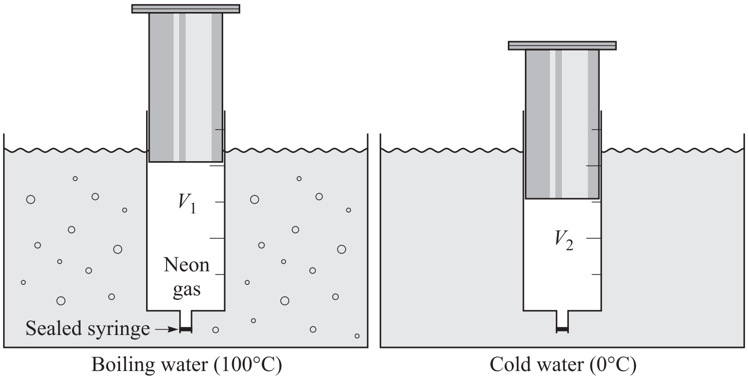


Fig. 5-3

See Fig. 5-4. Gay-Lussac's law gives us

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \qquad \text{or} \qquad P_2 = \frac{T_2}{T_1} P_1 = \frac{(100 + 273)\,\text{K}}{(27 + 273)\,\text{K}} (12.0\,\text{atm}) = 14.9\,\text{atm}$$

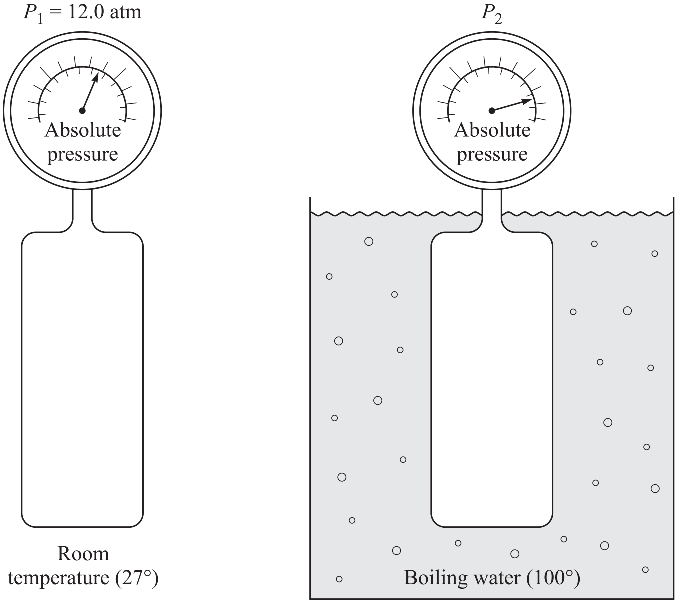


Fig. 5-4

5.6. Diesel engines run without the use of a spark plug because the fuel/air mixture is heated during compression to the flash point. Suppose the 6-cylinder, 6.0-L engine takes in the fuel/air mixture at 1 atm and 25°C, but is capable of 13.5 atm compression at the 220°C required to ignite the particular mixture. As the design engineer, calculate the volume per cylinder of the gas/air mixture that is necessary.

Since we have all three factors involved in gas action/reaction, we can apply the combined gas law. The 6-cylinder engine, 6.0 liters total volume, has 1.0-L cylinders, which is the value of V_1. The remainder of the factors are stated.

Remembering that all gas law problems require temperature expressed in the Kelvin scale, you can apply the combined gas law to determine the answer.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \qquad \text{or} \qquad V_2 = V_1\left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right) = (1.0\,\text{L})\left(\frac{493\,\text{K}}{298\,\text{K}}\right)\left(\frac{1\,\text{atm}}{13.5\,\text{atm}}\right) = 0.123\,\text{L}$$

5.7. Given 20.0 L of ammonia at 5°C and 760 torr, determine its volume at 30°C and 800 torr.

See Fig. 5-5 for some visual help. This problem is set up in the same manner as Problem 5.6.

$$V_2 = V_1\left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right) = (20.0\,\text{L})\left(\frac{303\,\text{K}}{278\,\text{K}}\right)\left(\frac{760\,\text{torr}}{800\,\text{torr}}\right) = 20.7\,\text{L}$$

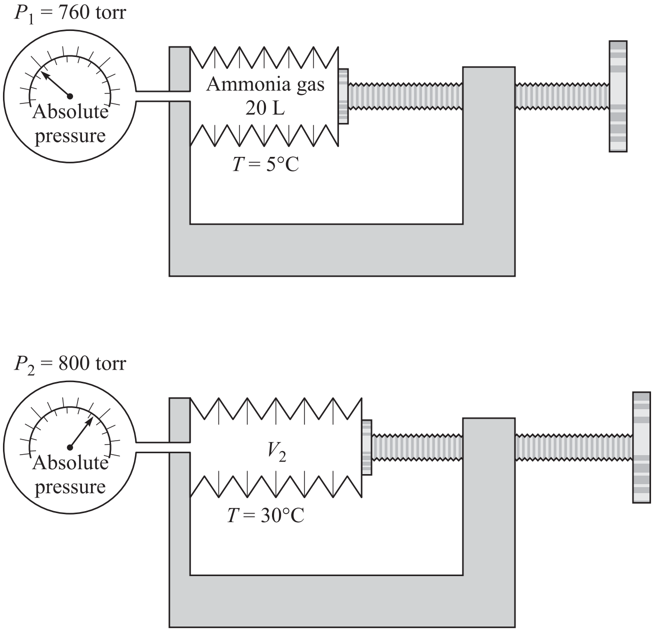


Fig. 5-5

5.8. One liter of gas, originally at 1.00 atm and −20°C, was warmed to 40°C. How many atmospheres pressure must it then be subjected to in order to reduce its volume to one-half liter?

The solution for this problem is derived from the use of the combined gas law.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \qquad \text{or} \qquad P_2 = P_1\left(\frac{V_1}{V_2}\right)\left(\frac{T_2}{T_1}\right) = (1\,\text{atm})\left(\frac{1\,\text{L}}{0.5\,\text{L}}\right)\left(\frac{313\,\text{K}}{253\,\text{K}}\right) = 2.47\,\text{atm}$$

5.9. Suppose just before taking a trip you filled your tires to 30 pounds pressure (psi; lb/in^2) and the temperature that day was 27°F. After the trip, you checked the pressure and found it to be 34.2 psi. Estimate the temperature in °F of the air in the tires. Assume that the tire gauge reads relative pressure, that the volume of the tires remains constant, and that the ambient pressure was 1.00 atm that day.

Problem 1.9 contains the calculation showing that 1 atm is equal to 14.7 psi. Making the conversion, we find that the beginning pressure was (30.0 + 14.7) psi and that the tire pressure at the end of the trip was (34.2 + 14.7) psi. Since absolute zero is −460°F (Fig. 1-1), the absolute temperature is (27 + 460) Fahrenheit degree intervals. Applying Gay-Lussac's law, which determines temperature and pressure changes with no volume changes,

$$T_2 = T_1 \times P_2/P_1 = (27 + 460)(34.2 + 14.7)/(30.0 + 14.7) = 533 \text{ Fahrenheit degree intervals}$$

$$\text{Final temperature} = \text{Fahrenheit degree intervals} - \text{absolute zero} = 533 - 460 = 73°\text{F}$$

Note that the absolute temperatures were used in this problem, as is required by gas law problems. The difference between this problem and others is that the scale is Fahrenheit rather than Kelvin.

5.10. A container holds 6.00 g of CO_2 at 150°C and 100 kPa pressure. How many grams of CO_2 will it hold at 30°C and the same pressure?

Charles' law will organize the information and provide us with the solution. However, we must assume that CO_2 behaves consistently with the change in the number of molecules (change in mass). Now, we can let the volume of the container be V_1 and the volume of the 6.00 g of CO_2 be V_2.

$$\text{By some rearrangement: } \frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad \text{or} \qquad V_1T_2 = V_2T_1 \qquad \text{or} \qquad \frac{V_2}{V_1} = \frac{T_2}{T_1}$$

$$V_2/V_1 = (30 + 273)/(150 + 273) = 0.716$$

Since 6.00 g of CO_2 occupies 0.716 V_1, to fill the container (V_1) will require

$$6.00\,\text{g}/0.716 = 8.38\,\text{g CO}_2$$

DENSITY OF A GAS

5.11. The density of helium is 0.1786 kg/m^3 at S.T.P. If a given mass of helium at S.T.P. is allowed to expand to 1.500 times the initial volume by changing the temperature and pressure, what will be the resultant density?

The density of a gas varies inversely with the volume.

$$\text{Resultant density} = (0.1786\,\text{kg/m}^3)\left(\frac{1}{1.500}\right) = 0.1191\,\text{kg/m}^3$$

Note that the problem could have been posed in terms of liters because 1 kg/m^3 = 1 g/L.

5.12. The density of oxygen is 1.43 g/L at S.T.P. What is the density of oxygen at 17°C and 700 torr?

The combined gas law shows that the density of an ideal gas varies inversely with the absolute temperature and directly with the pressure.

$$D_2 = D_1\left(\frac{T_1}{T_2}\right)\left(\frac{P_2}{P_1}\right) = (1.43\,\text{g/L})\left(\frac{273\,\text{K}}{290\,\text{K}}\right)\left(\frac{700\,\text{torr}}{760\,\text{torr}}\right) = 1.24\,\text{g/L}$$

PARTIAL PRESSURE

5.13. A mixture of gases at 760 torr contains 65.0% nitrogen, 15.0% oxygen, and 20.0% carbon dioxide by volume. What is the pressure of each gas in torr?

Dalton's law of partial pressure states that the total pressure is the result of the sum of the pressures of the component gases in a mixture. Therefore, if the total pressure is 760 torr, then the pressure of the nitrogen would be 65.0% of 760 torr. Using this approach results in the pressures of each of the gases.

For nitrogen: 760 torr × 0.650 = 494 torr due to N_2

For oxygen: 760 torr × 0.150 = 114 torr due to O_2

For carbon dioxide: 760 torr × 0.200 = 152 torr due to CO_2

Notice that the sum of the pressures (494 + 114 + 152) is 760, which is our check on the work.

5.14. In a gaseous mixture at 20°C the partial pressures of the components are: hydrogen, 200 torr; carbon dioxide, 150 torr; methane, 320 torr; and ethylene, 105 torr. What is (*a*) the total pressure of the mixture and (*b*) the volume percent of hydrogen?

(*a*) Total pressure = the sum of the partial pressure = 200 + 150 + 320 + 105 = 755 torr

(*b*) By applying Boyle's law, it can be shown that the fraction of the total pressure (all the gases in the mixture occupy the same volume—constant volume) is the same as the fraction of the total volume (when each gas is at the same pressure).

$$\text{Volume fraction of } H_2 = \frac{\text{partial pressure } H_2}{\text{total pressure of mixture}} = \frac{200\,\text{torr}}{775\,\text{torr}} = 0.258 \text{ (of total)} \qquad \text{or} \qquad 25.8\%$$

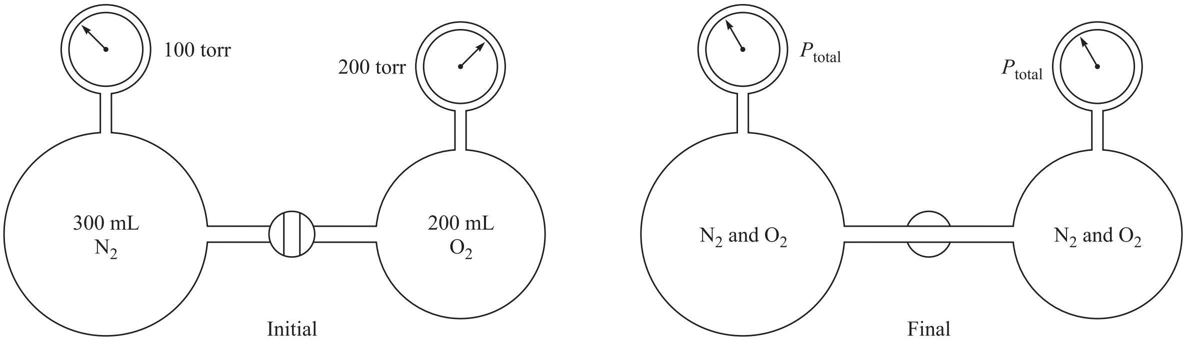


Fig. 5-6

5.15. A 200-mL flask contained oxygen at 200 torr, and a 300-mL flask contained nitrogen at 100 torr (Fig. 5-6). The two flasks were then interconnected so that gases flowed together in the combined volume. Assuming no change in temperature, (*a*) what was the partial pressure of each gas in the final mixture and (*b*) what was the total pressure?

Since the final volume is the sum of the two volumes, it is 500 mL. And, applying Dalton's law of partial pressure:

(*a*) For oxygen: $$P_{\text{final}} = P_{\text{initial}}\left(\frac{V_{\text{initial}}}{V_{\text{final}}}\right) = (200\,\text{torr})\left(\frac{200}{500}\right) = 80\,\text{torr}$$

For nitrogen: $$P_{\text{final}} = P_{\text{initial}}\left(\frac{V_{\text{initial}}}{V_{\text{final}}}\right) = (100\,\text{torr})\left(\frac{300}{500}\right) = 60\,\text{torr}$$

(*b*) Total pressure = sum of the partial pressures = 80 torr + 60 torr = 140 torr

COLLECTING GASES OVER A LIQUID

5.16. Exactly 100 cm^3 of oxygen are collected over water at 23°C and 800 torr. Compute the *standard volume* (volume at S.T.P.) of the dry oxygen. Vapor pressure of water at 23°C is 21.1 torr.

The gas collected in this experiment is not just oxygen, but also contains some water vapor which must be mathematically removed to determine the pressure of just the oxygen.

$$\begin{aligned}\text{Pressure of dry oxygen} &= \text{total pressure} - \text{vapor pressure of water}\\ &= 800\,\text{torr} - 21\,\text{torr} = 779\,\text{torr}\end{aligned}$$

Then, for dry oxygen, $V_1 = 100\,\text{cm}^3$, $T_1 = 23 + 273 = 296\,\text{K}$, and $P = 779\,\text{torr}$. In order to solve for the S.T.P. conditions, we can use the second set of variables (V_2, T_2, and P_2) in the combined gas law and solve it for V_2.

$$V_2 = V_1\left(\frac{T_2}{T_1}\right)\left(\frac{P_1}{P_2}\right) = (100\,\text{cm}^3)\left(\frac{273\,\text{K}}{296\,\text{K}}\right)\left(\frac{779\,\text{torr}}{760\,\text{torr}}\right) = 94.5\,\text{cm}^3$$

5.17. In a basal metabolism measurement timed at exactly 6 minutes, a patient exhaled 52.5 L of air, measured over water at 20°C. The vapor pressure of water at 20°C is 17.5 torr. The barometric pressure was 750 torr. The exhaled air analyzed at 16.75 volume % oxygen, and the inhaled air at 20.32 volume % oxygen (both on a dry basis). Neglecting any solubility of the gases in water and any difference in total volumes of inhaled and exhaled air, calculate the rate of oxygen consumption by the patient in cm^3 (S.T.P.) per minute.

$$\text{Volume of dry air at S.T.P.} = (52.5\,\text{L})\left(\frac{273\,\text{K}}{293\,\text{K}}\right)\left(\frac{750\,\text{torr} - 17.5\,\text{torr}}{760\,\text{torr}}\right) = 47.1\,\text{L}$$

$$\text{Rate of oxygen consumption} = \frac{\text{volume of oxygen (S.T.P.) consumed}}{\text{time in which the volume was consumed}}$$

$$= \frac{(0.2032 - 0.1675)(47.1\,\text{L})}{6\,\text{min}} = 0.280\,\text{L/min} = 280\,\text{cm}^3/\text{min}$$

5.18. A quantity of gas is collected in a graduated tube over mercury. The volume of gas at 20°C is $50.0\,\text{cm}^3$, and the level of the mercury in the tube is 200 mm above the outside mercury level (see Fig. 5-7). The barometer reads 750 torr. Find the volume at S.T.P. The vapor pressure of mercury is not significant at this temperature.

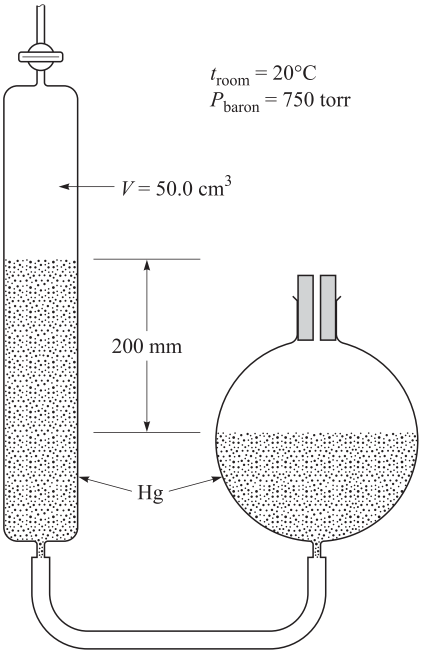


Fig. 5-7

After a gas is collected over a liquid, the receiver is often adjusted so that the level of the liquid inside and outside is the same. When this cannot be done conveniently, it is necessary to calculate the effect of the difference in levels.

Since the level of mercury inside the tube is 200 mm higher than outside, the pressure of the gas is 200 mm Hg = 200 torr less than the atmospheric pressure of 750 torr.

$$\text{Volume at S.T.P.} = (50.0\,\text{cm}^3)\left(\frac{273\,\text{K}}{293\,\text{K}}\right)\left(\frac{750 - 200\,\text{torr})}{760\,\text{torr}}\right) = 33.7\,\text{cm}^3$$

Supplementary Problems

5.19. A portable air tank has a note on its gauge stating that 125 psi cannot be exceeded. What is the ***total*** pressure in (*a*) atm, (*b*) torr, (*c*) mm Hg, and (*d*) millibars?

Ans. (*a*) 9.5 atm; (*b*) 722.6 torr; (*c*) 7222.6 mm Hg; (*d*) 9500 millibars

5.20. Provide Boyles' and Charles' gas laws starting with the combined gas law equation.

Ans. Boyles' law (constant temperature): $\dfrac{P_1V_1}{\cancel{T_1}} = \dfrac{P_2V_2}{\cancel{T_2}}$ becomes $P_1V_1 = P_2V_2$

Charles' law (constant pressure): $\dfrac{\cancel{P_1}V_1}{T_1} = \dfrac{\cancel{P_2}V_2}{T_2}$ becomes $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$

5.21. The vapor pressure of water at 25°C is 23.8 torr. Express this in (*a*) atm and (*b*) kPa.

Ans. (*a*) 0.0313 atm; (*b*) 3.17 kPa

5.22. Camphor has been found to undergo a crystalline modification at a temperature of 148°C and a pressure of 3.09×10^9 N/m^2. What is the transition pressure in atmospheres?

Ans. 3.05×10^4 atm

5.23. When solving gas law problems using the combined gas law, the pressure and volume units do not have to be as indicated by the authors of the laws and by the ideal gas law; they don't even have to be in the metric system. However, temperature must be in the Kelvin scale. Explain.

Ans. The conversion factors used to change units to liters (V) and atm (P) will cancel since they are used in the same manner on both sides of the equation (multiplication/division in the same location on both sides with no addition/subtraction). However, the conversions from either °F or °C to K include addition/subtraction, which does not cancel.

5.24. A hydrogen-filled weather balloon occupies 48.0 ft^3 at ground level where the pressure is 753 torr. Compute its volume at the top of the mountain where it is about to be launched when the temperature is the same as at ground level, but the pressure is only 652 torr. (We don't need to account for the elasticity of the skin.)

Ans. 55.4 ft^3

5.25. During a fire, the gases in a room will expand and can eventually break out of tight-fitting windows. Suppose a room 10 feet by 12 feet with a 7-foot ceiling originally at 1 atm and 25°C (room/lab conditions) begins to burn. The temperature in the room rises to 400°C (approximately 750°F). What will be the amount of pressure exerted by the heated air (no change in volume, yet)?

Ans. 2.26 atm

5.26. Ten liters of hydrogen under 1 atm pressure are contained in a cylinder which has a movable piston. The piston is moved in until the same mass of gas occupies 2 L with no temperature change. Find the pressure in the cylinder.

Ans. 5 atm

5.27. Chlorine gas is evolved at the anode of a commercial electrolysis cell at the rate of 3.65 L/min at a temperature of 647°C. On its way to the intake pump, it is cooled to 63°C. Calculate its rate of intake to the pump assuming the pressure has remained constant.

Ans. 1.33 L/min

5.28. A quantity of hydrogen is confined in a platinum chamber of constant volume. When the chamber is immersed in a bath of melting ice, the pressure of the gas is 1000 torr. (*a*) What is the Celsius temperature when the pressure manometer indicates an absolute pressure of 100 torr? (*b*) What pressure will be indicated when the chamber is brought to 100°C?

Ans. (*a*) −246°C; (*b*) 1366 torr

5.29. Since helium gas is a precious resource, the contents of a small passenger balloon were pumped to storage during an overhaul. Normally the balloon contains 18,700 ft^3 of helium at 31°C and 1.00 atm (14.7 lb/in^2 or 14.7 psi). How many steel cylinders will be required to store it if each cylinder holds 2.50 ft^3, the storage temperature is a constant 11°C, and the cylinders are rated safe up to 2000 psi?

Ans. 52 cylinders (calculated answer: 51.4 cylinders)

5.30. A gas at 50°C and 785 torr occupies 350 mL. What volume will the gas occupy at S.T.P.?

Ans. 306 mL

5.31. A reaction for the production of hydrogen gas suitable for use in a hydrogen-powered vehicle is given below. What volume of H_2 can be prepared from 1.00 kg CaH_2 (the final conditions are 25°C and 1 atm)?

$$CaH_2(s) + H_2O(l) \rightarrow Ca(OH)_2(aq) + 2H_2(g)$$

Ans. 1160 L

5.32. The gas evolved in a reaction was collected in a vessel like that shown in Fig. 5-7. Its volume was 47.3 cm^3 when first observed at 752 torr and 26°C. The Hg level in the bulb was 279 mm below that in the collection tube. The next day, with the temperature at 17°C and the pressure at 729 torr, the volume was measured again, but first the bulb was adjusted to equalize the levels. What volume reading is expected?

Ans. 29.8 cm^3

5.33. Exactly 500 cm^3 of nitrogen are collected over water at 25°C and 755 torr. The gas is saturated with water vapor. Compute the volume of the nitrogen in the dry condition at S.T.P. The vapor pressure of water at 25°C is 23.8 torr.

Ans. 441 cm^3

5.34. A dry gas occupied 127 cm^3 at S.T.P. If this same mass of gas were collected over water at 23°C (total gas pressure 745 torr), what volume would it occupy? Water's vapor pressure at 23°C is 21 torr.

Ans. 145 cm^3

5.35. A mass of gas occupies 0.825 L at −30°C and 556 Pa. What is the pressure if the volume becomes 1 L and the temperature 20°C?

Ans. 553 Pa

5.36. A 57.3-L pressure vessel has a safety valve set to open at 875 kPa. A chemical reaction is expected to yield 472 L of gaseous product at S.T.P. Would it be a good idea to store this in the vessel described if the ambient temperature can rise to 105°F?

Ans. No; the final pressure could be 959 kPa.

5.37. An attempt to identify a colorless liquid is made by heating it to 100°C at 754 torr in a partially sealed 250 flask to replace the air in the flask with only the vapor as the liquid is noted to boil at about 65°C. The volume of the flask is 271 mL, determined by filling it with water and measuring the volume. The mass of the flask has increased by 0.284 g. What is the molecular mass of the unknown liquid?

Ans. 32 g/mol; the BP and the molecular mass are clues to the identity, which might be methyl alcohol, CH_3OH.

5.38. The density of a gas at S.T.P. provides an easy measurement of molar mass (refer to Problem 6.1). For a normally liquid substance, however, it is necessary to measure the gas density at an elevated temperature and reduced pressure. Calculate the density in g/L (same as kg/m^3) at S.T.P. of a gas which has a density of 3.45 g/L at 90°C and 638 torr.

Ans. 5.59 g/L

5.39. Airplanes are known to have less lift in warm weather than in cold. Compare the density of air at 30°C to air at S.T.P.

Ans. The density of the air will be 0.9 of the density at S.T.P., resulting in a loss of lift.

5.40. A container holds 2.55 g of neon at S.T.P. What mass of neon will it hold at 100°C and 10.0 atm?

Ans. 18.7 g

5.41. Glass tubing is being chosen to produce a neon sign, but the glass must support 2.5 atm without breaking. The design for the sign requires the use of 10.5 g Ne gas in a total of 6.77 L volume for the entire sign. Operating temperature is expected to reach the highest at 78°C. Will this glass take the strain or should another tubing be located?

Ans. This tubing has sufficient strength to hold the pressure (2.2 atm is the expected), but not with much reserve. Common practice in design should allow for the chance that the pressure might increase; therefore, considering the use of a stronger tubing would be a prudent practice.

5.42. At the top of a mountain, the thermometer reads 10°C and the barometer reads 700 mm Hg. At the bottom of the same mountain, the temperature is 30°C and the pressure is 760 mm Hg. Compare the density of the air at the top with that at the bottom of the mountain.

Ans. 0.986 at the top and 1.000 at the bottom

5.43. A volume of 95 cm^3 of nitrous oxide at 27°C is collected over mercury in a graduated tube. The level of mercury inside the tube is 60 mm above the outside level when the barometer reads 750 torr. (*a*) Calculate the volume of the gas at S.T.P. (*b*) What volume would the gas occupy at 40°C with a barometric pressure of 745 torr and the mercury level inside the tube 25 mm below the outside?

Ans. (*a*) 78 cm^3; (*b*) 89 cm^3

5.44. At a certain altitude in the upper atmosphere, the temperature is estimated to be -100°C and the density just 10^{-9} that of the earth's atmosphere at S.T.P. Assuming a uniform atmospheric composition, what is the pressure in torr at this altitude?

Ans. 4.82×10^{-7} torr

5.45. At 0°C the density of nitrogen at 1 atm is 1.25 kg/m^3. The nitrogen which occupied 1500 cm^3 at S.T.P. was compressed at 0°C to 575 atm and the gas volume was observed to be 3.92 cm^3, in violation of Boyle's law. What is the final density of this nonideal gas?

Ans. 478 kg/m^3

5.46. One cylinder of a particular 8-cylinder engine has the largest volume of 625 mL. The fuel-air mixture in that cylinder (original pressure 1 atm) is compressed to 85 mL, then is ignited. (*a*) If the gases are present at the largest volume at 1 atm, what is the pressure on compression before ignition? (*b*) Express the compression ratio (volume ratio).

Ans. (*a*) 7.67 atm; (*b*) 7.35:1

5.47. Let us reconsider Problem 5.46 a little more realistically. The fuel-air mixture enters the engine at 18°C and, after compression, it is at 121°C just before being burned. If the original pressure before compression is 1 atm, (*a*) what is the pressure just before ignition? (*b*) Would the engine designed using the parameters in Problem 5.46 be suitable for the conditions of this problem?

Ans. 9.96 atm; (*b*) Considering that the pressure here is nearly 30% greater, some strengthening of the cylinder would be a wise move.

5.48. The respiration of a suspension of yeast cells was measured by observing the decrease in pressure of gas above the cell suspension. The apparatus shown in Fig. 5-8 was arranged so that the gas was confined to a constant volume of 16.0 cm^3 and the entire pressure change was caused by the uptake of oxygen by the cells. The pressure was measured with the use of a manometer, the fluid of which had a density of 1.034 g/cm^3. The supply of liquid was adjustable so that the level on the closed side was kept constant. The entire apparatus was maintained at 37°C. In a 30-minute observation period, the fluid in the open side of the manometer dropped 37 mm. Neglecting the solubility of oxygen in the yeast suspension, compute the rate of oxygen consumption by the cells in cubic millimeters of O_2 (S.T.P.) per hour.

Ans. 105 mm^3/hr

5.49. A mixture of N_2, NO, and NO_2 was analyzed by selective absorption of the oxides of nitrogen. The initial volume of the mixture was 2.74 cm^3. After treatment with water, which absorbed the NO_2, the volume was 2.02 cm^3. A solution of $FeSO_4$ in water was then shaken with the residual gas to absorb the NO, after which the volume was 0.25 cm^3. All the volumes were measured at the same pressure. Neglecting water vapor, what was the volume percentage of each gas in the original mixture?

Ans. 9.1% N_2; 64.6% NO; 26.3% NO_2

5.50. HCN can be toxic at a concentration of 150 ppm. (*a*) What is the percent composition of the HCN in the air at this concentration? (*b*) What is the partial pressure of HCN at this level if the total pressure is 1 atm?

Ans. (*a*) 0.015% HCN; (*b*) 0.00015 atm

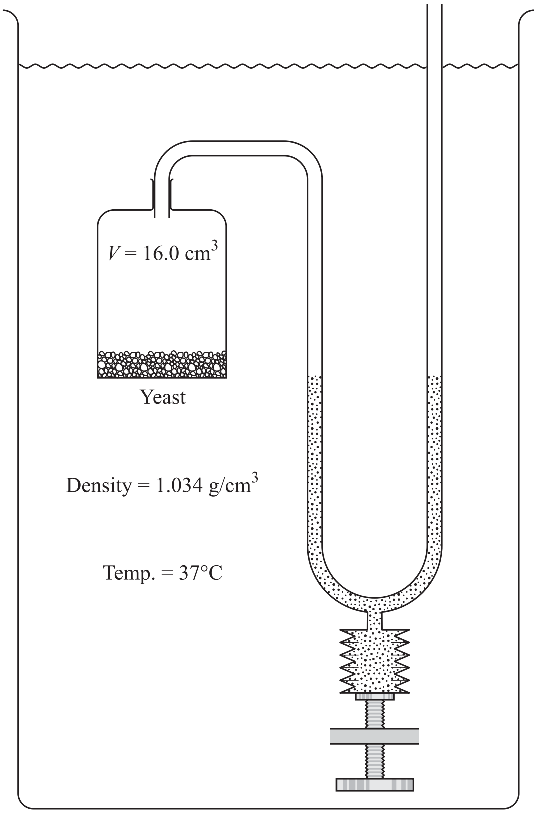


Fig. 5-8

5.51. A handball with the internal volume of 60 cm^3 was filled with air to a pressure of 1.35 atm. A dishonest player filled a syringe to the 25-cm^3 mark with air at 1.00 atm and injected it into the handball. Calculate the pressure inside the tampered handball, assuming no volume change.

Ans. 1.77 atm

5.52. A 250-mL flask contained krypton at 500 torr. A 450-mL flask contained helium at 950 torr. The contents of the two flasks were mixed by opening a stopcock connecting them. Assuming that all operations were carried out at a constant temperature, calculate the final pressure and the volume percent of each gas in the mixture. Neglect the volume of the stopcock.

Ans. 789 torr; 22.6% Kr and 77.4% He

5.53. A glass vacuum tube was sealed at the factory at 750°C with a residual pressure of air of 4.5×10^{-7} torr. Then a metal "getter" was used to remove all the oxygen (which is 21% by volume of air). What was the final pressure in the tube at 22°C?

Ans. 1.03×10^{-7} torr

5.54. The vapor pressure of water at 80°C is 355 torr. A 100-mL vessel contained water-saturated oxygen at 80°C, the total gas pressure being 760 torr. The contents of the vessel were pumped into a 50-mL vessel at the same temperature. Assuming no condensation, (*a*) What were the partial pressures of oxygen and of the water vapor? (*b*) What was the total pressure in the final equilibrium state?

Ans. (*a*) 810 torr, 355 torr; (*b*) 1165 torr

5.55. A gas sample was collected in an apparatus similar to that in Fig. 5-7 except that the confining liquid was water. At 17°C, the volume of gas was 67.3 cm^3, the barometric pressure was 723 torr, and the water level in the bulb was 210 mm below that in the collection tube. Later that day the room warmed to 34°C and the barometer went up to 741 torr. The experimenter slowly adjusted the bulb to equalize the levels. What was the new volume reading? The vapor pressure of water is 14.5 torr at 17°C and 39.9 torr at 34°C. The density of mercury is 13.6 times that of water.

Ans. 70.4 cm^3

CHAPTER 6

The Ideal Gas Law and Kinetic Theory

AVOGADRO'S HYPOTHESIS

Avogadro's hypothesis states that *equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules*. Such being the case, 1 L of oxygen contains the same number of molecules as 1 L of hydrogen (or any other gas). Also, 1 ft^3 of helium contains the same number of molecules as 1 ft^3 of nitrogen (or any other gas). Of course, these gases must be measured under the same conditions of temperature and pressure.

Avogadro's hypothesis can be applied to the problem of relative masses of molecules of two gases and, if one is known, the other can be determined as is shown in Example 1.

EXAMPLE 1 At standard conditions, 1 L of oxygen weighs 1.43 g and 1 L of an unknown gas that we know contains carbon and oxygen (C_xO_y) weighs 1.25 g. By applying Avogadro's hypothesis, we can state that 1 L of C_xO_y (S.T.P.) contains the same number of molecules as 1 L of O_2 (S.T.P.). This further tells us that a molecule of C_xO_y must weigh 1.25/1.43 times as much as a molecule of oxygen. According to the Periodic Table, O_2 weighs 32 grams per mole, so we can calculate the mass of C_xO_y.

$$\frac{1.25\,\text{g/L}}{1.43\,\text{g/L}} \times 32\,\text{g/mol}$$

It appears as though this compound, C_xO_y, is carbon monoxide ($C + O = 12 + 16 = 28\,\text{g/mol}$). By using this technique, we are able to determine atomic mass, especially for the lighter elements. Even crude gas density experiments may be used along with chemical composition data and known atomic masses to establish molecular mass, which leads us to the molecular formula of a gas.

EXAMPLE 2 A hydride of silicon that has the empirical formula SiH_3 (approximately 31 g/empirical formula) was found to have an approximate gas density at S.T.P. of 2.9 g/L. By comparison with oxygen, whose molecular mass and density are known, the molecular mass of the hydride is

$$\frac{2.9\,\text{g/L}}{1.43\,\text{g/L}} \times 32\,\text{g/mol} = 65\,\text{g/mol}$$

This is an approximate molecular mass and might be off by as much as 10 percent. Regardless, the value is sufficiently accurate to tell us that the molecular formula is approximately two times the empirical formula, Si_2H_6, with a molecular mass of 62 g ruling out other multiples of the empirical formula.

MOLAR VOLUME

If 1 mol of any gas has the same number of molecules, N_A, as 1 mol of any other gas (Chapter 2), and if equal numbers of molecules occupy equal volumes at S.T.P. (Avogadro's hypothesis), then 1 mol of any gas has the same volume at S.T.P. as 1 mol of any other gas. This standard *molar volume* has the value of 22.414 L.

As a caution to the reader: Of course, Avogadro's hypotheses and the gas laws assume that gases are all ideal gases. The gases in the real world are not all ideal gases; the molar volume at S.T.P. is most often a little below the 22.414 L indicated here. In the remainder of this chapter, the rounded value 22.4 L/mol will be used for all gases and, if not so identified, all the gases are ideal.

IDEAL GAS LAW

Let us take a look at the combined gas law (Chapter 5) and substitute in standard conditions (S.T.P.) for 1 mol gas. We can use the subscript of zero to specifically indicate standard conditions.

$$\frac{P_0V_0}{T_0} = \frac{(1\ \text{atm})(22.4\ \text{L/mol})}{273\ \text{K}} = 0.0821\frac{\text{L atm}}{\text{mol K}} \qquad \text{or} \qquad 0.0821\ \text{L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

This calculation provides us with the *universal gas constant*, R. If we were dealing with more than 1 mol of an ideal gas at S.T.P., the volume of the gas would be n times greater. The relationship can be expressed as $PV/T = nR$ or, by rearrangement,

$$PV = nRT \qquad \text{where} \qquad P \text{ is in atm; } V \text{ is in liters; } n \text{ is in moles; } T \text{ is in kelvins.}$$

This relationship is the *ideal gas law* and your knowledge of the law and the value of R is critical. When SI units are used for P and V (pascals and cubic meters), then

$$R = 8.3145\frac{\text{J}}{\text{mol K}} \qquad \text{or} \qquad R = 8.3145\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

must be used.

The mass, in grams, of gas present is given by

$$w = n\mathsf{M} \qquad \text{where} \qquad \mathsf{M} \text{ is the molar mass in g/mol;}$$

or by

$$w = dV \qquad \text{where} \qquad d \text{ is the gas density in g/L and } V \text{ is in liters.}$$

Performing the substitution of the above terms provides us with an alternative form of the ideal gas law, which is

$$PV = nRT \qquad \text{becomes} \qquad PV = \left(\frac{w}{\mathsf{M}}\right)RT$$

and, by further substitution,

$$P = \left(\frac{d}{\mathsf{M}}\right)RT$$

For an ideal gas, V is proportional to n when P and T are fixed. This means that the awkward concept of volume percentage (or fraction) discussed in Problem 5.12 can now be replaced with mole percentage or mole fraction. An assumption is that each gas occupies the entire volume of the mixture, but is at its own partial pressure.

GAS VOLUME RELATIONS FROM EQUATIONS

A chemical equation represents the relationship of the reactants and products through a numerical relationship expressed by the coefficients associated with the participants. The coefficients can be interpreted as telling us the number of molecules or moles of materials involved; but they also represent the volumes of those participants that are gases, assuming a constant temperature and pressure (T and P). An example of these relationships is as follows:

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

4 molecules	3 molecules	2 molecules	6 molecules
4 moles	3 moles	2 moles	6 moles
4 volumes	3 volumes	2 volumes	6 volumes
4 × 22.4 L	3 × 22.4 L	2 × 22.4 L	6 × 22.4 L
4 gal	3 gal	2 gal	6 gal
4 ft^3	3 ft^3	2 ft^3	6 ft^3

The interpretation of the relationships of water to the other substances is valid only if the water is also a gas (vapor) under the conditions of temperature and pressure specified. At S.T.P. the water would be condensed into a liquid (or may be solid) and its volume would be very small compared with its volume as a gas and could be ignored. So, at S.T.P. with water as a liquid or solid, the 7 volumes of reactants would only produce 2 volumes of products (water's volume being negligible).

GAS STOICHIOMETRY INVOLVING MASS

There are circumstances where weight is an important factor (Example 3), but the calculations involving gases may be in terms of volumes of gases involved. The conversion from volumes of gas to mass is done through the numbers of moles. The methods used in these problem solutions are as in Chapter 4 except that the numbers of moles converted to mass (g, lb, etc.) must be determined from the volume, temperature, and pressure of the gases.

EXAMPLE 3 Carbon dioxide can be removed from the recirculated air aboard a spaceship by passing it over lithium hydroxide.

$$2LiOH(s) + CO_2(g) \rightarrow Li_2CO_3(s) + H_2O(g)$$

Calculate the number of grams of LiOH consumed in the above reaction when 100 L of air containing 1.20% CO_2 at 29°C and 776 torr are treated by being passed through the LiOH.

It is important to note that the calculations are tied to the properly written and balanced equation. The equation sets the relationships between participants that we need to complete the solution.

$$n_{CO_2} = \frac{(0.0120)(100\,\text{L})\left(\dfrac{776\,\text{torr}}{760\,\text{torr/atm}}\right)}{\left(0.0821\dfrac{\text{L atm}}{\text{mol K}}\right)(302\,\text{K})} 0.0494\,\text{mol CO}_2$$

$$n_{LiOH} = 2(n_{CO_2}) = 2(0.0494\,\text{mol}) = 0.0988\,\text{mol LiOH}$$

$$\text{Mass of LiOH} = (0.0988\,\text{mol LiOH})\left(23.9\frac{\text{g LiOH}}{\text{mol LiOH}}\right) = 2.36\,\text{g LiOH}$$

BASIC ASSUMPTIONS OF THE KINETIC THEORY OF GASES

The ideal gas law can be derived solely from theoretical principles by making a few assumptions about the nature of gases and the meaning of temperature. The derivation can be found in any physical chemistry textbook.

The basic assumptions involved are as follows:

1. A gas consists of a very large number of molecules which are in a state of continual random motion. A molecule is extremely small and cannot even be seen. Pressure is due to the force of molecular collisions on a surface, such as the container walls or a diaphragm in a gauge used for measuring pressure.
2. Collisions between molecules or between a molecule and an inert surface are perfectly elastic. This means they bounce off each other with no loss of kinetic energy.
3. No forces are exerted between molecules except through collisions. Therefore, between collisions, a molecule travels in a straight line at constant speed.
4. The average kinetic energy per gas molecule, $(\frac{1}{2}mu^2)_{\text{avg}}$, is independent of the nature of the gas and is directly proportional to the temperature. In this case, the kinetic energy is defined by the standard physical formula in terms of molecule mass, *m*, and the molecular speed, *u*. This statement may be taken as a more exact definition of temperature than the qualitative one given in Chapter 1. A list of some common energy units is given in Table 6-1.

Table 6-1 Some Common Energy Units

Unit	Unit Symbol	Definition
joule (SI)	J	$\text{m}^2 \cdot \text{kg} \cdot \text{s}^{-2} = \text{N} \cdot \text{m}$
calorie	cal	4.184 J
kilocalorie	kcal	10^3 cal
Calorie (as in nutrition)	Cal	10^3 cal
British thermal unit	Btu	252 cal = 1054 J*

*Approximate definition.

PREDICTIONS OF THE KINETIC THEORY

(*a*) A mechanical argument based on Assumptions 1, 2, and 3 above shows that for a gas composed of *N* molecules,

$$PV = \frac{2}{3}N\left[\left(\frac{1}{2}mu^2\right)_{\text{avg}}\right]$$

(*b*) Using Assumption 4, the distribution of speeds over the assemblage of molecules is predicted in mathematical form known as the *Maxwell-Boltzmann* distribution. Figure 6-1 is the distribution for hydrogen and shows the plots of the fraction of molecules having velocities close to a given value, *u*, and as a function of *u* at two different temperatures. The *most probable velocity*, u_{mp}, is the maximum speed for that set of conditions. It is slightly smaller than the average velocity. Another velocity, slight larger than the u_{avg}, is the *root-mean-square speed*, u_{rms}, which is defined as that speed for which a molecule's kinetic energy would be equal to the average kinetic energy over the entire sample, which is represented by

$$\frac{1}{2}m(u_{\text{rms}})^2 = \left(\frac{1}{2}mu^2\right)_{\text{avg}}$$

For the Maxwell-Boltzmann distribution, recalling that raising to the 1/2 power is taking the square root:

$$u_{\text{mp}} = \left(\frac{2RT}{\mathsf{M}}\right)^{1/2} \qquad u_{\text{avg}} = \left(\frac{8RT}{\pi\mathsf{M}}\right)^{1/2} \qquad u_{\text{rms}} = \left(\frac{3RT}{\mathsf{M}}\right)^{1/2}$$

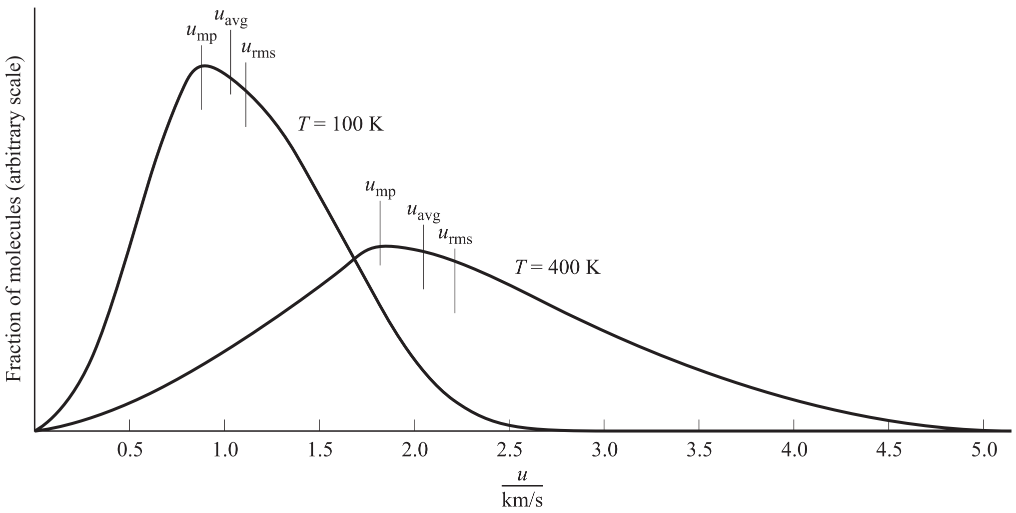


Fig. 6-1

(*c*) From the results of (*a*) and (*b*), using $N = nN_A$ and $N_A m = \mathsf{M}$, *we can derive the ideal gas law.*

$$PV = \frac{2N}{3}\left(\frac{mu_{\text{rms}}^2}{2}\right) = \frac{2nN_A}{3}\left(\frac{3mRT}{2\mathsf{M}}\right) = nRT$$

The agreement of this expression with the empirically determined (lab-determined) ideal gas law validates the important definition of temperature in Assumption 4 above.

(*d*) The frequency of molecular collisions with a particular area of the container wall is predicted by

$$Z = \frac{N_A P}{(2\pi \mathsf{M}RT)^{1/2}} \qquad \text{or} \qquad Z = \frac{N_A P}{\sqrt{2\pi \mathsf{M}RT}}$$

Imagine a small hole in the container. The rate at which a gas passes through that hole (effuses) into a vacuum is exactly the rate at which the molecules are predicted to collide with a portion of the wall the size of the hole. This means that the equation directly above can be used to describe the effusion rates of two gases at the same pressure and temperature by the ratio

$$\frac{Z_1}{Z_2} = \left(\frac{\mathsf{M}_2}{\mathsf{M}_1}\right)^{1/2} \qquad \text{or} \qquad \frac{Z_1}{Z_2} = \sqrt{\frac{\mathsf{M}_2}{\mathsf{M}_1}}$$

where M is the molar mass. This explains *Graham's law of effusion*, which is the experimental finding that the rates of effusion of gases at equal pressures and temperatures are inversely proportional to the square roots (1/2 power) of their densities. This can also be stated in terms of gas densities because the density of a gas is proportional to the molar mass.

(*e*) The inverse relationship discussed in (*d*) also applies in the areas of *diffusion*, *thermal conduction*, and *nonturbulent flow*, although the theory is not as exact in these phenomena as with Graham's law of effusion. A reason for the variation from the theoretical is that the consideration of the nature of intermolecular collisions must be made, which is a process involved in the understanding of some of the nonideal behavior of gases. Problem 6.68 looks at an important process in which one gas penetrates another on the way to equalization of concentrations throughout the mixture. Although the relationship is more accurate for effusion, the assumption will be made in this book that the relative diffusion rates of two gases are inversely proportional to the square roots of their molar masses.

Solved Problems

VOLUMES AND MOLAR MASSES OF GASES

6.1. Determine the approximate molar mass of a gas if 560 cm^3 weighs 1.55 g at S.T.P.

$$PV = nRT \qquad \text{and} \qquad n = \frac{g_{\text{sample}}}{\mathsf{M}} \qquad \text{results in} \qquad PV = \frac{g_{\text{sample}}}{\mathsf{M}}RT$$

$$\mathsf{M} = \frac{g_{\text{sample}}RT}{PV} = \frac{(1.55\,\text{g})\left(0.0821\dfrac{\text{L atm}}{\text{mol K}}\right)(273\,\text{K})}{(1\,\text{atm})(0.560\,\text{L})} = 62.0\,\text{g/mol}$$

Alternate Method

Molar mass = weight of 1 L at S.T.P. × number of liters at S.T.P. per mole

$$\text{Molar mass} = \left(\frac{1.55\,\text{g}}{0.560\,\text{L}}\right)(22.4\,\text{L/mol}) = 62.0\,\text{g/mol}$$

Of course, the second method is faster; but you have to have the data for S.T.P. and converting would definitely slow down the process.

6.2. At 18°C and 765 torr, 1.29 L of gas weighs 2.71 g. Calculate the approximate molar mass of the gas.

This problem is similar to 6.1 and is given to demonstrate a different approach. First, let us convert the gas data to moles.

$$PV = nRT \qquad \text{rearranges to} \qquad n = \frac{PV}{RT} \qquad \text{and} \qquad P = \frac{765}{760}\,\text{atm}; \qquad T = (18 + 173)\text{K} = 291\,\text{K}$$

$$n = \frac{\left(\dfrac{765}{760}\text{atm}\right)(1.29\,\text{L})}{\left(0.0821\dfrac{\text{L atm}}{\text{mol K}}\right)(291\,\text{K})} = 0.0544\,\text{mol}$$

Using this information ($n = 0.0544$ mol) and given the sample size (2.71 g), solve the problem.

$$\mathsf{M} = \frac{2.71\,\text{g}}{0.0544\,\text{mol}} = 49.8\,\text{g/mol}$$

Note that $\dfrac{(\text{L atm})}{(\text{mol K})}$ is used as the units of R. A commonly used alternative is $\text{L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

6.3. Determine the volume occupied by 4.0 g of oxygen at S.T.P. (molar mass of O_2 is 32).

The volume of 4.0 g O_2 at S.T.P. = number of moles in 4.0 g O_2 × standard molar volume.

$$V = \left(\frac{4.0\,\text{g}}{32\,\text{g/mol}}\right)(22.4\,\text{L/mol}) = 2.8\,\text{L}$$

6.4. What volume would 15.0 g Ar occupy at 90°C and 735 torr?

$$V = \frac{g_{\text{sample}}RT}{\mathsf{M}P} = \frac{(15.0\,\text{g})\left(0.0821\dfrac{\text{L atm}}{\text{mol K}}\right)(363\,\text{K})}{(39.9\,\text{g/mol})\left(\dfrac{735}{760}\,\text{atm}\right)} = 11.6\,\text{L}$$

6.5. Compute the approximate density of methane, CH_4, at 20°C and 5.00 atm. The molar mass of methane is 16.0.

$$PV = \left(\frac{g_{\text{sample}}}{\mathsf{M}}\right) RT \qquad \text{becomes} \qquad P = \left(\frac{g_{\text{sample}}}{V\mathsf{M}}\right) RT = \left(\frac{D}{\mathsf{M}}\right) RT$$

By rearrangement,

$$D = \frac{\mathsf{M}P}{RT} = \frac{(16.0\,\text{g/mol})(5.00\,\text{atm})}{\left(0.0821\dfrac{\text{L atm}}{\text{mol K}}\right)(293\,\text{K})} = 3.33\,\text{g/L}$$

Alternate Method

$$\text{Density} = \frac{\text{mass of 1 mol}}{\text{volume of 1 mol}} = \frac{16.0\,\text{g}}{(22.4\,\text{L})\left(\dfrac{1.00\,\text{atm}}{5.00\,\text{atm}}\right)\left(\dfrac{293\,\text{K}}{273\,\text{K}}\right)} = 3.33\,\text{g/L}$$

6.6. Dry air consists of approximately 21% O_2, 78% N_2, and 1% Ar by moles. (*a*) What is the average (i.e., "apparent") molar mass of dry air? (*b*) Calculate the density of dry air at S.T.P.

(*a*) One mole of air contains 0.21 mol O_2, 0.78 mol N_2, and 0.01 mol Ar. By incorporating the molecular masses, we can determine the apparent mass of one mole of dry air.

$$(0.21\,\text{mol}\,O_2)\left(32.0\frac{\text{g}\,O_2}{\text{mol}\,O_2}\right) + (0.78\,\text{mol}\,N_2)\left(28.0\frac{\text{g}\,N_2}{\text{mol}\,N_2}\right) + (0.01\,\text{mol Ar})\left(39.95\frac{\text{g Ar}}{\text{mol Ar}}\right) = 29\,\text{g air}$$

(*b*) The mass of 22.4 L of a gas at S.T.P. (assuming dry air) is its molar mass.

$$D = \frac{\text{molar mass}}{\text{molar volume}} = \frac{29\,\text{g}}{22.4\,\text{L}} = 1.29\,\text{g/L}$$

6.7. An organic compound had the following analysis: C = 55.8%, H = 7.03%, and O = 37.2%. A 1.500-g sample was vaporized and was found to occupy 530 cm^3 at 100°C and 740 torr. What is the molecular formula of the compound?

The approximate molar mass, calculated from the gas density data, is 89 g/mol. The empirical formula, calculated from the percentage composition data, is C_2H_3O with the empirical formula unit mass of 43.0. The exact molar mass must be (2)(43) = 86.0 g/mol since this is the only multiple of 43.0 (whole-number multiple) reasonably close to the approximate molecular formula of 89 g/mol. The molecule must be the equivalent of 2 empirical formulas: C_4H_6O.

Alternate Method

The percentage composition of each component, along with the molecular mass of 89 g/mol, can be used to determine the moles of atoms of each element in the compound.

$$n(\text{C}) = \frac{(0.558)(89\,\text{g})}{12.0\,\text{g/mol}} = 4.1 \qquad n(\text{H}) = \frac{(0.0703)(89\,\text{g})}{1.01\,\text{g/mol}} = 6.2 \qquad n(\text{O}) = \frac{(0.372)(89\,\text{g})}{16.0\,\text{g/mol}} = 2.1$$

These numbers approximate the numbers of atoms in the molecule with small deviations from values resulting from the *approximate* nature of the molar mass measurement. The molecular formula, $C_4H_6O_2$, is obtained without going through the intermediate evaluation of an empirical formula.

6.8. Mercury diffusion pumps may be used in the lab to produce a high vacuum. Cold traps are generally placed between the pump and the system to be evacuated. The traps cause the condensation of mercury vapor, which prevents diffusion back into the system. The maximum pressure of mercury that can exist in the system is the vapor pressure of mercury at the temperature of the cold trap. Calculate the number of mercury vapor molecules per unit of volume in a cold trap maintained at $-120°C$. The vapor pressure of mercury at this temperature is 10^{-16} torr.

$$\text{Moles per liter} = \frac{n}{V} = \frac{P}{RT} = \frac{(10^{-16}/760)\,\text{atm}}{\left(0.0821\,\dfrac{\text{L atm}}{\text{mol K}}\right)(153\,\text{K})} = 1.0 \times 10^{-20}\,\text{mol/L}$$

$$\text{Molecules/L} = (1.0 \times 10^{-20}\,\text{mol/L})(6.0 \times 10^{23}\,\text{molecules/mol}) = 6 \times 10^{3}\,\text{molecules/L or 6 molecules/mL}$$

REACTIONS INVOLVING GASES

In each of the four problems in this section, all gases are measured at the same temperature and pressure.

6.9. (*a*) What volume of hydrogen will combine with 12 L of chlorine to form hydrogen chloride? (*b*) What volume of hydrogen chloride will be formed?

We must write a balanced equation for this problem, which is

$$H_2(gas) + Cl_2(gas) \rightarrow 2HCl(gas)$$

(*a*) The equation shows that 1 molecule (or mole) H_2 reacts with 1 molecule (or mole) Cl_2 to form 2 molecules (or moles) HCl. By Avogadro's hypothesis, equal numbers of molecules of *gases* under the same conditions of temperature and pressure occupy equal volumes. Therefore, the equation also indicates that 1 volume of H_2 reacts with 1 volume of Cl_2 to form 2 volumes of HCl.

(*b*) Since 12 L of Cl_2 are used in the reaction and looking at the logic in part (*a*), $2 \times 12\,\text{L} = 24\,\text{L}$ of HCl are formed.

6.10. (*a*) What volume of hydrogen will react with 6 ft^3 of nitrogen to form ammonia? (b) What volume of ammonia will be produced?

$$N_2(gas) + 3H_2(gas) \rightarrow 2NH_3(gas)$$

(*a*) Applying Avogadro's hypothesis as in 6.9(*a*), since 1 volume of nitrogen (6 ft^3) requires 3 volumes of hydrogen for complete reaction, 3 volumes × 6 ft^3/volume = 18 ft^3 of hydrogen.

(*b*) One volume of nitrogen leads to the formation of 2 volumes of ammonia. Therefore, 6 ft^3 of nitrogen gas will form $2 \times 6 = 12$ ft^3 of ammonia gas.

6.11. Sixty-four liters of NO are mixed with 40 L of O_2 and allowed to react. What is the total volume of gas present after completion of the reaction?

$$2NO(gas) + O_2(gas) \rightarrow 2NO_2(gas)$$

The equation tells us that the volume of oxygen required is only half that of NO (2NO:O_2), $\frac{1}{2}(64) = 32$ L O_2 will be required and $(40 - 32)$ O_2 = 8 L O_2 will be in excess. The equation also tells us that the volume of NO_2 formed is the same as that of the NO reacted (2NO:2NO_2). The final volumes are 0 L NO + 8 L O_2 + 64 L NO_2 = 72 L gas.

6.12. (*a*) What volume of O_2 at S.T.P. is required for the complete combustion of 1 mol of carbon disulfide, CS_2? (*b*) What volumes of CO_2 and SO_2 are produced (also at S.T.P.)?

$$CS_2(liquid) + 3O_2(gas) \rightarrow CO_2(gas) + 2SO_2(gas)$$

(*a*) Under the conditions of S.T.P., 1 mole of gas takes up 22.4 liters. Since there are 3 moles of oxygen required to use up 1 mole of carbon disulfide,

$$\text{For the oxygen used:}(3\,\text{mol gas})(22.4\,\text{L/mol gas}) = 67.2\,\text{L } O_2.$$

(*b*) In the same manner as (*a*),

$$\text{For the carbon dioxide produced: } (1\text{ mol gas})(22.4\text{ L/mol gas}) = 22.4\text{ L } CO_2$$

$$\text{For the sulfur dioxide produced: } (2\text{ mol gas})(22.4\text{ L/mol gas}) = 44.8\text{ L } SO_2$$

6.13. How many liters of oxygen, at standard conditions, can be obtained from the heating of 100 g of potassium chlorate?

$$\underset{2\text{ moles}}{2KClO_3(solid)} \rightarrow 2KCl(solid) + \underset{3\text{ moles}}{3O_2(gas)}$$

Molar Method

Note that the equation tells us that 2 mol $KClO_3$ produce 3 mol O_2. As in previous chapters, the symbol n represents the number of moles and M the molecular mass.

$$n(KClO_3) = \frac{g_{\text{sample}}}{\mathsf{M}} = \frac{100\text{ g}}{122.6\text{ g/mol}} = 0.816\text{ mol } KClO_3$$

$$n(O_2) = \frac{3}{2}n(KClO_3) = \frac{3}{2}(0.816) = 1.224\text{ mol } O_2$$

Alternate Method

The equations shows that 2 mol $KClO_3$, 2(122.6) = 245.2 g, gives 3 mole volumes O_2, 3(22.4) = 67.2 L. Then, at S.T.P.,

	245.2 g $KClO_3$	gives	67.2 L O_2
	1 g $KClO_3$	gives	$\frac{67.2}{245.2}$ L O_2
and	100 g $KClO_3$	gives	$100\left(\frac{67.2}{245.2}\text{ L}\right) = 27.4\text{ L } O_2$

Note that neither method requires calculations involving the *mass* of oxygen formed.

6.14. What volume of oxygen can be obtained from the decomposition of 100 g $KClO_3$? The conditions of 18°C and 750 torr are held constant in this experiment.

This problem is identical with Problem 6.13, except that the volume of oxygen must be recalculated using conditions that are not standard.

$$\text{Volume at } 18^\circ\text{C and } 750\text{ torr} = (27.4\text{ L})\left[\frac{(273+18)\text{ K}}{273\text{ K}}\right]\left(\frac{760\text{ torr}}{750\text{ torr}}\right) = 29.6\text{ L } O_2$$

Alternate Method

When we are not concerned with S.T.P., we can calculate the volume directly from moles.

$$V = \frac{nRT}{P} = \frac{(1.224\text{ mol})\left(0.0821\ \frac{\text{L atm}}{\text{mol K}}\right)(291\text{ K})}{\frac{750}{760}\text{ atm}} = 29.6\text{ L } O_2$$

6.15. How many grams of zinc must react with sulfuric acid in order to obtain 500 cm^3 (0.5 L) of hydrogen at 20°C and 770 torr?

$$Zn(solid) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(gas)$$

Let us find the number of moles of hydrogen gas produced by using the *ideal gas law*.

$$n(H_2) = \frac{PV}{RT} = \frac{\left(\frac{770}{760}\text{ atm}\right)(0.500\text{ L})}{\left(0.0821\frac{\text{L atm}}{\text{mol K}}\right)(293\text{ K})} = 0.0211\text{ mol } H_2$$

We can now use dimensional analysis (factor-label method) to arrive at the answer to the problem using the mole ratio ($1\text{Zn}{:}1\text{H}_2$) from the balanced equation.

$$0.0211\ \text{mol H}_2 \times \frac{1\ \text{mol Zn}}{1\ \text{mol H}_2} \times \frac{65\ \text{g Zn}}{1\ \text{mol Zn}} = 1.38\ \text{g Zn}$$

6.16. A natural gas sample contains 84% CH_4, 10% C_2H_6, 3% C_3H_8, and 3% N_2, all determined by percent volume. If a series of catalytic reactions could be used for converting all the carbon atoms of the gas into butadiene, C_4H_6, with 100% efficiency, how much butadiene could be prepared from 100 g of the natural gas?

This problem starts out as an application of mole volume. If we had 100 moles of the mixture, then we would have 84 mol CH_4, 10 mol C_2H_6, 3 mol C_3H_8, and 3 mol N_2. We can calculate the amount of natural gas in 100 moles of the mixture by utilizing the molecular weights.

$$\begin{aligned}100\ \text{mol mixture} &= 84\ \text{mol CH}_4\left(16\ \frac{\text{g}}{\text{mol}}\right) + 10\ \text{mol C}_2\text{H}_6\left(30\ \frac{\text{g}}{\text{mol}}\right) + 3\ \text{mol C}_3\text{H}_8\left(44\ \frac{\text{g}}{\text{mol}}\right) + 3\ \text{mol N}_2\left(28\ \frac{\text{g}}{\text{mol}}\right)\\ &= 1860\ \text{g natural gas mixture}\end{aligned}$$

The number of moles of carbon in 100 mol mixture is $84(1) + 10(2) + 3(3) + 3(0) = 113$ mol C. Since 4 mol C gives us 1 mol C_4H_6, 54 g, 113 mol C provides us with

$$\left(\frac{113}{4}\ \text{mol}\right)(54\ \text{g/mol}) = 1530\ \text{g C}_4\text{H}_6$$

Then

$$1860\ \text{g natural gas yields } 1530\ \text{g C}_4\text{H}_6$$

and

$$100\ \text{g natural gas yields } \frac{100}{1860}(1530\ \text{g}) = 82\ \text{g C}_4\text{H}_6$$

6.17. A reaction for the combustion of SO_2 was prepared by opening a stopcock connecting two separate chambers. One of the chambers has a volume of 2.125 L and is filled at 0.750 atm with SO_2. The second chamber has the volume of 1.500 L filled at 0.500 atm with O_2. The temperature of both is 80°C. (*a*) What were the mole fraction of SO_2 in the mixture, the total pressure, and the partial pressures? (*b*) If the mixture were to be passed over a catalyst that promoted the formation of SO_3 and then was returned to the original two connected vessels, what were the mole fractions in the final mixture, and what was the final total pressure? Assume that the final temperature is 80°C and that the conversion of the SO_2 is complete to the extent of the availability of O_2.

(*a*)

$$n(\text{SO}_2) = \frac{PV}{RT} = \frac{(0.750\ \text{atm})(2.125\ \text{L})}{\left(0.0821\ \frac{\text{L atm}}{\text{mol K}}\right)(353\ \text{K})} = 0.0550\ \text{mol SO}_2$$

$$n(\text{O}_2) = \frac{PV}{RT} = \frac{(0.500\ \text{atm})(1.500\ \text{L})}{\left(0.0821\frac{\text{L atm}}{\text{mol K}}\right)(353\ \text{K})} = 0.0259\ \text{mol O}_2$$

Each mole fraction is evaluated by dividing the number of moles of the component by the total number of moles in the mixture. Let X be the symbol for mole fraction.

$$X(\text{SO}_2) = \frac{n(\text{SO}_2)}{n(\text{SO}_2) + n(\text{O}_2)} = \frac{0.0550\ \text{mol}}{(0.0550 + 0.259)} = \frac{0.0550}{0.0809} = 0.680$$

$$X(\text{O}_2) = \frac{0.0259}{0.0809} = 0.320$$

Note that the mole fraction is dimensionless (no units) and that the sum of the mole fractions is 1.

The total pressure before the reaction can be evaluated by using total volume ($2.125\,\text{L} + 1.500\,\text{L} = 3.625\,\text{L}$) and the total number of moles, $n = 0.0809$ mol.

$$P_{\text{total}} = \frac{nRT}{V} = \frac{(0.0809\,\text{mol})\left(0.0821\,\dfrac{\text{L atm}}{\text{mol K}}\right)(353\,\text{K})}{3.625\,\text{L}} = 0.647\,\text{atm}$$

Knowing the total pressure, the calculation of the partial pressure of each substance (X) in the mixture is computed by multiplying the respective mole fractions (X) by the total pressure. This statement can be proven by

$$\frac{P(\text{X})}{P_{\text{total}}} = \frac{n(\text{X})RT/V}{nRT/V} = \frac{n(\text{X})}{n} = x(\text{X}) \qquad \text{and} \qquad P(\text{X}) = x(\text{X})P_{\text{total}}$$

then

$$P(\text{SO}_2) = X(\text{SO}_2) \times P_{\text{total}} = (0.680)(0.647\,\text{atm}) = 0.440\,\text{atm SO}_2$$

$$P(\text{O}_2) = X(\text{O}_2) \times P_{\text{total}} = (0.320)(0.647\,\text{atm}) = 0.207\,\text{atm O}_2$$

The sum of the partial pressures, of course, must equal the total pressure.

(*b*) The chemical reaction for the equation is required for this part of the problem.

$$2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$$

All substances are gases under the experimental conditions. The number of moles of oxygen required is half the number of moles of sulfur dioxide; but this experiment had 0.0259 mol O_2, which was less than half of the mol SO_2 (0.0550 mol SO_2). This means that the oxygen is a limiting reactant and there is an excess of sulfur dioxide. The calculation of the O_2 is first, then that of the SO_2 used.

$$n(\text{O}_2) = 0.0259\,\text{mol O}_{21}$$

$$n(\text{SO}_2)\text{ used} = 2 \times n(\text{O}_2) = \left(2\,\frac{\text{mol SO}_2\text{ used}}{\text{mol O}_2}\right)(0.0259\,\text{mol O}_2) = 0.0518\,\text{mol SO}_2\text{ used (required)}$$

The amount of product, SO_3, will be the same amount as the SO_2 used, according to the balanced equation. Therefore, the amount of SO_3 produced will be 0.0518 mol, assuming a 100% efficient reaction. There would be 0.0032 mol SO_2 in excess (0.0550 original − 0.0518 used).

The amounts of gas on completion of the reaction (100% efficiency assumed) are 0.0032 mol SO_2, 0 mol O_2, and 0.0518 mol SO_3. On the basis of this information, we calculate the mole fractions of each.

$$X(\text{SO}_2) = \frac{n(\text{SO}_2)}{n(\text{SO}_2) + n(\text{SO}_3)} = \frac{0.0032\,\text{mol}}{(0.0032 + 0.0518)\,\text{mol}} = \frac{0.0032\,\text{mol}}{0.0550\,\text{mol}} = 0.058$$

$$X(\text{SO}_3) = \frac{n(\text{SO}_3)}{n(\text{SO}_2) + n(\text{SO}_3)} = \frac{0.0518\,\text{mol}}{(0.0032 + 0.0518)\,\text{mol}} = \frac{0.0518\,\text{mol}}{0.0550\,\text{mol}} = 0.942$$

The final total pressure is calculated on the basis of the total number of moles on completion of the reaction.

$$P_{\text{total}} = \frac{n_{\text{total}}RT}{V} = \frac{(0.0550\,\text{mol})\left(0.0821\,\dfrac{\text{L atm}}{\text{mol K}}\right)(353\,\text{K})}{3.625\,\text{L}} = 0.440\,\text{atm}$$

On the other hand, if we were to notice that the chemical equation tells us that the amount of SO_3 produced is the same as the amount of SO_2 used, then we can also realize that the final *total* pressure is the same as the initial *partial* pressure of SO_2. This happens because the only gases present at the end are SO_2 (excess amount) and SO_3. Further, the amount of SO_3 produced is exactly the amount of SO_2 used; there is no change in the total amount of gas present before and after the reaction as far as they are concerned. The difference in the final pressure is due to using up the oxygen; this means that the total pressure will be dropped by the amount of oxygen used—all of it.

KINETIC THEORY

6.18. (*a*) Show how the value of R, $8.3145\dfrac{\text{J}}{\text{mol K}}$, in $\dfrac{\text{L atm}}{\text{mol K}}$ can be derived from the value in SI units. (*b*) Express R in terms of calories.

(*a*)
$$R = 8.3145\,\frac{\text{J}}{\text{mol K}} = 8.3145\,\frac{\text{N m}}{\text{mol K}}$$

$$R = \left(8.3145\,\frac{\text{N m}}{\text{mol K}}\right)\left(\frac{1\text{ atm}}{1.013\times10^5\text{N}\cdot\text{m}^{-2}}\right)\left(\frac{10^3\text{dm}^3}{1\text{ m}^3}\right)\left(\frac{1\text{ L}}{1\text{ dm}^3}\right) = 0.0821\,\frac{\text{L atm}}{\text{mol K}}$$

(*b*)
$$R = \left(8.3145\frac{\text{J}}{\text{mol K}}\right)\left(\frac{1\text{ cal}}{4.184\text{ J}}\right) = 1.987\,\frac{\text{cal}}{\text{mol K}}$$

6.19. Calculate the root-mean-square velocity of H_2 at 0°C.

$$u_{\text{rms}} = \left(\frac{3RT}{\mathsf{M}}\right)^{1/2} = \left[\frac{3\left(8.3145\dfrac{\text{J}}{\text{mol K}}\right)(273\text{ K})}{\left(1.016\dfrac{\text{g}}{\text{mol}}\right)\left(\dfrac{1\text{ kg}}{1000\text{ g}}\right)}\right]^{1/2} = 1837\ (\text{J/kg})^{1/2}$$

$$u_{\text{rms}} = 1.84\times10^3\left(\frac{\text{kg}\cdot\text{m}^2/\text{s}^2}{\text{kg}}\right)^{1/2} = 1.84\times10^3\text{m/s}\quad\text{or}\quad 1.84\text{ km/s}$$

6.20. Calculate the relative rates of effusion of H_2 and CO_2 through a fine pinhole.

$$\frac{r(\text{H}_2)}{r(\text{CO}_2)} = \sqrt{\frac{\mathsf{M}(\text{CO}_2)}{\mathsf{M}(\text{H}_2)}} = \sqrt{\frac{44\text{ g/mol}}{2.0\text{ g/mol}}} = \sqrt{22} = 4.7$$

Supplementary Problems

VOLUMES, MOLAR MASSES, AND REACTIONS OF GASES

6.21. Let us assume that octane (C_8H_{18}) burns explosively (gasoline certainly can) and that rubbing alcohol (C_3H_7OH) does, too. Which will explode more violently on the basis of gas expansion on complete burning?

Ans. Octane will produce much more gas than the alcohol (34:14 on the mole basis), producing a more violent explosion.

6.22. If 200 cm^3 of a gas at S.T.P. weighs 0.268 g, what is its molar mass?

Ans. 30.0 g/mol

6.23. A design of a tank for holding nitrous oxide, N_2O, for automobile racing requires the choice of a material that will support the stress of 1500 g stored in a volume of 7.5 liters. The temperature is not expected to exceed 125°C. Calculate the stress (atm) to which the tank may be exposed.

Ans. 218 atm

6.24. What is the volume of 16 g of nitrous oxide, N_2O, at S.T.P.?

Ans. 8.1 L

6.25. What volume will 1.216 g of SO_2 gas occupy at 18°C and 755 torr?

Ans. 456 cm^3

6.26. A chemist had to determine the molar mass of a compound in the liquid state, but was concerned that it would decompose if heated. So he used a syringe to inject 0.436 grams of the liquid sample into a 5.00-L flask with argon at 17°C and connected an open-tube manometer. The liquid vaporized completely and the mercury in the manometer went from 16.7 mm to 52.4 mm. What is the molar mass of the compound?

Ans. 44.2 g/mol

6.27. Calculate the weight of 2.65 L of carbon dioxide gas at 34°C and 1.047 atm.

Ans. 4.84 g

6.28. Determine the density of H_2S gas at 27°C and 2.00 atm.

Ans. 2.77 g/L

6.29. What is the mass of 1 mole of a gas whose density at 40°C and 785 torr is 1.286 kg/m^3?

Ans. 32.0 g/mol

6.30. A large piece of magnesium, 20 kg, is accidentally dropped into a vat containing 500 liters of concentrated HCl solution. What will be the volume of hydrogen gas released (1 atm, 32°C)?

Ans. 2.1×10^4 L H_2

6.31. Phosgene, $COCl_2$, inhalation is suspected as a cause of death. Gas from the lungs was dried, the components separated and identified. A small sample of a puzzling component was placed in a 25-mL container which changed in weight from 18.6600 g to 18.7613 g. The temperature was stable at 24°C and the final pressure was 1 atm. Determine the molecular mass.

Ans. 99 u—this is close enough to phosgene's mass of 98.9164 u to be a candidate.

6.32. A collapsed balloon and its load weighs 216 kg. Calculate how many cubic meters of hydrogen gas is required so that the balloon is sufficiently inflated to launch it from a mountain top at -12°C and at a pressure of 628 torr. The density of air on the mountain is 1.11 g/L.

Ans. 210 m^3

6.33. One of the methods for estimating the temperature of the center of the sun is based on the ideal gas law. What is the calculated temperature if the sun's center is assumed to consist of gases whose average molar mass is 2.0, the density is 1.4×10^3 kg/m^3, and the pressure is 1.3×10^9 atm?

Ans. 2.3×10^7 K

6.34. A 100-cm^3 experimental chamber was sealed off at a pressure of 1.2×10^{-5} torr and 27°C. What is the number of gas molecules remaining in the tube?

Ans. 3.9×10^{13} molecules

6.35. Photochemical smog contains NO_2, the gas responsible for the "brown blanket" over larger cities. This gas can produce a *dimer* (two identical units chemically bonded) by the reaction, $2NO_2 \rightarrow N_2O_4$. If the reaction of 750 g NO_2 goes all the way to the right, what will be the pressure in a 10-L chamber at 42°C?

Ans. 21 atm

6.36. One of the important considerations of hydrogen as automotive fuel is its compactness. Compare the number of hydrogen atoms per cubic meter available in (*a*) hydrogen gas under a pressure of 14.0 MPa at 300 K; (*b*) liquid hydrogen at 20 K at a density of 70.0 kg/m^3; (*c*) the solid compound $DyCo_3H_5$, which has a density of 8200 kg/m^3 at 300 K, from which all of the hydrogen can be made available for combustion.

Ans. (*a*) 0.68×10^{28} atoms/m^3; (*b*) 4.2×10^{28} atoms/m^3; (*c*) 7.2×10^{28} atoms/m^3

6.37. A 28-L tank designed for storing compressed gas can hold no more than 15 atm pressure. (*a*) What number of moles of helium can that tank hold at standard temperature (0°C)? (*b*) What number of moles of helium can the tank hold at 140°F (60°C, the temperature of a car on a hot summer day)?

Ans. (*a*) 19 mol He at 0°C; (*b*) 12 mol He at 60°C

6.38. A plastic bottle is designed to hold 1 liter of carbonated beverage, but pressure is a problem. The air space above the beverage holds 100 mL volume and the bottle can support 7.5 atm of pressure. How much CO_2 can be in that space at room temperature (25°C) in moles and grams?

Ans. 0.030 mol or 1.3 g CO_2

6.39. An empty 1.5-ft^3 steel gas tank and its valve weighed 125 lb. The tank was filled with oxygen to 2000 lbf/in^2 absolute at 25°C. (*a*) What percent of the total weight of the full tank was O_2? Assume the ideal gas law applies. (*Note*: 1 atm = 14.7 lb/in^2.)

For parts (*b*), (*c*), and (*d*), note that pure oxygen gas is not necessarily the most compact source of oxygen for a confined fuel system because of the weight of the cylinder necessary to confine the gas. Other compact sources are hydrogen peroxide and lithium peroxide. The oxygen-yielding reactions are

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad 2Li_2O_2 \rightarrow 2Li_2O + O_2$$

(*b*) Rate 65% by weight solution of H_2O_2 in H_2O, and (*c*) rate pure Li_2O_2 in terms of % of total weight which is "available" oxygen. Neglect the weights of the containers. (*d*) Compare with (*a*).

Ans. (*a*) 12%; (*b*) 31%; (*c*) 35%; (*d*) Both (*b*) and (*c*) are more efficient than (*a*) on a weight % basis.

6.40. A 0.331-g sample of hydrated ammonium carbonate was placed in an evacuated 30.0 cm^3 pyrolysis tube rated at 45.0 atm. It was heated at 250°C until complete decomposition by

$$(NH_4)_2CO_3 \cdot H_2O \rightarrow 2NH_3 + CO_2 + 2H_2O$$

(*a*) Was there any liquid water in the tube? (*b*) Knowing that the vapor pressure of water at 250°C is 39.2 atm, did the tube explode?

Ans. (*a*) No, P(water) = 8.30 atm; (*b*) No, P(total) = 20.7 atm

6.41. An iron meteorite was analyzed for its isotopic argon constant. The amount of ^{36}Ar was 0.200 mm^3 (S.T.P.) per kilogram of meteorite. If each ^{36}Ar atom had been formed by a single cosmic event, how many such events must there have been per kilogram of meteorite?

Ans. 5.4×10^{15}

6.42. Three volatile compounds of a certain element have gaseous densities calculated back to S.T.P. as follows: 6.75, 9.56, and 10.08 kg/m^3. The three compounds contain 96.0%, 33.9%, and 96.4% of the element in question, respectively. What is the element's most probable atomic mass?

Ans. 72.6, although the data do not exclude 72.6/n, where n is a positive integer.

6.43. During short spaceflights, chemical absorbers can be used to remove space travelers' exhaled CO_2. Li_2O is very efficient in terms of absorbing capacity per unit weight. What is the absorption efficiency of pure Li_2O as stated in liters CO_2 (S.T.P.) per kilogram Li_2CO_3 reacting as below?

$$Li_2O + CO_2 \rightarrow Li_2CO_3$$

Ans. 752 L/kg

6.44. A mixture of methane, CH_4, and ethane, C_2H_6, exerted a pressure of 2.33 atm when confined within a reaction vessel at a fixed pressure and temperature. It was mixed with an excess of oxygen and burned completely to CO_2 and H_2O. After removing all the H_2O and excess oxygen, the CO_2 was returned to the vessel where its pressure was 3.02 atm, when measured at the same pressure and temperature as the original mixture. Calculate the mole fractions of the gases in the original mixture.

Ans. $X(CH_4) = 0.704$, $X(C_2H_6) = 0.296$

6.45. Exactly 500 cm^3 of a gas at S.T.P. weighs 0.581 g. The gas composition is C = 92.24% and H = 7.76%. Derive the molecular formula of the gas.

Ans. C_2H_2

6.46. A hydrocarbon has the composition of 82.66% carbon and 17.34% hydrogen. The density of the vapor is 0.2308 g/L at 30°C and 75 torr. Determine its molar mass and its molecular formula.

Ans. 58.2 g/mol, C_4H_{10}

6.47. How many grams of O_2 are contained in 10.5 L of oxygen measured over water at 25°C and 740 torr? The vapor pressure of water at 25°C is 24 torr.

Ans. 12.9 g

6.48. An empty flask open to the air weighed 24.173 g. The flask was filled with the vapor of an organic liquid and was sealed off at 100°C. At room temperature, the flask then weighed 25.002 g. The flask was then opened and filled with water at room temperature, after which it weighed 176 g. The barometric reading was 725 mm Hg. All weighings were taken at room temperature, which was 25°C. What is the molar mass of the organic vapor? Allow for the buoyancy of the air in the weighing of the sealed-off flask using 1.18 g/L for the density of air at 25°C and 1 atm.

Ans. 213 g/mol

6.49. A student decides that the proverbial "lead balloon" can be built and proceeds to the design stage. He assumes a spherical shape of radius r and a skin weight of 5.00 g/cm^2. The balloon is to be filled with helium at 25°C and 711 torr. At these conditions the density of air is 1.10 g/L. For a sphere of radius r, the surface (skin) area is $4\pi r^2$ and the volume is $4\pi r^3/3$. Calculate how large the radius must be to get the balloon off the ground and the final weight.

Ans. $r = 158$ m, weight $= 1.82 \times 10^7$ kg, including the skin and the helium

6.50. A 50-cm^3 sample of a hydrogen-oxygen mixture was placed in a gas buret at 18°C and confined at ambient pressure. A spark was passed through the sample so that the formation of water could go to completion. The resulting pure gas had a volume of 10 cm^3 at ambient pressure. What was the initial mole fraction of hydrogen in the mixture (*a*) if the residual gas after sparking was hydrogen? (*b*) if the residual gas was oxygen?

Ans. (*a*) 0.73; (*b*) 0.53

6.51. How much water vapor is contained in a cubic room 4.0 m along an edge if the relative humidity is 50% and the temperature is 27°C? The vapor pressure of water at 27°C is 26.7 torr. The relative humidity expresses the partial pressure of water as a percentage of the water vapor pressure.

Ans. 0.82 kg

6.52. A batch of wet clothes in a dryer contains 0.983 kg water. Assuming the air leaves the dryer saturated with water vapor at 48°C and 738 torr total pressure, calculate the volume of dry air at 24°C and 738 torr required to dry the clothes. The vapor pressure of water at 48°C is 83.7 torr.

Ans. 1.070×10^4 L

6.53. Ethane gas, C_2H_6, burns in air as indicated by the equation $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$. Determine the number of (*a*) moles CO_2 and of H_2O forms when 1 mol of C_2H_6 burned, (*b*) liters of O_2 required to burn 1 L of C_2H_6, (*c*) liters of CO_2 formed when 25 L of C_2H_6 are burned, (*d*) liters (S.T.P.) of CO_2 formed when 1 mole C_2H_6 is burned, (*e*) moles CO_2 formed when 25 L (S.T.P.) of C_2H_6 are burned, and (*f*) grams of CO_2 formed when 25 L (S.T.P.) of C_2H_6 are burned.

Ans. (*a*) 2 mol CO_2, 3 mol H_2O; (*b*) 3.5 L; (*c*) 50 L; (*d*) 44.8 L; (*e*) 2.23 mol; (*f*) 98.2 g

6.54. Pure nitrogen can be prepared by the decomposition in aqueous solution of ammonium nitrite.

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

If 56.0 mL of N_2 were collected over water at 42°C and a total pressure of 778 torr, what mass of NH_4NO_2 must have been decomposed? The vapor pressure water at 42°C is 61 torr.

Ans. 0.131 g

6.55. CO_2 can be collected over water; however, since CO_2 is very soluble in water and reacts with it, the water must be saturated with CO_2. A volume of 372 mL gas are collected over CO_2-saturated water. The conditions are 1.001 atm and 23.40°C. The CO_2 is obtained by the reaction below. What mass of $CaCO_3$ decomposed? (Vapor pressure of water at 23.40°C is 21.58 mm Hg.)

$$CaCO_3(s) + 2HCl(aq) = CaCl_2(aq) + CO_2(g) + H_2O(l)$$

Ans. 1.50 g $CaCO_3$

6.56. Lithium reacts with hydrogen to produce the hydride, LiH. Sometimes the product is contaminated with unreacted lithium metal. The extent of the contamination can be measured by measuring the amount of hydrogen gas generated by reacting a sample with water.

$$LiH + H_2O \rightarrow LiOH + H_2$$
$$2Li + 2H_2O \rightarrow 2\,LiOH + H_2$$

A 0.205-g sample of contaminated LiH yielded 561 mL of gas measured over water at 22°C and a total pressure of 731 torr. Calculate the percent by weight of lithium metal in the sample. The vapor pressure of water at 22°C is 20 torr.

Ans. 37%

6.57. A mixture of 5.00 g of water, 5.00 g of methanol (CH_3OH), and 5.00 g of ethanol (C_2H_5OH) was put into a large sealed vessel that had been previously evacuated. The vessel was heated until all traces of liquid had evaporated. If the total pressure was 2.57 atm, what was the partial pressure of the ethanol?

Ans. 0.514 atm

6.58. Fifty grams of aluminum are to be treated with a 10% excess of H_2SO_4.

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

(*a*) What volume of concentrated sulfuric acid (density of 1.80 g/cm^3) containing 96.5% H_2SO_4 by weight must be taken? (*b*) What volume of hydrogen would be collected over water at 20°C and 785 torr? The vapor pressure of water at 20°C is 17.5 torr.

Ans. (*a*) 173 cm^3; (*b*) 66.2 L

6.59. A 0.750-g sample of solid benzoic acid, $C_7H_6O_2$, was placed in a 0.500-L pressurized reaction vessel filled with O_2 at 10.0 atm pressure and 25°C. The benzoic acid was burned completely to water and CO_2. What were the final mole fractions of CO_2 and H_2O vapor in the resulting gas mixture brought to the initial temperature? The vapor pressure of water at 25°C is 23.8 torr. Neglect both the volume occupied by nongaseous substances and the solubility of CO_2 in water. The water pressure in the gas phase cannot exceed the vapor pressure of water, so most of the water is condensed to the liquid.

Ans. $X(CO_2) = 0.213$, $X(H_2O) = 0.0032$

6.60. Two gases in adjoining vessels were brought into contact by opening a stopcock between them. One vessel measured 0.250 L and contained NO at 800 torr and 220 K; the other measured 0.100 L and contained O_2 at 600 torr and 220 K. The reaction to form N_2O_4 as a solid exhausted the limiting reactant completely. (*a*) Neglecting the vapor pressure of N_2O_4, what was the pressure and composition of the gas remaining at 220 K after completion of the reaction? (*b*) What weight of N_2O_4 was formed?

Ans. (*a*) 229 torr NO; (*b*) 0.402 g N_2O_4

6.61. The industrial production of ammonia by use of natural gas feedstock can be represented by the following simplified set of reactions:

$$(1) \qquad CH_4 + H_2O \rightarrow CO + 3H_2$$
$$(2) \qquad 2CH_4 + O_2 \rightarrow 2CO + 4H_2$$
$$(3) \qquad CO + H_2O \rightarrow CO_2 + H_2$$
$$(4) \qquad N_2 + 3H_2 \rightarrow 2NH_3$$

By assuming (i) that only the above reactions take place, plus the chemical absorption of CO_2, (ii) that natural gas consists of only CH_4, (iii) that air consists of 0.80 mole fraction N_2 and 0.20 mole fraction O_2, and (iv) that the ratio of conversion of CH_4 by processes (*1*) and (*2*) is controlled through admitting oxygen for reaction (*2*) by adding just enough air so that the mole ratio of N_2 to H_2 is exactly 1:3, consider the overall efficiency of a process in which 1200 m^3 (S.T.P.) of natural gas yields 1.00 metric tons of NH_3. (*a*) How many moles of NH_3 would be formed from each mole of natural gas if there were to be the complete conversion of natural gas subject to the stated assumptions? (*b*) What percentage of the maximum yield calculated in (*a*) is the actual yield?

Ans. (*a*) 2.29 mol NH_3/mol CH_4; (*b*) 48% yield

KINETIC THEORY

6.62. Calculate the ratio of (*a*) u_{rms} to u_{mp} and (*b*) u_{avg} to u_{mp}.

Ans. (*a*) 1.22; (*b*) 1.13

6.63. At what temperature do N_2 molecules have the same average speed as He atoms at 300 K?

Ans. 2100 K

6.64. At what temperature would the most probable speed of CO molecules be twice that at 0°C?

Ans. 819°C

6.65. Two gases were introduced into a 3-meter glass tube, NH_3 from the right and an unknown from the left. When the two met, a white smoke appeared and deposited inside the tubing a distance of 2.1 from the right end. (*a*) What is the molecular mass of the unknown? (*b*) Make a proposal as to the unknown's formula.

Ans. (*a*) 36 g/mol; (*b*) The mass is very close to that of HCl, 36.46

6.66. Two toxic gases are placed in an argon-filled tube. The relative rates for the travel of the tube are 0.80 for #1 and 1.0 for #2. The first gas is known to be hydrogen bromide, HBr, and the second is suspected to be diborane, B_2H_6, cyanogen chloride, ClCN, or cyanogen, $(CN)_2$. Which is the second gas most likely to be?

Ans. Cyanogen, $(CN)_2$, is the closest with cyanogen chloride, ClCN, at 0.87:1.

6.67. What is the ratio of the average molecular kinetic energy of UF_6 to that of He, both at 300 K?

Ans. 1.000

6.68. What is the kinetic energy of a mole of CO_2 at 400 K (*a*) in kJ and (*b*) in kcal?

Ans. (*a*) 4.99 kJ; (*b*) 1.192 kcal (Cal)

6.69. Uranium isotopes have been separated by taking advantage of the different rates of diffusion of the two isotopic forms of UF_6. One form contains uranium of atomic mass 238 and the other of atomic mass 235. What are the relative rates of diffusion of these two molecules if Graham's law applies?

Ans. UF_6 with ^{235}U is faster by a factor of 1.004.

6.70. A gas sample is suspected to be HCN, H_2S, or CO. The sample is mixed with N_2; the mixture is placed at one end of a tube containing only argon. It is determined that nitrogen arrives at the other end of the tube 1.1 times faster than the unknown. Which is the most likely formula for the unknown gas?

Ans. H_2S

6.71. The pressure of a vessel that contained pure oxygen dropped from 2000 torr to 1500 torr in 47 minutes as the oxygen leaked through a small hole into a vacuum. When the same vessel was filled with another gas, the pressure dropped from 2000 torr to 1500 torr in 74 minutes. What is the molar mass of the second gas?

Ans. 79 g/mol

6.72. A large cylinder of helium filled at 2000 lbf/in^2 has a small thin orifice through which helium escaped into an evacuated space at the rate of 3.4 millimoles per hour. How long would it take for 10 millimoles of CO to leak through a similar orifice if the CO were confined at the same pressure?

Ans. 7.8 hours

6.73. Calculate the average speed of a nitrogen molecule in air at room temperature (25°C). *Hint*: If you use SI units for R and for the molar mass, u will come out in m/s.

Ans. 475 m/s

6.74. How does the average speed of a nitrogen molecule in air compare to that of an oxygen molecule in air? (Air is approximately 20% oxygen and 80% nitrogen by moles.)

Ans. The N_2 molecules move at 1.07 times the speed of the O_2 molecules (7% faster).

6.75. You learned that in a mixture each gas exerted a partial pressure in proportion to its mole fraction. Yet, in a box of air the average N_2 molecule, because of its greater speed, hits the walls more frequently than the average

O_2 molecule. This suggests that nitrogen might contribute more than 80% of the pressure. Explain the apparent discrepancy.

Ans. Although the average O_2 molecule collides with the wall less frequently (by a factor of 1/1.07), it carries a momentum (mu) which is 1.07 times greater than that of the average N_2 molecule (see Problem 6.74). The force of an impact depends on momentum.

CHAPTER 7

Thermochemistry

HEAT

Of all of the forms of energy, heat can be considered as the most basic. The other forms of energy, such as chemical, light, radio, and electrical, tend to be transformed into heat by natural processes. When any energy type is converted into heat or when heat is converted into another type of energy, there is no loss in the total amount of energy. Additionally, the amount of heat energy necessary to raise the temperature of a substance is exactly the same as the energy lost when the substance cools to the original temperature. And the amount of energy necessary for a physical state change, such as melting or becoming a gas, is the same as the energy lost in the reverse process (solidification or liquefaction).

The concepts mentioned above all lead to the measurement of energy, energy types, energy conversions, and the effects of the gains and losses of energy. The units most commonly used are listed in Table 6-1. The use of the SI unit, the joule, emphasizes the interconvertibility of the various forms of energy. Chemists have long used the calorie and the kilocalorie (Calorie), but the joule and the kilocalorie have become the preferred units. Engineers are the principal users of the Btu.

HEAT CAPACITY

The *heat capacity* of a body is the amount of heat required to raise the temperature of that body 1 K (1°C). For pure substances, it is most convenient to refer to quantities of *molar heat capacity* (heat capacity per mole) and, as discussed above, the *specific heat capacity* or, more commonly, the *specific heat* (heat capacity per unit of mass). As an example, the average specific heat of water is

$$1.00\,\text{cal/g}\cdot\text{K} = 4.184\,\text{J/g}\cdot\text{K} \qquad \text{or} \qquad 1.00\,\text{kcal/kg}\cdot\text{K} = 4.184\,\text{kJ/kg}\cdot\text{K}$$

[*Note*: The *k*'s (×1000) will cancel]

Using these data for water, the molar heat capacity is 18.02 cal/mol · K (approximately 75.40 J/mol · K). Note that the deviations from this average are all less than 1 percent between the freezing and boiling points. The point being made is that the heat capacity may depend (slightly) on temperature, but is a reasonably stable value making it possible to consider heat capacity as a constant, as it is in this book.

CALORIMETRY

The amount of heat energy entering or leaving a substance undergoing a temperature change can be measured. The relationship for a body under consideration is

$$\text{Heat exchange} = (\text{heat capacity}) \times (\text{temperature change})$$

The heating or cooling of a body of matter of known heat capacity can be used in *calorimetry*, the measurement of quantities of heat. Conversely, given all of the information about a substance except the heat capacity (two of the three variables), it can be calculated by the application of the above relationship.

ENERGY AND ENTHALPY

When a system absorbs heat, part of the absorbed energy may be used for doing work. Examples of work in this context are accelerating an automobile, compressing a gas, charging a battery, and changing water from a liquid to a gas. Part of the total amount of energy within a system is associated with rearrangements of the atoms that occur in chemical reactions, the energy of interactions among atoms and molecules, and the energy associated with simply having a temperature (any temperature above absolute zero). This stored portion is known at the *internal energy*, E. The amount of heat absorbed by any system undergoing a modification, such as an increase in temperature, a change in physical state, or a chemical reaction, depends somewhat on the conditions under which the process occurs. As an example: The amount of heat absorbed is exactly equal to the increase in E if no work is done by the system. This would be the case in an ordinary chemical reaction, not linked to a battery, carried out in a closed reactor vessel so that no expansion against the outside atmosphere occurred. The change in E can be represented by ΔE. (Delta, Δ, is the mathematical symbol representing a change. ΔE is the difference in E accompanying a process, defined as the final value of E minus the initial value.)

Most of the chemical reactions run in laboratory courses are to be performed in open systems. This means that there won't be a build-up of pressure and some work will be done by the reacting system on the surroundings or, possibly, by the surroundings on the system. In such cases, the principle of conservation of energy requires that the amount of heat shifted must adjust itself to provide for the small, but significant, amount of this work. A new function, the *enthalpy*, H, can be defined which is related simply to the heat flow in an open or constant-pressure vessel by the definition, $H = E + PV$. The amount of heat absorbed (or released) in a constant-pressure process is exactly equal to ΔH, the increase (or decrease) in H.

In summary, if q is the amount of heat **absorbed** by the system from its surroundings,

$$q \text{ (at constant volume)} = \Delta E$$
$$q \text{ (at constant pressure)} = \Delta H$$

These equations are exact so long as they are not in use by work-generating devices, such as batteries, motors, and the like. Any of the terms in these equations may have either sign (+ or −). The process can be *exothermic*, one for which q is negative, where heat is being lost from the system. An *endothermic* process is one for which q is positive, indicating that heat is being taken up by the system. If the system under investigation is neither exothermic nor endothermic, the system is at equilibrium with the quantitative value zero (0). Most of the thermochemical problems in this book will be looking at H. Even though we may not know the absolute value of ΔE or ΔH, the above equations provide the experimental basis for measuring changes in these functions.

ENTHALPY CHANGES FOR VARIOUS PROCESSES

Change of temperature

If a substance of heat capacity, C, is heated or cooled through a temperature interval ΔT,

$$q = C\Delta T$$

assuming (as throughout this book) that C is independent of temperature. Subscripts are often used to designate a heat capacity measured at constant pressure, C_p, and at constant volume, C_v. Using C_p,

$$\Delta H = C_p \Delta T$$

The quantities C and H are *extensive*, meaning that they are proportional to the amount of material involved in the process or reaction. We choose to let c, c_p, and c_v represent specific heat capacities with the lower case symbol, w, for the sample's mass. Then,

$$C = cw$$

Where the subscript is omitted in the problems in this book, C_p (constant pressure) is implied. Further, note that, depending on the author, symbols often used for specific heat are c, C, C_s, SH, or s.

Change of phase of a substance

The heat that must be absorbed to melt a substance may be called the *latent heat of fusion* or, in the shortened form, the *heat of fusion*. For the melting of ice at 0°C, for example, the process may be written as

$$\mathrm{H_2O}(s) \rightarrow \mathrm{H_2O}(l) \qquad \text{at } 0°\text{C, 1 atm } q(\text{fusion}) = 80 \text{ cal/g}$$

Just as (*gas*) or (*g*) in Chapter 6 referred to the gaseous state, (*s*) refers to the solid state and (*l*) to the liquid state.

$$\Delta H = q(\text{fusion}) = (80 \text{ cal/g})(18.0 \text{ g/mol}) = 1.44 \text{ kcal/mol H}_2\text{O} \qquad \text{or} \qquad 6.02 \text{ kJ/mol H}_2\text{O}$$

There is a *latent heat of vaporization* (shortened to *heat of vaporization*), ΔH(vaporization), carried out at constant temperature and pressure. The latent heat of vaporization of water at 100°C and 1 atm is 540 cal/g or 9.72 kcal/mol (40.7 kJ/mol).

There is a ΔH for the process of sublimation, called the *latent heat of sublimation* (*heat of sublimation*). Sublimation is the conversion from the solid state to the gaseous physical state, skipping the liquid state. Elemental iodine, I_2, and CO_2 are substances that sublime at 1 atm pressure.

Chemical reaction

There is a change in enthalpy that accompanies a chemical reaction. The ΔH_f° is the *standard heat of formation*, the enthalpy change that occurs when one mole of a substance is formed from its component elements, as shown below.

$$\mathrm{C(graphite)} + \mathrm{O_2}(g) \rightarrow \mathrm{CO_2}(g) \qquad \Delta H_f^{\circ} = -393.51 \text{ kJ}$$

$$\mathrm{H_2}(g) + \mathrm{I_2}(s) \rightarrow 2\mathrm{HI}(g) \qquad \Delta H = +52.72 \text{ kJ}$$

In the first reaction, 393.51 kJ are *liberated* (exothermic reaction) when 1 mol of gaseous CO_2 is formed from graphite and oxygen. When 2 mol HI are formed from gaseous hydrogen and solid iodine, there are 52.72 kJ *absorbed* (endothermic reaction). In the case of the second reaction, the standard heat of formation is +26.36 kJ/mol HI formed; the total amount of energy involved in the reaction as written is twice the standard heat of formation because there were two moles of product formed. The reason why ΔH is the symbol instead of ΔH_f° is that the reaction does not address the formation of one mole of product; therefore, ΔH_f°, which is calculated on a per-mole basis, is not an appropriate symbol for the reaction. Further, notice that the $^{\circ}$ is used in ΔH_f° and with other factors (S°, ΔG_f°, or ΔE°) to indicate the standard condition of pressure, 1 atm (1 bar), usually 25°C and, for dissolved substances, of concentration 1 molal (refer to Chapter 12). For easy reference, selected standard heats of formation for selected substances are located in Table 7-1; however, notice that there are no elements listed in the table.

Table 7-1 Standard Enthalpies of Formation at 25°C

Substance	ΔH_f°/kcal · mol^{-1}	ΔH_f°/kJ · mol^{-1}	Substance	ΔH_f°/kcal · mol^{-1}	ΔH_f°/kJ · mol^{-1}
$Al_2O_3(s)$	−400.50	−1675.7	$HNO_3(l)$	−41.61	−174.10
$B_2O_3(s)$	−304.20	−1272.8	$H_2O(g)$	−57.80	−241.81
$Br(g)$	+26.73	+111.84	$H_2O(l)$	−68.32	−285.83
C (*diamond*)	+0.45	+1.88	$H_2O_2(l)$	−44.88	−187.8
$CF_4(g)$	−220.9	−924.7	$H_2S(g)$	−4.93	−20.6
$CH_3OH(g)$	−47.96	−200.7	H_2S (*aq,undiss.*)	−9.5	−39.7
$C_9H_{20}(l)$	−65.85	−275.5	$I_2(g)$	+14.92	+62.4
$(CH_3)_2N_2H_2(l)$	+13.3	+55.6	$KCl(s)$	−104.42	−436.9
$C(NO_2)_4(l)$	+8.8	+36.8	$KClO_3(s)$	−95.06	−397.7
$CO(g)$	−26.42	−110.53	$KClO_4(s)$	−103.6	−433.5
$CO_2(g)$	−94.05	−393.51	$LiAlH_4(s)$	−24.21	−101.3
$CaC_2(s)$	−14.2	−59.4	$LiBH_4(s)$	−44.6	−186.6
$CaO(s)$	−151.6	−634.3	$Li_2O(s)$	−143.1	−598.7
$Ca(OH)_2(s)$	−235.80	−986.6	$N_2H_4(l)$	+12.10	+50.63
$CaCO_3(s)$	−288.5	−1206.9	$NO(g)$	+21.45	+89.75
$ClF_3(l)$	−45.3	−190	$NO_2(g)$	+8.60	+35.98
$Cl^-(aq)$	−39.95	−167.16	$N_2O_4(g)$	+2.19	+9.16
$Cu^{2+}(aq)$	+15.49	+64.8	$N_2O_4(l)$	−4.66	−19.50
$CuSO_4(s)$	−184.36	−771.36	$O_3(g)$	+34.1	+142.7
$Fe^{2+}(aq)$	−21.3	−89.1	$OH^-(aq)$	−54.97	−229.99
$Fe_2O_3(s)$	−197.0	−824.2	$PCl_3(l)$	−76.4	−319.7
$FeS(s)$	−23.9	−100.0	$PCl_3(g)$	−68.6	−287.0
$H^+(aq)$	0.0	0.0	$PCl_5(g)$	−89.6	−374.9
$HBr(g)$	−8.70	−36.38	$POCl_3(g)$	−133.48	−558.48
$HCl(g)$	−22.06	−92.31	$SO_2(g)$	−70.94	−296.81
$HF(g)$	−64.8	−271.1	$SO_3(g)$	−94.58	−395.72
$HI(g)$	+6.30	+26.36	$Zn^{2+}(aq)$	−36.78	−153.89

Although there is a standard heat of formation for compounds, the standard heat of formation for elements in their ground state at 25°C and 1 atm is taken to be zero. For example, the standard state of H_2, O_2, Cl_2 or N_2 is gaseous; Fe, Na, I_2, or Cr is solid; and Br_2, Hg, or Cs is liquid—zero (0) is the standard heat of formation for these substances. As a point of interest, the standard state of carbon is graphite, not diamond (heat of formation = +0.45 kcal/mol)!

The standard state had been calculated at 1 atm for many decades before it was changed to 1 bar. Because of this, most available tables are based on 1 atm, which is very close to 1 bar. Fortunately, ΔH is not strongly dependent on pressure, so the numerical values show little or no differences, and any which appear are small enough to be ignored for most purposes.

RULES OF THERMOCHEMISTRY

The internal energy and the enthalpy of a system depend on the *state* of the system under specific conditions of temperature and pressure. As an example, recall from Chapter 6 that the kinetic energy contribution to E for an ideal gas is uniquely determined by the temperature. Further, when there is a change in a system, ΔE and ΔH depend only on the original and final states, not the path taken between them. This path-independence implies two important rules of thermochemistry.

1. ΔE and ΔH for processes that are the reverse of each other have the same magnitude (number), but have opposite signs.

EXAMPLE 1 For melting ice: ΔH for the fusion of ice is 1440 cal/mol, since it is found experimentally that 1440 cal are absorbed in the melting of 1 mol at constant temperature, 273 K, and at constant pressure, 1 atm. For freezing water: The ΔH for freezing is -1440 cal/mol because this amount of heat must be lost from the water to the surrounding in order to freeze. (*Note*: Energy in = energy out.)

2. If a process can occur in successive steps, ΔH for the overall process is equal to the sum of the enthalpy changes for the individual steps. This rule is *Hess' law* or, more formally, *Hess' law of constant heat summation*.

EXAMPLE 2 We cannot measure accurately the heat given off when C burns to CO because the reaction (combustion) cannot be stopped at CO with no CO_2 being produced. However, we can accurately measure the heat given off when C burns to produce CO_2 (we use an excess of O_2), which is 393.5 kJ/mol CO_2. We can also measure the heat given off when CO burns to CO_2 (283.0 kJ per mol CO_2). Using this information, we can calculate the enthalpy change for the burning of C to CO by recognizing that when we add thermochemical equations, the enthalpies are also additive. The same treatment applies if equations are subtracted. *Balanced equations are an absolute necessity.*

$$2\mathrm{C(graphite)} + 2\mathrm{O}_2(g) \rightarrow 2\mathrm{CO}_2(g) \qquad \Delta H = (2\ \mathrm{mol})(-393.5\ \mathrm{kJ/mol}) = -787.0\ \mathrm{kJ}$$

$$\cancel{2\mathrm{CO}(g) + \mathrm{O}_2(g) \rightarrow 2\mathrm{CO}_2(g) \qquad \Delta H = (2\mathrm{mol})(-283.0\mathrm{kJ/mol}) = -566.0\mathrm{kJ}}$$

$$\text{reversed} \qquad 2\mathrm{CO}_2(g) \rightarrow 2\mathrm{CO}(g) + \mathrm{O}_2(g) \qquad \Delta H = \qquad = +566.0\ \mathrm{kJ}$$

We reverse the second equation so that the CO is on the right (crossing out the original equation), but that also cancels the $2CO_2$ and one of the oxygen molecules (cross them out). Also, when we reverse the chemical equation, we reverse the sign associated with the ΔH of the second equation of +566.0 kJ.

$$2\mathrm{C(graphite)} + \mathrm{O}_2(g) \rightarrow 2\mathrm{CO}(g) \qquad \Delta H = -787.0 + 566.0 = -221.0\ \mathrm{kJ}$$

Since there are 2 mol CO produced, then the heat of formation for CO is calculated by

$$\Delta H_f^{\mathrm{o}} = (-221.0\ \mathrm{kJ})/(2\ \mathrm{mol\ CO}) = -110.5\ \mathrm{kJ/mol\ CO}$$

EXAMPLE 3 The heat of sublimation of a substance (gas → solid and vice verse) is the sum of the heats of fusion and vaporization of that substance *at the same temperature*.

EXAMPLE 4 Hess' law provides us with the application based on the following:

> *The enthalpy change of any reaction is equal to the sum of the enthalpies (heats) of formation of all the products minus the sum of the enthalpies of formation of all of the reactants, each ΔH_f^{o} being multiplied by the number of moles of substance in the balanced equation.*

Let us look at a reaction and perform the calculations on the basis of the heats (enthalpies) of formation.

$$\mathrm{PCl}_5(g) + \mathrm{H}_2\mathrm{O}(g) \rightarrow \mathrm{POCl}_3(g) + 2\mathrm{HCl}(g)$$

We are to write the reactions reflecting the formation of the compounds involved from their elements. Further, we must do so conforming with the units from Table 7-1, which are written in a per-mole basis.

$$\begin{array}{lrl}
(1) & \mathrm{P(white)} + \tfrac{3}{2}\mathrm{Cl}_2(g) + \tfrac{1}{2}\mathrm{O}_2(g) \rightarrow \mathrm{POCl}_3(g) & \Delta H^{\mathrm{o}} = -558.5\ \mathrm{kJ} \\
(2) & \mathrm{H}_2(g) + \mathrm{Cl2}(g) \rightarrow 2\mathrm{HCl} & \Delta H^{\mathrm{o}} = -184.6\ \mathrm{kJ} \\
(3) & \mathrm{PCl}_5(g) \rightarrow \mathrm{P(white)} + \tfrac{5}{2}\mathrm{Cl}_2(g) & \Delta H^{\mathrm{o}} = +374.9\ \mathrm{kJ} \\
(4) & \mathrm{H}_2\mathrm{O}(g) \rightarrow \mathrm{H}_2(g) + \tfrac{3}{2}\mathrm{O}_2(g) & \Delta H^{\mathrm{o}} = +241.8\ \mathrm{kJ} \\
\hline
\text{Summation reaction} & \mathrm{PCl}_5(g) + \mathrm{H}_2\mathrm{O}(g) \rightarrow \mathrm{POCl}_3(g) + 2\mathrm{HCl}(g) & \Delta H = -126.4\ \mathrm{kJ}
\end{array}$$

Note that two of the reactions (*2*) and (*3*) had to be reversed in order to produce the summation reaction. The use of the fractional coefficients is for convenience so that the chlorine and the oxygen will cancel, but also so that we are matching the equation we were given in the problem statement above. The use of fractions in the balancing of equations is common, especially when balancing thermochemical reactions and electrochemical reactions (Chapter 19).

COMMENT ON THERMOCHEMICAL REACTIONS

Often times, it looks as though we study concepts, but there are no real-world applications that hit home. Example 4 gives us a piece of information that does have a useful application. Suppose you had to open a container of PCl_5 and a room had a high humidity. The water vapor mixing with the PCl_5 might just cause the highly exothermic reaction discussed. And if this reaction progresses at a high rate, the results could be very dangerous—a fire or even an explosion; at the very least, there would be hydrogen chloride gas in the air you'd be breathing. Hydrogen chloride gas is very irritating to your lungs and in a high enough concentration (not very high at all), hydrogen chloride will damage your lungs and can kill.

The calculation of the ΔH is important also because it is, along with ΔG (Chapter 16), useful in determining whether or not a reaction is spontaneous and provides information about reactions that are at equilibrium. Further, although ΔH has been calculated in this chapter for standard states and at basically room temperature and 1 atm, it can be calculated under other circumstances, as is done in Physical Chemistry and other upper-level chemistry courses.

Solved Problems

HEAT CAPACITY AND CALORIMETRY

7.1. (*a*) How many joules are required to heat 100 g of copper ($c = 0.389$ J/g · K) from 10°C to 100°C? (*b*) The same quantity of heat as in (*a*) is added to 100 g of aluminum ($c = 0.908$ j/g · K) at 100°C. Which gets hotter, the copper or aluminum?

(*a*)
$$\Delta H = C\Delta T = (0.389 \text{ J/g} \cdot \text{K})(100 \text{ g})[(100 - 10)\text{K}] = 3500 \text{ J}$$

(*b*) Since the specific heat of copper is less than that of aluminum, less heat is required to raise the temperature of a mass of copper by 1 K than is required for an equal mass of aluminum; the copper gets hotter.

7.2. One kilogram of anthracite coal when burned evolves about 30,500 kJ. Calculate the amount of coal required to heat 4.0 kg of water from 20°C to the boiling point at 1 atm pressure, assuming no loss of heat in the process.

For the heating of the water:

$$\Delta H = C\Delta T = (4.184 \text{ kg} \cdot \text{K})(4.0 \text{ kg})[(100 - 20)\text{K}] = 1339 \text{ kJ}$$

$$\text{Amount of coal required} = \frac{1339 \text{ kJ}}{30{,}500 \text{ kJ/kg}} = 0.044 \text{ kg} = 44 \text{ g}$$

7.3. A steam boiler is made of steel and weighs 900 kg. The boiler contains 400 kg of water. Assuming that 70% of the heat is delivered to the boiler and water, how much heat is required to raise the temperature of the whole from 10°C to 100°C? The specific heat of steel is 0.11 kcal/kg · K.

For heating the boiler:

$$\Delta H = C_{\text{total}}\Delta T = [C_{\text{boiler}} + \mathrm{C}_{\text{water}}]\Delta T$$

$$= [(0.11)(900)\ \text{kcal/K} + (1.00)(400)\ \text{kcal/K}](90\ \text{K}) = 44{,}900\ \text{kcal}$$

$$\text{Input required} = \frac{44{,}900\ \text{kcal}}{0.70} = 64{,}000\ \text{kcal}$$

Note: Beginning with Problem 7.3 and continuing throughout this chapter, we will be using subscript notation rather than notation in parentheses after a symbol. As an example: C(total) becomes C_{total}.

7.4. Exactly three grams of carbon were burned to CO_2 in a copper calorimeter. The mass of the calorimeter is 1500 g and the mass of the water in the calorimeter is 2000 g. The initial temperature was 20.0°C and the temperature rose to 31.3°C. Calculate the heat of combustion of carbon in joules per gram. The specific heat of copper is 0.389 J/g · K.

$$\begin{aligned} q_{\text{calorimeter}} = C_{\text{total}}\Delta T &= [C_{\text{copper}} + C_{\text{water}}]\Delta T \\ &= [(0.389\ \text{J/g}\cdot\text{K})(1500\ \text{g}) + (4.184\ \text{J/g}\cdot\text{K})(2000\ \text{g})][(31.3 - 20.0)\ \text{K}] \\ &= 1.102 \times 10^5\ \text{J/g} \end{aligned}$$

$$\text{Heat value, carbon} = \frac{1.102 \times 10^5\ \text{J/g}}{3.00\ \text{g}} = 3.37 \times 10^4\ \text{J/g}$$

7.5. A 1.250-g sample of benzoic acid, $C_7H_6O_2$, was placed in a combustion bomb. The bomb was filled with an excess of oxygen at high pressure, sealed, and immersed in a pail of water which served as a calorimeter. The heat capacity of the entire apparatus (bomb, pail, thermometer, and water) was found to be 10,134 J/K. The oxidation of the benzoic acid was triggered by passing an electric spark through the sample. After complete combustion, the thermometer immersed in the water registered a temperature 3.256 K greater than before the combustion. What is ΔE per mole of benzoic acid burned?

$$q_{\text{acid}} = -q_{\text{calorimeter}} = -(10{,}134\ \text{J/K})(3.256\ \text{K}) = -33.00\ \text{kJ}$$

$$\Delta E_{\text{combustion}} = \frac{q_{\text{acid}}}{\text{number of moles acid}} = \frac{-33.00\ \text{kJ}}{(1.250\ \text{g})/(122.1\ \text{g/mol})} = -3223\ \text{kJ/mol}$$

7.6. A 25.0-g sample of an alloy was heated to 100.0°C and dropped into a beaker containing 90 g of water at 25.32°C. The temperature of the water rose to 27.18°C. Assuming 100% efficiency, what is the specific heat of the alloy?

$$\text{Heat loss by alloy} = \text{heat absorbed by water}$$

$$\text{Specific heat}_{\text{alloy}} \times \text{mass}_{\text{alloy}} \times \Delta T_{\text{alloy}} = \text{specific heat}_{\text{water}} \times \text{mass}_{\text{water}} \times \Delta T_{\text{water}}$$

$$C_{\text{alloy}} \times w_{\text{alloy}} \times \Delta T_{\text{alloy}} = C_{\text{water}} \times w_{\text{water}} \times \Delta T_{\text{water}}$$

$$(C)(25.0\ \text{g})[(100.0 - 27.2)\text{K}] = (4.184\ \text{J/g}\cdot\text{K})(90\ \text{g})[(27.18 - 25.32)\text{K}]$$

and, solving for C, $C = 0.385$ J/g · K.

7.7. Determine the final temperature when 150 g of ice at 0°C is mixed with 300 g of water at 50°C.

Step 1. Consider the heat absorbed by the ice and by the melted water (0°C to T_{final}). Recalling that 1°C is the same size as 1 in the Kelvin scale, we can substitute 1 K for 1°C.

$$\Delta H_{\text{fusion}} = (80\ \text{cal/g})(150\ \text{g}) = 1.20 \times 10^4\text{cal}$$
$$\Delta H_{\text{heating water}} = C\Delta T = (1.00\ \text{cal/g}\cdot{}^\circ\text{C})(150\ \text{g})[(T_{\text{final}} - 0)^\circ\text{C}]$$

Step 2. Let us consider the change in enthalpy of the hot water.

$$\Delta H_{\text{hot water}} = C\Delta T = (1.00\ \text{cal/g}\cdot{}^\circ\text{C})(300\ \text{g})[(T_{\text{final}} - 50)^\circ\text{C}]$$

where, presumably, $T_{\text{final}} < 50^\circ\text{C}$, consistent with a loss of heat from the hot water.
Step 3. The sum of the ΔH's must equal zero since heat is assumed not to leak into or out of the system discussed in parts 1 and 2 above.

$$1.20 \times 10^4 + 150T_{\text{final}} + 300(T_{\text{final}} - 50) = 0$$

from which $T_{final} = 6.7^\circ\text{C}$
Note: If the amount of ice were to be 200 g, rather than 150 g, the above procedure would have yielded the result, $T_{\text{final}} = -2^\circ\text{C}$. This answer is impossible because the final temperature cannot lie outside the range of the initial temperatures. In this case, the result means that there is insufficient hot water to melt all the ice. The final temperature must be 0°C due to the mixture of ice and water. You can calculate that there is 12.5 g of unmelted ice on completion of the experiment.

7.8. How much heat is given up when 20 g of steam at 100°C is condensed and cooled to 20°C?

The heat of vaporization of water at 100°C is

$$(40.7\ \text{kJ/mol})\left(\frac{1\ \text{mol}}{18.02\ \text{g}}\right) = 2.26\ \text{kJ/g}$$

$$\Delta H_{\text{condensation}} = -(\text{mass}) \times (\text{heat of vaporization}) = -(20\ \text{g})(2.26\ \text{kJ/g}) = -45.2\ \text{kJ}$$

$$\Delta H_{\text{cooling}} = C\Delta T = (4.184\ \text{J/g}\cdot{}^\circ\text{C})(20\ \text{g})[(20 - 100)^\circ\text{C}] = -6.7\ \text{kJ}$$

$$\Delta H_{\text{total}} = \Delta H_{\text{condensation}} + \Delta H_{\text{cooling}} = -45.2\ \text{kJ} - 6.7\ \text{kJ} = -51.9\ \text{kJ}$$

The amount of heat given up is 51.9 kJ.

7.9. How much heat is required to convert 40 g of ice (C = 0.5 cal/g · K) at −10°C to steam ($c = 0.5$ cal/g · K) at 120°C? (Refer to 7.7, (1): 1°C can be substituted for 1 K.)

Heating ice, − 10°C to 0°C	$\Delta H = C\Delta T = (0.5\ \text{cal/g}\cdot \text{K})(40\ \text{g})(10\ \text{K})$	= 0.2 kcal
Melting ice at 0°C	$\Delta H = w \times H_{\text{fusion}} = (40\ \text{g})(80\ \text{cal/g})$	= 3.2 kcal
Heating water, 0°C to 100°C	$\Delta H = C\Delta T = (1.00\ \text{cal/g}\cdot \text{K})(40\ \text{g})(100\ \text{K})$	= 4.0 kcal
Vaporization to steam, 100°C	$\Delta H = w \times \text{H}_{\text{vaporization}} = (40\ \text{g})(540\ \text{cal/g})$	= 21.6 kcal
Heating steam, 100°C to 120°C	$\Delta H = C\Delta T = (0.5\ \text{cal/g}\cdot \text{K})(40\ \text{g})(20\ \text{K})$	= 0.4 kcal

$$\Delta H_{\text{total}} = (0.2 + 3.2 + 4.0 + 21.6 + 0.4)\text{kcal} = 29.4\ \text{kcal}$$

THERMOCHEMICAL EQUATIONS

7.10. What is the heat of vaporization of water per gram at 25°C and 1 atm?

We can write the thermochemical equation for the process, which is

$$H_2O(l) \rightarrow H_2O(g)$$

ΔH^o can be evaluated by subtracting ΔH_f^o of reactants from the ΔH_f^o of the products (Table 7-1).

$$\Delta H^o = \Delta H_{f\,\text{products}}^o - \Delta H_{f\,\text{reactants}}^o = -241.81 - (-285.83) = 44.02\text{ kJ/mol}$$

The enthalpy of vaporization per gram is

$$\frac{44.02\text{ kJ/mol}}{18.02\text{ g/mol}} = 2.44\text{ kJ/g}$$

Note that the heat of vaporization at 25°C is greater than the value (2.26 kJ/g) at 100°C.

7.11. The thermochemical equation for the combustion of ethylene gas, C_2H_4, is

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l) \qquad \Delta H^o = -1410\text{ kJ}$$

Assuming 70% efficiency, how many kilograms of water at 20°C can be converted into steam at 100°C by burning 1 m^3 of C_2H_4 gas measured at S.T.P.?

$$n(C_2H_4) = \frac{(1\text{ m}^3)(1000\text{ L/m}^3)}{22.4\text{ L/mol}} = 44.6\text{ mol}$$

$$\Delta H(1\text{ m}^3) = n(C_2H_4) \times \Delta H(1\text{ mol}) = (44.6\text{ mol})(-1410\text{ kJ/mol}) = -6.29 \times 10^4\text{ kJ}$$

The useful heat at 70% efficiency is $(0.70)(6.29 \times 10^4\text{ kJ}) = 4.40 \times 10^4$ kJ.
The next step is to consider the conversion of water from 20°C to 100°C, which occurs in two stages.

$$\begin{array}{lrl}
H_2O(l, 20°C) \rightarrow H_2O(l, 100°C) & \Delta H = (4.184\text{ kJ/kg}\cdot\text{K})(80\text{ K}) & = 335\text{ kJ/g} \\
H_2O(l, 100°C) \rightarrow H_2O(g, 100°C) & \underline{\Delta H = (40.7\text{ kJ/mol})/(0.01802\text{ kg/mol})} & = \underline{2259\text{ kJ/g}} \\
 & \Delta H_{\text{total}} & = 2594\text{ kJ/g}
\end{array}$$

The mass of water converted, w, is equal to the amount of heat available divided by the heat required per kilogram of water to be converted.

$$w(H_2O) = \frac{4.40 \times 10^4\text{ kJ}}{2594\text{ kJ/kg}} = 17.0\text{ kg}$$

7.12. Calculate the ΔH^o for reduction of ferric oxide by aluminum (thermite reaction) at 25°C.

There is a chemical reaction associated with the problem and that reaction must be written as the starting place for the solution to the problem. We can also place the enthalpy of formation (heat of formation) for the participants in the reaction from Table 7-1, multiplied by the coefficient used in balancing the equation. Recall that for an element in the ground state, the ΔH_f^o is zero.

$$\begin{array}{cccc}
2Al+ & Fe_2O_3 & \rightarrow 2Fe+ & Al_2O_3 \\
2(0) & 1(-824.2) & 2(0) & 1(-1675.7)
\end{array}$$

We must keep in mind what the units are and what happens to them. As an example, look at the value for Fe_2O_3, which is 1 mol × (−824.2 kJ/mol) = −824.2 kJ.

The formal statement of the ΔH_f° of the reaction is given by

$$\Delta H^\circ = (\text{sum of the } n\Delta H_f^\circ \text{ of the products}) - (\text{sum of the } n\Delta H_f^\circ \text{ of the reactants})$$

$$\Delta H^\circ = (-1675.7) - (-824.2) = -851.5 \text{ kJ for one mole } Fe_2O_3 \text{ reduced}$$

Note that keeping the general formula for ΔH° above in the correct order can be done by noticing that during the reaction the products are gained (positive) and the reactants are lost (negative sign).

7.13. The ΔH_f° for N(g) (not the standard state of nitrogen) has been determined as 472.7 kJ/mol, and as 249 kJ/mol for O(g). Calculate the ΔH° in (a) kJ and (b) kcal for a hypothetical reaction in the upper atmosphere,

$$N(g) + O(g) \rightarrow NO(g)$$

(a) As with the Problem 7.12, we write the heats of formation (multiplied by 1 mole due to the coefficients in the balanced equation) from Table 7-1. Then, we perform the calculation resulting in the value of ΔH° for the reaction.

$$\begin{array}{ccccc} N(g) & + & O(g) & \rightarrow & NO(g) \\ +472.7 & & +249.2 & & +89.7 \end{array}$$

$$\Delta H^\circ = +89.7 - (+472.7 + 249.2) = -632.2.\text{ kJ}$$

(b) The calculation for the conversion from kJ to kcal for this exothermic reaction ($-\Delta H^\circ$) is

$$(-632 \text{ kJ})/(4.184 \text{ kJ/kcal}) = -151.1 \text{ kcal}$$

7.14. Calculate the enthalpy of decomposition of $CaCO_3$ into CaO and CO_2.

The first step is to write the balanced equation for the reaction. The second step is to place all the values for the heats of formation noting that the coefficients are all 1's. Then, we can calculate ΔH°.

$$\begin{array}{lccccc} & CaCO_3(s) & \rightarrow & CaO(s) & + & CO_2(g) \\ \left(n\Delta H_f^\circ\right) \text{ kcal:} & -288.5 & & -151.6 & & -94.0 \end{array}$$

$$\Delta H^\circ = (-151.6 - 94.0) - (-288.5) = +42.9 \text{ kcal} \quad \text{or} \quad +179.5 \text{ kJ}$$

Note that the positive value for the enthalpy of this decomposition tells us that this reaction is endothermic.

7.15. (a) Calculate the enthalpy of neutralization of a strong acid by a strong base in water. (b) The heat liberated on neutralization of HCN, a weak acid, by NaOH is 12.1 kJ/mol. How many kilojoules are absorbed during the ionizing of 1 mol of HCN in water?

(a) The basic equation for the neutralization of an acid by a base is

$$\begin{array}{lccc} & H^+(aq)+ & OH^-(aq) \rightarrow & H_2O(l) \\ (n\Delta H_f^\circ)/\text{kJ} & \text{O} & -230.0 & -285.8 \end{array}$$

and

$$\Delta H^\circ = -258.8 - (-230.0) = -55.8 \text{ kJ (exothermic reaction)}$$

(b) The neutralization of HCN(aq) by NaOH(aq) can be considered as the result of two processes; this means that the ΔH° values of the processes can be added for the summation reaction. The processes are the ionization of HCN(aq) and the neutralization of $H^+(aq)$ with $OH^-(aq)$. Note that since NaOH is a strong base when dissolved in water, we assume complete ionization and a separate thermochemical equation for the ionization need not be written. We can write the following reactions:

$$\begin{array}{llll} & HCN(aq) \rightarrow H^+(aq) + CN^-(aq) & \Delta H^\circ = x & \text{(ionization reaction)} \\ & \underline{H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad\qquad} & \underline{\Delta H^\circ = -55.8\text{ kJ}} & \\ \text{Summation:} & HCN(aq) + OH^-(aq) \rightarrow H_2O(l) + CN^-(aq) & \Delta H^\circ = -12.1\text{ kJ} & \text{(exothermic reaction)} \end{array}$$

The summation reaction is endothermic; however, the ionization reaction is endothermic because the value of ΔH° for the ionization reaction is

$$x + (-55.8) = -12.1 \qquad \text{and, by rearrangement} \qquad x = -12.1 + 55.8 = +43.7\text{ kJ}$$

7.16. The heat evolved on combustion of acetylene gas, C_2H_2, at 25°C is 1299 kJ/mol. Determine the enthalpy of formation of acetylene gas.

Because we are asked for information for 1 mol C_2H_2, let us balance the chemical reaction using only 1 mol C_2H_2. We can also place the heats of formation in preparation for the final calculation requested.

$$\begin{array}{lcccc} & C_2H_2(g) + & \frac{5}{2}O_2(g) \rightarrow & 2CO_2(g) + & H_2O(l) \\ (n\Delta H_f^\circ)/\text{kJ} & 1(x) & \frac{5}{2}(0) & 2(-393.5) & 1(-285.8) \end{array}$$

and

$$\Delta H^\circ = -1299.1\text{ kJ/mol} = [2(-393.5) + (-285.8)] - x$$
$$x = n\Delta H_f^\circ \text{ for } C_2H_2(g) = +226.3\text{ kJ}$$

7.17. How much heat will be required to make 1 kg of CaC_2 according to the reaction given below?

$$CaO(s) + 3C(s) \rightarrow CaC_2(s) + CO(g)$$

As above, the heats of formation are placed and the calculation is performed.

$$\begin{array}{lcccc} & CaO(s) & + 3C(s) \rightarrow & CaC_2(s) + & CO(g) \\ (n\Delta H_f^\circ)/\text{kJ} & 1(-634.3) & 3(0) & 1(-59.4) & 1(-110.5) \end{array}$$

$$\Delta H^\circ = (-59.4 - 110.5) - (-634.3) = +464.4\text{ kJ/mol } CaC_2$$

This is the heat required to make 1 mol CaC_2 (endothermic reaction). One kilogram of CaC_2 requires

$$\left(\frac{1000\text{ g } CaC_2}{64.10\text{ g } CaC_2/\text{mol } CaC_2}\right)(464.4\text{ kJ/mol } CaC_2) = 7245\text{ kJ}$$

7.18. How many kilojoules of heat will be evolved in making one mole of H_2S from FeS and dilute hydrochloric acid?

$$\begin{array}{cccc} FeS(s) & + 2H^+(aq) \rightarrow & Fe^{2+}(aq) + & H_2S(g) \\ -100.0 & 0 & -89.1 & -20.6 \end{array}$$

Since HCl and $FeCl_2$ are strong electrolytes (ionize well in water), the chloride ion, which does not participate in the reaction (a spectator ion), can be omitted from the balanced equation.

$$\Delta H^\circ = (-89.1 - 20.6) - (-100.0) = -9.7\text{ kJ/mol } H_2S$$

Supplementary Problems

HEAT CAPACITY AND CALORIMETRY

7.19. How many calories are required to heat each of the following from 15°C to 65°C: (*a*) 1.0 g water; (*b*) 5.0 g Pyrex® glass; (*c*) 20 g platinum? (The specific heat of the glass is 0.20 cal/g · K; of platinum, 0.032 cal/g · K.)

Ans. (*a*) 50 cal; (*b*) 50 cal; (*c*) 32 cal

7.20. The ability to convert between calories and joules is extremely important. Express the answers in Problem 7.19 in joules and in kJ.

Ans. (*a* and *b*) 209.2 J and 0.2092 kJ; (*c*) 133.9 J and 0.1339 kJ

7.21. The combustion of 5.00 g of coke raised the temperature of water of 1.00 kg of water from 10°C to 47°C. Calculate the heating value of coke.

Ans. 7.4 kcal/g or 31 kJ/g

7.22. Assuming that 50% of the heat is useful, how many kilograms of water at 15°C can be heated to 95°C by burning 200 L of methane, CH_4, measured at S.T.P.? The heat of combustion for methane is 891 kJ/mol.

Ans. 12 kg water

7.23. The heat of combustion of ethane gas, C_2H_6, is 1561 kJ/mol. Assuming that 60% of the heat is useful, how many liters of ethane (S.T.P.) must be burned to supply enough heat to convert 50 kg of water at 10°C to steam at 100°C?

Ans. 3150 L

7.24. A substance, metallic in nature, is to be identified, and heat capacity is one of the clues to its identity. A block of the metal weighing 150 g required 38.5 cal to raise its temperature from 22.8°C to 26.4°C. Calculate the specific heat capacity of the metal and determine if it is the correct alloy, which has a specific heat capacity of 0.0713 cal/g · K.

Ans. Yes, it is the same alloy on the basis of heat capacity; it is a match at 0.0713 cal/g · K.

7.25. An ore has been refined and the metal produced is suspected of being gold. A test is to determine the specific heat of the metal and compare against that of gold allowing a 2% *tolerance* (2% above or below). The amount of heat necessary to raise 25.0 grams of the metal from 10.0°C to 23.6°C was 10.78 cal. The specific heat of gold is 0.0314 cal/g°C.

Ans. The specific heat of the sample is 0.0317 cal/g°C, which is just 1% from the specific heat of gold.

7.26. A 45.0-g sample of an alloy was heated to 90.0°C and then dropped into a beaker containing 82 g of water at 23.50°C. The temperature of the water rose to 26.25°C. What is the specific heat of the alloy?

Ans. 0.329 J/g · K or 0.079 cal/g · K

7.27. A fired lead bullet weighed 35.4 g after cleaning; it was heated to 91.50°C, then placed in 50.0 mL of water at 24.73°C. The temperature of the water rose to 26.50°C. A sample bullet was secured from a potential suspect and was found to have a specific heat of 0.03022 cal/g°C. What is the specific heat of the fired bullet and could it be from the same batch of bullets?

Ans. The specific heat of the sample is 0.03946. The specific heats are 0.0.00924 cal/g°C apart. An interpretation is that the collected bullet is 31% higher in specific heat than the sample bullet, which would tend to eliminate the suspected similarity.

7.28. If the specific heat of a substance is *h* cal/g · K, what is its specific heat in Btu/lb · °F?

Ans. *h* Btu/lb · °F

7.29. How much water at 20°C would be necessary to cool a 34-g piece of copper, specific heat 0.0924 cal/g · K, from 98°C to 25°C?

Ans. 46 g H_2O

7.30. Determine the resulting temperature when 1 kg of ice at 0°C is mixed with 9 kg of water at 50°C. The heat of fusion of ice is 80 cal/g (355 J/g).

Ans. 37°C

7.31. An automatic fire sprinkler depends on a piece of metal with a low melting point to release water when necessary. How much heat would be required to melt a 5 g piece of lead (MP = 327°C, specific heat of 0.03 cal/g · K) used as a plug in a sprinkler normally at room temperature (25°C)? Express in calories and joules.

Ans. 45.3 cal or 189.5 J

7.32. How much heat is required to change 10 g of ice at 0°C to steam at 100°C? The heat of vaporization of water at 100°C is 540 cal/g (2259 J/g).

Ans. 7.2 kcal or 30 kJ

7.33. A boiler that supplies a steam turbine used in an electric power plant must raise the temperature of water from the ambient temperature passing through a physical state change and then to live (very hot) steam. How much energy (kcal and kJ) would be required to raise 15,000 L of water from 25°C to steam at 175°C? (steam requires 0.5 cal/g · K)?

Ans. 9,800 kcal or 41,000 kJ

7.34. A Styrofoam™ coffee cup serves as an inexpensive calorimeter for measurements that do not require high accuracy. One gram of KCl(*s*) was added to 25.0 ml of water in such a cup at 24.33°C. It dissolved completely and quickly with gentle stirring. The minimum temperature reached was 22.12°C. Estimate the ΔH° of the heat of solution of KCl in kJ/mol. You may assume the solution has the same heat capacity as water and that the heat capacity of the cup and thermometer need not be considered.

Ans. $\Delta H^\circ_{\text{solution}} = +17.2$ kJ/mol

7.35. In an ice calorimeter, a chemical reaction is allowed to occur in thermal contact with an ice-water mixture at 0°C. Any heat liberated by the reaction is used to melt ice; the volume change of the ice-water mixture indicates the amount of melting. When solutions containing 1.00 millimole each of $AgNO_3$ and NaCl were mixed in such a calorimeter, both solutions having been precooled to 0°C, 0.20 g of ice melted. Assuming complete reaction, what is ΔH for the reaction $Ag^+ + Cl^- \rightarrow AgCl$?

Ans. -67 kJ or -16 kcal

7.36. A 15.3-g portion of an organic liquid at 26.2°C was poured into the reaction chamber of an ice calorimeter and cooled to 0.0°C. The rise in water level indicated that 3.09 g of ice melted. Calculate the specific heat of this organic liquid.

Ans. 0.616 cal/g · K or 2.58 J/g · K

THERMOCHEMICAL EQUATIONS

7.37. What is the heat of sublimation of solid iodine at 25°C?

Ans. 14.92 kcal/mol I_2 or 62.4 kJ/mol I_2

7.38. Calculate the amount of energy involved in the change of 650 g I_2 from a gas to a solid at 25°C.

Ans. 32.67 kcal or 136.7 kJ

7.39. Is the process of dissolving H_2S gas in water endothermic or exothermic? To what extent?

Ans. Exothermic, 4.6 kcal/mol (19.1 kJ/mol) (*Note*: The actual answer is −4.6 cal/mol. Recall that a negative value indicates that the reaction (physical or chemical) is exothermic.)

7.40. How much heat is released on dissolving 1 mol of HCl(*g*) in a large amount of water? (*Hint*: HCl is completely ionized in dilute solution.)

Ans. 17.9 kcal or 74.8 kJ

7.41. The standard enthalpy of formation of H(*g*) has been determined to be 218.0 kJ/mol. Calculate the ΔH° in kilojoules for the following two reactions: (*a*) $H(g) + Br(g) \rightarrow HBr(g)$; (*b*) $H(g) + Br_2(l) \rightarrow HBr(g) + Br(g)$

Ans. (*a*) −366.2 kJ; (*b*) −142.6 kJ

7.42. Determine the ΔH° of decomposition of 1 mol of solid $KClO_3$ into solid KCl and oxygen gas.

Ans. −10.9 kcal or −45.5 kJ

7.43. The heat released on neutralization of CsOH with all strong acids is 13.4 kcal/mol. The heat released on neutralization of CsOH with HF (weak acid) is 16.4 kcal/mol. Calculate the ΔH° of the ionization of HF in water.

Ans. −3.0 kcal/mol

7.44. Find the heat evolved in slaking 1 kg of quicklime (CaO) according to the reaction

$$\text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca(OH)}_2(s)$$

Ans. 282 kcal or 1180 kJ

7.45. The heat liberated on complete combustion of 1 mol of CH_4 gas to $CO_2(g)$ and $H_2O(l)$ is 890 kJ. Determine the enthalpy of formation of 1 mol of CH_4 gas.

Ans. −75 kJ/mol

7.46. The heat evolved on combustion of 1 g of starch, $(C_6H_{10}O_5)_n$, into $CO_2(g)$ and $H_2O(l)$ is 17.48 kJ. Compute the standard enthalpy of formation of 1 g starch.

Ans. −5.88 kJ

7.47. The amount of heat evolved on dissolving $CuSO_4$ is 73.1 kJ/mol. What is ΔH_f° for $SO_4^{2-}(aq)$?

Ans. −909.3 kJ/mol

7.48. The heat of solution of $CuSO_4 \cdot 5H_2O$ in a large amount of water is 5.4 kJ/mol (endothermic). Refer to Problem 7.47 and calculate the heat of reaction for

$$\text{CuSO}_4(s) + 5\text{H}_2\text{O}(l) \rightarrow \text{CuSO}_4\cdot 5\text{H}_2\text{O}(s)$$

Ans. 78.5 kJ (exothermic and expressed as −78.5 kJ or −18.8 kcal)

7.49. The heat evolved during the combustion of 1 mol $C_2H_6(g)$ into $CO_2(g)$ and $H_2O(l)$ is 1559.8 kJ, and for complete combustion of 1 mol $C_2H_4(g)$ is 1410.8 kJ. Calculate ΔH for the following reaction:

$$\text{C}_2\text{H}_4(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g)$$

$\Delta H = -97.0$ kJ. What is the heat of solution of $CaCl_2$ (anhydrous) in a large volume of water?

Ans. −136.8 kJ

7.50. The solution of $CaCl_2 \cdot 6H_2O$ in a large volume of water is endothermic to the extent of 14.6 kJ/mol. For the reaction below, $\Delta H = -97.0$ kJ. What is the heat of solution of $CaCl_2$ (anhydrous) in a large volume of water?

$$\text{CaCl}_2(s) + 6\text{H}_2\text{O}(l) \rightarrow \text{CaCl}_2\cdot 6\text{H}_2\text{O}(s)$$

Ans. 82.4 kJ/mol (exothermic)

7.51. Hydrolysis is an important organic reaction in which a large molecule utilizes a water molecule to split into two smaller molecules. Since the same number and kind of chemical bonds are present in both reactants and products, one might expect only a small energy change. Calculate ΔH° for the gas phase hydrolysis of dimethyl ether based on Table 7-1 and the additional heat of formation values following: $CH_3OCH_3(g) = -185.4$ kJ/mol and $CH_3OH(g) = -201.2$ kJ/mol. The reaction is

$$\text{CH}_3\text{OCH}_3(g) + \text{H}_2\text{O}(g) \rightarrow 2\text{CH}_3\text{OH}(g)$$

Ans. $\Delta H^\circ = +24.8$ kJ

7.52. The commercial production of water gas utilizes the reaction $C(s) + H_2O(g) \rightarrow H_2(g) + CO(g)$. The required heat for this endothermic reaction may be supplied by adding a limited amount of oxygen and burning some carbon to CO_2. How many grams of carbon must be burned to CO_2 to provide enough heat for the water gas conversion of 100 g of carbon? Assume no heat is lost to the environment.

Ans. 33.4 g

7.53. This reaction can be reversed.

$$Na_2SO_4 \cdot 10H_2O \rightarrow Na_2SO_4 + 10H_2O \Delta H = +18.8\text{kcal}$$

The reaction goes completely to the right at temperatures above 32.4°C, and remains completely on the left below this temperature. This system has been used in some solar homes for heating at night with the energy absorbed from the sun's radiation during the day. How many cubic feet of fuel gas could be saved per night by the reversal of the dehydration of a fixed charge of 100 lb $Na_2SO_4 \cdot 10H_2O$? Assume that the fuel value of the gas is 2000 Btu/ft^3.

Ans. 5.3 ft^3

7.54. A lot of heat is produced when gunpowder burns. A mixture can be produced from charcoal (carbon), $KClO_4$, and sulfur. By the reactions below, calculate the amount of energy given off when a mole of gunpowder burns (assume 1 mole of each substance adds up to 1 mol gunpowder).

Hints: (*i*) Balance equations—fractions are OK; (*ii*) O_2 can come from the air.

$$\begin{array}{llll} \text{Charcoal} & C + O_2 \rightarrow CO & \text{Sulfur} & S + O_2 \rightarrow SO_2 \\ \text{and} & CO + O_2 \rightarrow CO_2 & \text{and} & SO_2 + O_2 \rightarrow SO_3 \\ & \text{On heating} & KClO_4 \rightarrow KCl + O_2 & \end{array}$$

Ans. −189.5 kcal or −792.6 kJ

7.55. An important criterion for the desirability of fuel reactions for rockets is the fuel value in kilojoules, either per gram of reactant, or per cubic centimeter of reactant. Compute both of these quantities for each of the following reactions:

(*a*) $N_2H_4(l) + 2H_2O_2(l) \rightarrow N_2(g) + 4H_2O(g)$

(*b*) $2LiBH_4(s) + KClO_4(s) \rightarrow Li_2O(s) + B_2O_3(s) + KCl(s) + 4H_2(g)$

(*c*) $6LiAlH_4(s) + 2C(NO_2)_4(l) \rightarrow 3Al_2O_3(s) + 3Li_2O(s) + 2CO_2(g) + 4N_2(g) + 12H_2(g)$

(*d*) $4HNO_3(l) + 5N_2H_4(l) \rightarrow 7N_2(g) + 12H_2O(g)$

(*e*) $7N_2O_4(l) + C_9H_{20}(l) \rightarrow 9CO_2(g) + 10H_2O(g) + 7N_2(g)$

(*f*) $4ClF_3(l) + (CH_3)_2N_2H_2(l) \rightarrow 2CF_4(g) + N_2(g) + 4HCl(g) + 4HF(g)$

Use the following density values: $N_2H_4(l)$, 1.01 g/cm^3; $H_2O_2(l)$, 1.46 g/cm^3; $LiBH_4(s)$, 0.66 g/cm^3; $KClO_4(s)$, 2.52 g/cm^3; $LiAlH_4(s)$, 0.92 g/cm^3; $C(NO_2)_4(l)$, 1.65 g/cm^3; $HNO_3(l)$, 1.50 g/cm^3; $N_2O_4(l)$, 1.45 g/cm^3; $C_9H_{20}(l)$, 0.72 g/cm^3; $ClF_3(l)$, 1.77 g/cm^3; $(CH_3)_2N_2H_2(l)$, 0.78 g/cm^3. When computing the volume of each reaction mixture, assume that the reactants are present in stoichiometric proportions.

Ans. (*a*) 6.4 kJ/g, 8.2 kJ/cm^3; (*b*) 8.3 kJ/g, 12.4 kJ/cm^3; (*c*) 11.4 kJ/g, 14.6 kJ/cm^3; (*d*) 6.0 kJ/g, 7.5 kJ/cm^3; (*e*) 7.2 kJ/g, 8.9 kJ/cm^3; (*f*) 6.0 kJ/g, 9.1 kJ/cm^3

7.56. Fires often times are hotter than normal due to the use of an accelerant; nonane, C_9H_{20}, is an example. How much additional heat would there be in a fire contributed to by the complete combustion of 500 g nonane (gases for products)?

Ans. 1358.6 kcal or 5684.2 kJ

7.57. An early-model Concorde supersonic airplane consumed 4700 gallons of aviation fuel per hour at cruising speed. The density of the fuel was 6.65 pounds per gallon and the ΔH of combustion was −10,500 kcal/kg. Express the power consumption in megawatts ($1\text{ MW} = 10^6\text{ W} = 10^6\text{ J/s}$) during cruise.

Ans. 173 MW

7.58. Two solutions, initially at 25.08°C, were mixed in an insulated bottle. One consisted of 400 mL of a weak monoprotic acid solution of concentration 0.200 mL. The other consisted of 100 mL of a 0.800 mol of NaOH per liter of solution. The temperature rose to 26.25°C. How much heat is evolved in the neutralization of one mole of the acid? Assume that the densities of all solutions are 1.00 g/cm^3 and that their specific heat capacities are all 4.2 J/g · K. Actually, these assumptions are in error by several percent, but they nearly cancel each other.

Ans. 31 kJ/mol

7.59. An old type of miner's lamp burns acetylene, C_2H_2, which is made as needed by dropping water onto calcium carbide, CaC_2. The lamp designer needs to be concerned about how hot the calcium carbide chamber will get because the lamp is worn on the miner's hat and an explosion is not a good idea. Calculate the heat produced per liter (kJ/L at S.T.P.) of C_2H_2 generated. (Refer to Problem 7.16.)

$$CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$$

Ans. 5.77 kJ/L ($\Delta H^o = -129.3$ kJ/mol)

7.60. The miner's lamp discussed in Problem 7.59 is the basis for this problem. (*a*) How does the heat of combustion of the C_2H_2 compare to the heat generated in making it from calcium carbide? (*b*) If we add the generating reaction to the combustion reaction, the overall reaction of the lamp becomes

$$CaC_2(s) + H_2O(l) + \left(\frac{5}{2}\right)O_2(g) \rightarrow Ca(OH)_2(s) + 2CO_2(g)$$

Calculate the ΔH^o for the above reaction and compare it to the results of the separate calculations made in Problems 7.59 and 7.60(*a*).

Ans. (*a*) Heat of combustion = 58.0 kJ/L ($\Delta H = -1299$ kJ/mol). This is about ten times the result of Problem 7.59. (*b*) The result is exactly the sum of the previous calculations ($-129.3 - 1299.1$); $\Delta H^o = -1428$ kJ/mol.

7.61. Calcium carbonate reacts with HCl gas, and the reaction can neutralize a release of the corrosive gas. Calculate and interpret the thermodynamic value for the neutralization of 200 kg HCl gas by the reaction: $2HCl(g) + CaCO_3(s) \rightarrow CaCl_2(s) + CO_2(g) + H_2O(g)$. (The heat of formation for $CaCl_2$ is -190.0 kcal/mol.)

Ans. -25.3 kcal (-106 kJ). The negative value tells us it is an exothermic reaction.

CHAPTER 8

Atomic Structure and the Periodic Law

ABSORPTION AND EMISSION OF LIGHT

Modern atomic theory received a “shot in the arm” when it was recognized that the individual atom has light absorption and emission spectra occurring at narrow *lines* of the spectrum at specific wavelengths, as opposed to the broad *bands* typical of the polyatomic molecules and compounds. Since the line spectrum of each element is characteristic of that element, atomic spectroscopy can be used for precise elementary analysis of many types of chemically simple and complex materials. These studies make use of the wave character of light, as well as light’s particle character.

Wave character of light

A light beam can be viewed as a form of energy emitted from a source. A light beam can be imagined in the form of a sine wave, as shown in Fig. 8-1. The distance between two waves, usually measured from the peak of the waves, is the *wavelength*, given the symbol lambda, λ. The *frequency* is a statement of the number of waves passing a point in space per second; it is given the symbol nu, ν. The *hertz* is commonly used as the unit for frequency; $1\ \text{Hz} = 1\ \text{s}^{-1}$.

The product of the wavelength and the frequency is equal to the velocity of light, usually designated by c:

$$c = \lambda\nu$$

The velocity of light in a vacuum is the same for all wavelengths, 2.998×10^8 m/s. The formula above tells us that there is a simple inverse relationship of wavelength and frequency, $\lambda = c/\nu$ or $\nu = c/\lambda$. The velocity of light in the atmosphere is a little slower than in a vacuum; however, the drop in velocity is less than 0.1 percent of that in a vacuum, making 2.998×10^8 m/s acceptable for most applications due to the low percent error introduced. Another term is often used, the *wave number*, $\tilde{\nu}$, defined as $1/\lambda$ (or as ν/c). The most common unit for wave number is cm^{-1}.

Particle character of light

The energy of light is emitted, absorbed, or converted to other forms of energy in individual units referred to as *quanta* (singular: *quantum*). The unit of light energy is often referred to as the particle of light called the *photon*.

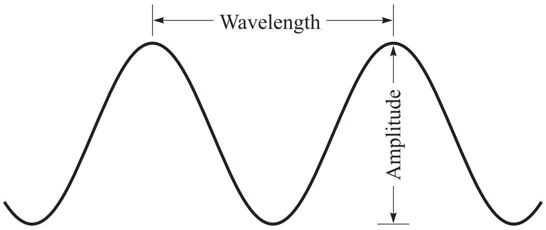


Fig. 8-1

The energy of a photon is proportional to the frequency:

$$\varepsilon = h\nu = (6.626 \times 10^{-34}\,\mathrm{J \cdot s})\nu$$

Planck's constant, h, is the universal proportionality constant.

Chemists' studies are performed using radiation whose wavelengths vary from 0.1 nm (x-rays) to several centimeters (microwaves). Note that visible light is in the range of 400 to 700 nm.

INTERACTION OF LIGHT WITH MATTER

A major step toward the understanding of atomic structure was Bohr's explanation of hydrogen's spectrum. His postulates were

1. The electron of the hydrogen atom revolves around the nucleus in stable circular orbits.
2. In each stable orbit the electrostatic attraction between the negatively charged electron and the positively charged nucleus provides the centripetal force (pulling the electron toward the nucleus) needed for the circular motion of the electron. The energy of the atom is the sum of the potential energy of the electrostatic interaction between the nucleus and the electron and the kinetic energy of the motion of the electron.
3. Only certain stable orbits are allowed—those for which the angular momentum of the electron is an integer, n, times the constant $h/2\pi$. (The h is Planck's constant introduced above.)
4. An electron can move from one stable orbit to another only by absorbing or releasing an amount of energy exactly equal to the difference between the energies of the two orbits. Energy is absorbed when going to a higher level (out from the nucleus) and released (not necessarily the same wavelength) when the electron falls back to the original orbit. If this energy is absorbed or released as light, a single photon of absorbed or emitted light must account for the required energy difference as

$$h\nu = |\Delta E|$$

where ΔE is the difference between the energies of the final and initial orbits.

Bohr satisfactorily accounted for the observed series of spectral lines for hydrogen with this theory. The predicted orbit energies in the simplest form of the theory are given by

$$E(n) = -\frac{me^4Z^2}{8\varepsilon_0^2 h^2 n^2}$$

where m and e are the mass and charge of the electron, ε_0 is permittivity of free space, and Z is the atomic number of the nucleus (1 for hydrogen). Note that the energy is negative with respect to the state in which the electron and nucleus are widely separated, which is the zero energy state. In SI units,

$$m = 9.1095 \times 10^{-31}\,\mathrm{kg} \qquad e = 1.602 \times 10^{-19}\,\mathrm{C} \qquad \varepsilon_0 = 8.854 \times 10^{-12}\,\mathrm{C^2/N \cdot m^2}$$

The predicted allowed wave numbers observed in the spectrum are

$$\tilde{\nu} = \frac{|E(n_2) - E(n_1)|}{hc} = \frac{me^4 Z^2}{8\varepsilon_0^2 h^3 c} \left| \frac{1}{n_1^2} - \frac{1}{n_2^2} \right| = RZ^2 \left\| \frac{1}{n_1^2} - \frac{1}{n_2^2} \right|$$

where $n_1 < n_2$ in absorption and $n_1 > n_2$ in emission. The quantity R, the *Rydberg constant*, is defined purely in terms of universal constants and has the value of 109,737 cm^{-1}:

$$R = \frac{me^4}{8\varepsilon_0^2 h^3 c} = 109{,}737\ \text{cm}^{-1}$$

Note: The observed value for ^{1}H is 0.06 percent lower because of the *reduced mass* effect. In accordance with a refinement of the simple Bohr theory, R increases with increasing nuclidic mass toward a maximum of 109,737 cm^{-1}. The predicted radii of the orbits are

$$r(n) = \frac{n^2}{Z} a_0 \qquad \text{where} \qquad a_0 = \frac{h^2 \varepsilon_0}{\pi m e^2}$$

The predicted value for hydrogen's first Bohr orbit ($n = 1$) is $a_0 = 5.29 \times 10^{-11}\ \text{m} = 0.529\ \text{Å}$.

A note of caution: The Bohr theory, even when improved and amplified, applies only to hydrogen and hydrogen-like species, such as He^+ and Li^+. The theory explains neither the spectra of atoms containing even as few as two electrons, nor the existence and stability of chemical compounds. The next advance in the understanding of atoms requires an understanding of the wave nature of matter.

PARTICLES AND WAVES

De Broglie proposed that not only does light have the dual properties of waves and particles, but also particles of matter have properties of waves. The wavelength of those particle waves is given by

$$\lambda = \frac{h}{mv}$$

where m and v are the mass and velocity of the particle. Planck's constant, h, is so small that the wavelengths are in an observable range only for particles of atomic or subatomic mass.

An experimental confirmation of the de Broglie relation for a beam of uniformly energetic electrons was followed by a theoretical development of *quantum mechanics*, also referred to as *wave mechanics*. Not only was Bohr's successful prediction of the stable energy levels of the hydrogen atoms reproduced, but the concept can be applied to many-electron atoms and to many-atom molecules. The Bohr postulates are replaced by the *Schrödinger equation*, which must be solved by the methods of partial differential equations. The equation has mathematical similarities to descriptions of physics waves, and the arbitrary introduction of integers in the Bohr theory receives justification in quantum mechanics in the requirement that wave-like solutions of the equation must be continuous, finite, and single-valued. The steady-state solutions of the wave equation corresponds to states of fixed energy, as in the Bohr theory, and in many cases, including the hydrogen atom, of fixed angular momentum. Many other descriptive properties, like the location of an electron, are not definitely fixed, but are represented by probabilities of distribution over a range of numerical values. In the hydrogen atom, the electron is not confined to a two-dimensional orbit, but is represented by a wave that extends over three-dimensional space. The wave amplitude indicates the varying probability of finding the electron at different locations with respect to the nucleus.

Orbitals

A solution to the Schrödinger equation for an electron must satisfy three quantum conditions corresponding to the three dimensions of space. Each quantum condition introduces an integer, called a *quantum number*, into the solution. A separate solution, describing a probability distribution of finding the electron at various locations, exists for each allowed set of three quantum numbers. Such a solution is called an *orbital*; it is similar to a hypothetical time-exposure photograph of an electron taken over a time interval large enough so that each region of space is represented by the weighted probability of finding the electron in that region. These three quantum numbers are usually designated as follows:

1. n, *principal quantum number*: This number almost exclusively determines the energy of the orbital in one-electron systems, and is still the principal determinant of energy in many-electron systems.
2. l, *angular momentum quantum number*: This number defines the shape of the orbital and, together with n, defines the average distance of the electron from the nucleus.
3. m_l, *magnetic quantum number*: This number determines the orientation of the orbital in space.

In addition to the three dimensions in space describing the relative positions of the electron and the nucleus, there is a fourth dimension internal to the electron itself, related to the spin of the electron around an internal axis and characterized by the magnetic moment associated with this spin. The quantum number associated with electron spin is usually designated as m_s.

Each of the four quantum numbers may have only certain values, which are:

(*a*) n may be any positive integer. Electrons having a given n-value are said to be in the same *shell* (orbit). Shells are designated by capital letters as follows:

n	1	2	3	4	5	6	7
Designation	K	L	M	N	O	P	Q

(*b*) The value of l varies from 0 to $n - 1$. The values of l are designated by letters as follows:

l	0	1	2	3	4
Designation	s	p	d	f	g

An orbital is usually referred to by its principal quantum number (n) followed by the letter corresponding to its l-value. Examples are $2s$,$2p$, $4d$, and $5f$.

(*c*) m_l may have any integral value from $-l$ to $+l$. This rule gives the *number* of orbitals, $2l + 1$, associated with a given (n, l) combination. There are three p orbitals corresponding to $m_l = 1, 0$, and -1. However, it is usually more convenient in chemistry to use a new set of three orbitals oriented along the x, y, and z axes to display the shapes and directions of these orbitals. Further, there are 5 d orbitals and 7 f orbitals having different shapes and orientations in space.

(*d*) The values of m_s may either be $+\frac{1}{2}$ or $-\frac{1}{2}$.

The probabilities of finding an electron at various distances, r, from the hydrogen nucleus are given in Fig. 8-2 for several (n, l) combinations. The shapes of the s, p, and d orbitals are shown in Fig. 8-3. An inspection of Fig. 8-2 shows a detail which emerges as an exact mathematical consequence of the theory: when $l = n - 1$, the most probable distance of the electron from the nucleus is exactly equal to the radius of the Bohr orbit, n^2a_0. In general, the average distance of the electron from the nucleus increases with increasing n. This same figure shows another interesting feature for all allowed l values, except the maximum for a given n; namely, the existence of minima of zero probability, corresponding to spherical *nodal surfaces* around the nucleus, at which the electron will not be found. Figure 8-3 shows that s orbitals take the shape of a sphere with the nucleus in the center. Each p orbital is concentrated along the $+$ and $-$ portions of one of the Cartesian axes (x, y, or z) with a *nodal plane* of zero probability perpendicular to that axis at the nucleus. Of the five allowed d orbitals for a given n, only four have the same shape—a three dimensional four-leaf clover—with the highest probability along the x

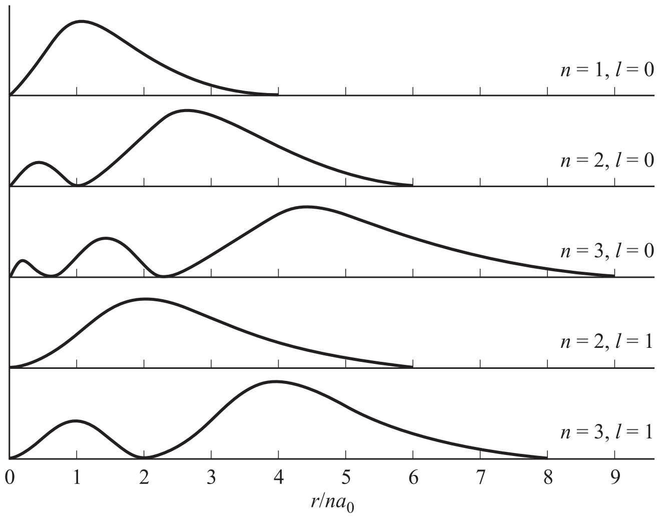


Fig. 8-2

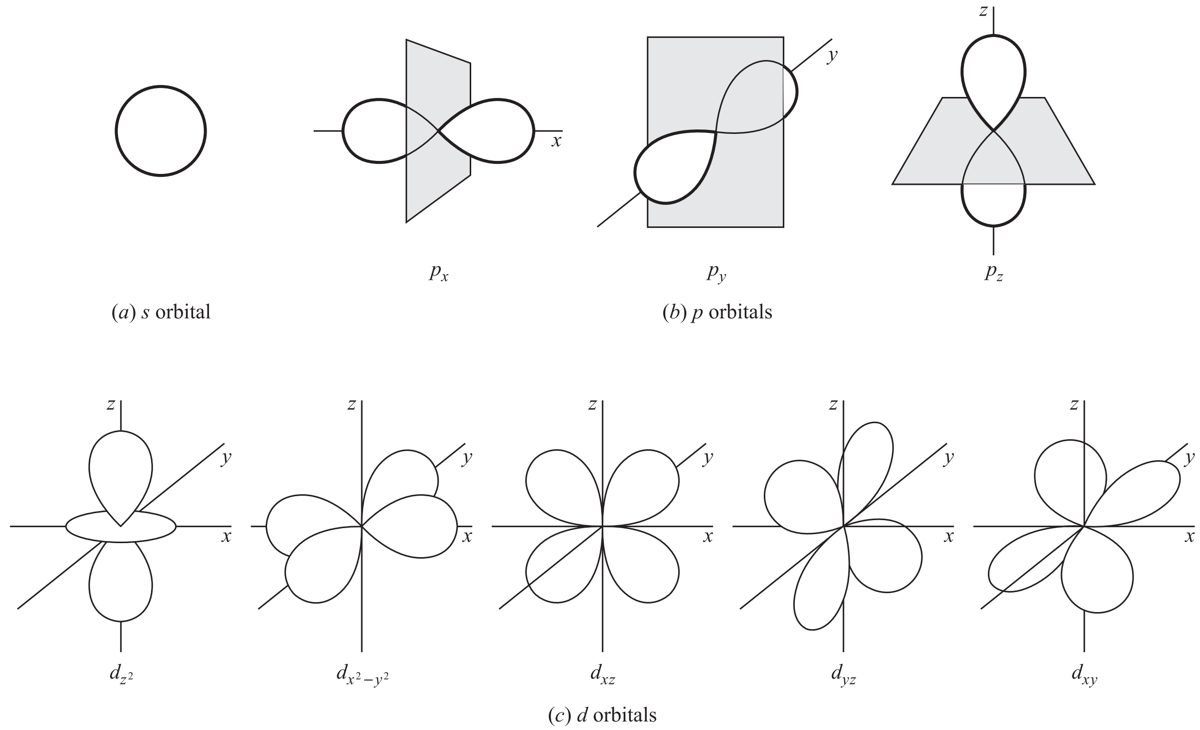


Fig. 8-3 Angular dependence of orbitals.

and y axes in the case of $d_{x^2-y^2}$ and in between the axes in the case of d_{xy}, d_{xz}, and d_{yz}. Each of these orbitals has two perpendicular nodal planes through the nucleus. The fifth d orbital, d_{z^2}, has maxima in the $+z$ and $-z$ directions and a secondary concentration in the (x, y) plane. This orbital has two conical nodal surfaces through the nucleus, one projecting above the (x, y) plane and one below. This separates the $+z$ and $-z$ lobes from the doughnut-shaped ring of probability concentrated in that plane.

THE PAULI PRINCIPLE AND THE PERIODIC LAW

The *Pauli exclusion principle* states that no two electrons in an atom may have the same set of all four quantum numbers. This principle places the following limits on the number of electrons for the various (n, l) orbital designations:

Orbital	Maximum Number of Electrons $2(2l + 1)$
s	2
p	6
d	10
f	14

Because the Schrödinger equation cannot be solved exactly for polyelectron atoms, it has become the practice to approximate the electron configuration by assigning electrons to *hydrogen-like* orbitals. These orbitals are designated by the same labels as for hydrogen's orbitals and have the same spatial characteristics described in the previous section, "Orbitals."

AUFBAU PRINCIPLE

The filling of the orbitals recognizes that electrons will first occupy those orbitals having the lowest energy. The *build-up* (*Aufbau*, German) principle describes the way electrons assort into the orbitals. Both n and l are accounted for by the process; however *screening* occurs, which reduces the nuclear charge in addition to the reduction due to distance. Essentially, an inner electron cloud screens the positive nuclear charge so that the electrons in successive orbitals are attracted less than predicted by the inverse square law (electromagnetic phenomena drop in intensity as the inverse of the square of the distance changes). Due to these factors and others which influence the process, the order for filling of the orbits can be taken as $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s$, etc., which is difficult to memorize. Figure 8-4 displays a layout that is easy to set up and remember. Note that the rows are the orbitals predicted to fill and the filling order is indicated by a set of diagonal arrows. The Aufbau principle predictions are for the configurations in their ground (lowest energy) state. An exception to the sequence exists and is covered by Problem 8.10.

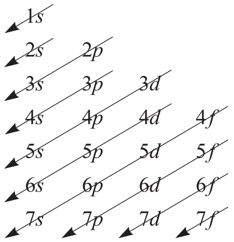


Fig. 8-4

Note: All electron configurations in this book are in the ground state unless otherwise indicated.

ELECTRON CONFIGURATIONS

The position of an element in the Periodic Table of the Elements (inside front cover) is a clue to the configuration of the outermost electron shell. Let n be the number of the period in which the element is found on the table and the superscript on s state the number of electrons in the s orbital. The group IA and IIA (1 and 2) electron configurations are ns^1 and ns^2. The other A groups, IIIA to VIIIA (13 to 18), have the configurations ns^2np^1 to ns^2np^6. These two sets of elements are the main group elements and are often referred to as the *s-block* and *p-block* elements. The exception to the pattern is helium ($1s^2$), which, although in group VIIIA, does not have sufficient electrons to conform to the group's configuration.

The *transition metals* in periods 4 and 5 have the outer configurations of $ns^2(n-1)d^1$ to $ns^2(n-1)d^{10}$, but there are some anomalies and the filling of the d shell is not uniform; refer to your text. The transition metals in periods 6 and 7 fill the $(n-2)f$ oribtals before the $(n-1)d$'s are completed. There are many anomalies in the course of filling the f shell. The *lanthanides*, period 6, and the *actinides*, period 7, are displayed separately below the body of the table and are handled by the guidelines outlined.

The outermost electrons, often called the *valence electrons*, are primarily responsible for the chemical properties of the elements. It follows that the elements in a specific group will show similar characteristic *oxidation numbers* (*charges*, also called *valences*) and display a trend in characteristics. Even though electron configurations were not known when the earliest periodic tables were formulated, the elements were placed by similarity of characteristics.

When considering the filled orbitals, it is important to note that electrons are in pairs as shown below. However, the individual orbitals fill one electron at a time until the orbital is completed. The electrons in unfilled orbitals can be represented by upward and downward arrows that indicate the opposite spins of the electrons in a pair. Figure 8-5 shows the placement of the p electrons in order represented by superscripts and the filled orbital with the electrons represented by the arrows commonly sketched; the d and f orbitals are handled similarly. Arrows are placed upward in the order of filling (1→3), then downward (4→6) to form pairs.

Fill order: $p_x^1 p_x^2 p_z^3$ then $p_x^4 p_y^5 p_z^6$ providing $p_x^{1,4} p_x^{2,5} p_x^{3,6}$

For the filled orbitals: $p_x^{\uparrow\downarrow} p_y^{\uparrow\downarrow} p_z^{\uparrow\downarrow}$

Fig. 8-5

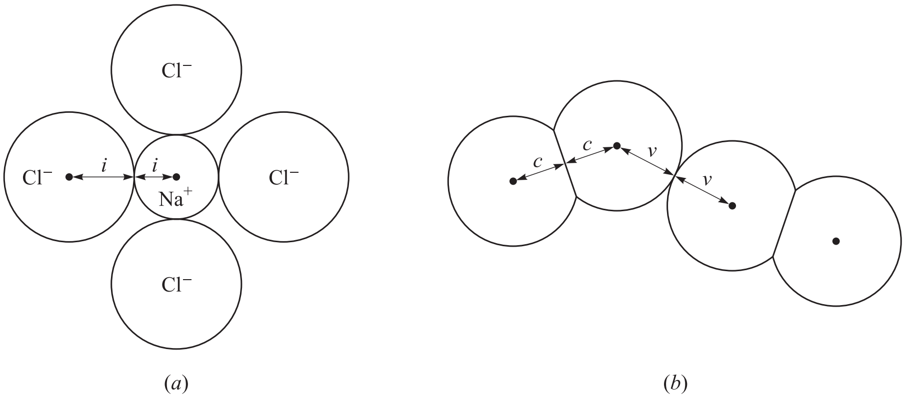
The inner electrons, those below the valence electrons, are arranged as is the noble gas element (Group VIIIA) before the element under consideration. If we were to consider titanium (Ti, $Z = 22$), the electron configuration could be expressed as $[\mathrm{Ar}]3d^2 4s^2$. Note that, although the Aufbau principle indicates the $4s$ filling before the $3d$, it is common practice to present the electron configuration in numerical order with respect to n, rather than the filling order.

ATOMIC RADII

The electron cloud around an atom makes the concept of atomic size somewhat imprecise. Even so, it is useful to refer to an atomic size or an atomic radius. Operationally, one can divide the experimentally determined distance between the centers of two chemically bonded atoms to arrive at the two atomic radii. If the bonding is covalent (see Chapter 9), the radius is called a *covalent radius*; if the bonding is ionic, the radius is an *ionic radius*. The radius for a nonbonded situation may also be defined in terms of the distance of closest nonbonding approach and is called a *van der Waals radius*. These concepts of size are illustrated in Fig. 8-6.

The following generalizations are observed regarding atomic size:

1. Within a given group of the Periodic Table, the radius increases with increasing atomic number. This fact is related to the increased n of the outermost shell.
2. Within a given period of the Periodic Table, the covalent radii generally decrease with increasing atomic number. This is related to the facts that (i) the size of an atom depends on the average distance of its outermost electron(s), (ii) there is no change in n of the outermost electron(s) within a given period, and (iii) there is increasing nuclear charge with increasing atomic number.
3. Ionic radii of *cations* (positive ions) are fairly small compared to the covalent radii for the corresponding atoms since all the outermost electrons (highest n) are usually removed. The radii of *anions* (negative ions) are only slightly larger than the van der Waals radii for the corresponding atoms since the extra electron(s)



(*a*) (*b*)

Fig. 8-6 (*a*) Portion of NaCl crystal showing the ionic radii (*i*). (*b*) Two Cl_2 molecules in contact in liquid chlorine showing the covalent radii (*c*) and the van der Waals radii (*v*).

have the same *n*. However, the covalent radii of these atoms are appreciably less since they are bonded to their neighbors by electron sharing.

4. Within a given group, ionic radii increase with increasing atomic number. Within a given period, the radii of cations decreases with increasing atomic number, as do the radii of anions. Note that the radius of the last cation and the first anion in a given period do not conform to the trend. The reason is that an ion becomes a cation by electron(s) loss, but an anion is the result of the gain of an electron(s).

IONIZATION ENERGIES

The Bohr formula for the hydrogen atom energy levels predicts that higher energy levels get closer and closer together and tend to approach a limit of zero as $n \to \infty$. At this limit, the atom has been ionized. The minimum energy required to ionize an isolated gaseous atom may be determined by spectroscopic, thermochemical, or electrical means. In the electrical method, a measurement is made of the accelerating potential that will impart to a *projectile electron* (not the electron within the atom) an amount of kinetic energy just sufficient to dislodge the bound electron from its atom. This means that the ionization energy can be measured directly in electrical terms. The *electron volt*, *ev*, is the energy imparted to one electron accelerated by a potential difference of 1 V (*Note*: 1 V = 1 J/C). The value of an electron volt is expressed as follows:

$$1\,\text{eV} = (e^{-}\text{'s charge}) \times (\text{potential difference}) = (1.6022 \times 10^{-19}\,\text{C}) \times (1\,\text{J/C}) = 1.6022 \times 10^{-19}\,\text{J}$$

Ionization energies, I.E., have been measured for all the atoms. They are all positive, corresponding to an endothermic process. Some interesting trends have been observed.

1. Within a given group of the periodic table, the first ionization energy decreases with increasing atomic number. This is related to the increase in atomic radius and the decreasing attraction of the nucleus for the increasingly distant outermost electron. It should be mentioned that this trend is not uniformly noted for the transition metals.

2. Within a given period, the trend is an increase in ionization energy with increasing atomic number. However, atoms just beginning a new subshell or the second half of a subshell may have a smaller ionization energy than the previous atom.

3. The ionization of each succeeding stage of ionization is always greater than for the preceding state. As an example, the second ionization energy of magnesium is considerably greater than the first (about twice

as great) because the Mg^{2+} has twice the electron static attraction for the removed electron as does Mg^{1+}. However, the second ionization energy of sodium is many times the first because the second electron must be removed from the $n = 2$ shell rather than the $n = 3$ shell (further from the nucleus).

ELECTRON AFFINITY

Some free atoms can capture an extra electron to form a stable gaseous anion, particularly with elements having almost-completed *p* subshells (Groups VIA and VIIA, especially). For example,

$$\text{Cl}(g) + e^-(g) \rightarrow \text{Cl}^-(g) \qquad \Delta H = -349\,\text{kJ/mol (exothermic)}$$

For most elements, the first electron gained is *exothermic* (energy given off). Chlorine's electron affinity (E.A.) is −349 kJ per mole of electrons gained. The higher the first electron affinity (chlorine's is high), the more likely the element is to form an anion. The electron affinities of the elements display loose trends to increase in a period with the atomic number.

MAGNETIC PROPERTIES

The magnetic properties of matter depend on the properties of the individual atoms. We have noted that electron spin has a magnetic moment associated with it. Two electrons occupying the same orbital (same n, l, and m_l) have their magnetic moments canceled out because the two values of m_s are of equal magnitude and have opposite spin angular momentum (equal but opposed magnet moment). This means that atoms, ions, or compounds in which at least one orbital is singly occupied then have a net magnetic moment. Such a substance is said to be *paramagnetic* and is attracted into a magnetic field. The magnitude of the magnetic moment (and the number of unpaired electron spins) can be determined experimentally by measuring the force of attraction of an externally imposed magnetic field for the substance. Substances without unpaired electron spins do not have magnetic moments and are repelled by a magnetic field; they are referred to as being *diamagnetic*. The repulsion of diamagnetic substances is much smaller in magnitude than the attraction of paramagnetic substances.

Magnetic measurement is an important experimental tool for determining the electron assignment into orbitals for atoms, ions, and compounds. Several rules have been developed for the assignment of electrons within a subshell.

1. Electrons within a subshell for which $l > 0$ tend to avoid pairing within the same orbital. This rule is Hund's rule and reflects the relatively greater electrostatic repulsion between two electrons in the same orbital as compared with occupancy of two orbitals having differing values for m_l.
2. Electrons in singly occupied orbitals tend to have their spins in the same direction so as to maximize the net magnetic moment.
3. Looking at the electron configuration allows for a prediction whether or not an atom (or ion) is paramagnetic. Note that the prediction only applies to the free individual atom. Any firm conclusion based on the prediction is risky when applied to collections of atoms (or ions). For example, the aluminum atom has one unpaired electron, but a piece of aluminum is diamagnetic.

Solved Problems

ENERGY RELATIONSHIPS

8.1. Determine the frequencies of electromagnetic radiation of the following wavelengths: (*a*) 0.10 nm; (*b*) 5000 Å; (*c*) 4.4 μm; (*d*) 89 m; (*e*) 562 nm.

The basic equation is

$$\nu = \frac{2.998 \times 10^8\ \text{m/s}}{\lambda}$$

(*a*) $$\nu = \frac{2.998 \times 10^8\ \text{m/s}}{0.10 \times 10^{-9}\ \text{m}} = 3.0 \times 10^{18}\text{s}^{-1} = 3.0 \times 10^{18}\ \text{Hz}$$

(*b*) $$\nu = \frac{2.998 \times 10^8\ \text{m/s}}{(5000\ \text{Å})(10^{-10}\ \text{m/Å})} = 5.996 \times 10^{14}\ \text{Hz} = 599.6\ \text{THz}$$

(*c*) $$\nu = \frac{2.998 \times 10^8\ \text{m/s}}{4.4 \times 10^{-6}\ \text{m}} = 6.8 \times 10^{13}\ \text{Hz} = 68\ \text{THz}$$

(*d*) $$\nu = \frac{2.998 \times 10^8\ \text{m/s}}{89\ \text{m}} = 3.4 \times 10^{6}\ \text{Hz} = 3.4\ \text{MHz}$$

(*e*) $$\nu = \frac{2.998 \times 10^8\ \text{m/s}}{562 \times 10^{-9}\ \text{m}} = 5.33 \times 10^{14}\ \text{Hz} = 533\ \text{THz}$$

8.2. (*a*) What change in molar energy (J/mol) would be associated with an atomic transition giving rise to radiation at 1 Hz? (*b*) For any given photon, what is the numerical relationship between its wavelength in nanometers and its energy in electron volts?

(*a*) If each of N_A atoms gives off one 1-Hz photon,

$$\Delta E = N_A(h\nu) = (6.022 \times 10^{23}\ \text{mol}^{-1})(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})(1\ \text{s}^{-1}) = 3.990 \times 10^{-10}\ \text{J}\cdot\text{mol}^{-1}$$

Since ΔE and ν are proportional, we may treat the ratio

$$\frac{3.990 \times 10^{-10}\ \text{J}\cdot\text{mol}^{-1}}{1\ \text{Hz}}$$

as a "conversion factor" between Hz and $\text{J}\cdot\text{mol}^{-1}$, provided we understand just what this "conversion" means. Then, for 1-MHz (10^6 Hz) radiation,

$$\Delta E = (10^6\ \text{Hz})(3.990 \times 10^{-10}\ \text{J}\cdot\text{mol}^{-1}\cdot\text{Hz}^{-1}) = 3.990 \times 10^{-4}\ \text{J}\cdot\text{mol}^{-1}$$

(*b*) First, let us find the frequency equivalent of 1 eV from the Planck equation, then find the wavelength from the frequency.

$$\nu = \frac{\varepsilon}{h} = \frac{1.6022 \times 10^{-19}\ \text{J}}{6.626 \times 10^{-34}\ \text{J}\cdot\text{s}} = 2.4180 \times 10^{14}\ \text{s}^{-1}$$

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8\ \text{m}\cdot\text{s}^{-1}}{2.4180 \times 10^{14}\ \text{s}^{-1}} = (1.2398 \times 10^{-6}\ \text{m})(10^9\ \text{nm/m}) = 1239.8\ \text{nm}$$

Because of the inverse proportionality between wavelength and energy, the relationship may be written as

$$\lambda\varepsilon = hc = 1239.8\ \text{nm}\cdot\text{eV}$$

8.3. In the photoelectric effect, an absorbed quantum of light results in the ejection of an electron from the absorber. The kinetic energy of the ejected electron is equal to the energy of the absorbed photon minus the energy of the longest-wavelength photon that causes the effect. Calculate the kinetic energy of a photoelectron (eV) produced in cesium by 400-nm light. The critical (maximum) wavelength for the photoelectric effect in cesium is 660 nm.

Using the result of Problem 8.2(*b*),

$$\text{Kinetic energy of electron} = h\nu - h\nu_{\text{crit}} = \frac{hc}{\lambda} - \frac{hc}{\lambda_{\text{crit}}}$$
$$= \frac{1240\,\text{nm}\cdot\text{eV}}{400\,\text{nm}} - \frac{1240\,\text{nm}\cdot\text{eV}}{660\,\text{nm}} = 1.22\,\text{eV}$$

8.4. It has been found that gaseous iodine molecules dissociate into separate atoms upon absorption of light at wavelengths less than 499.5 nm. If each quantum is absorbed by one molecule of I_2, what is the minimum input, in kJ/mol, needed to dissociate I_2 by this photochemical process?

$$E_{\text{per mol}} = N_A(h\nu) = \frac{N_A hc}{\lambda} = \frac{(6.022\times10^{23}\,\text{mol}^{-1})(6.626\times10^{-34}\,\text{J}\cdot\text{s})(2.998\times10^{8}\,\text{m}\cdot\text{s}^{-1})}{499.5\times10^{-9}\,\text{m}}$$
$$= 239.5\,\text{kJ/mol}$$

8.5. A beam of electrons accelerated through 4.64 V in a tube containing mercury vapor was partly absorbed by the vapor. As a result of absorption, electronic changes occurred within a mercury atom and light was emitted. If the full energy of a single incident electron was converted into light, what was the wave number of the emitted light?

Using the result of Problem 8.2(*b*),

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{h\nu}{hc} \quad \text{and} \quad \tilde{\nu} = \frac{4.64\,\text{eV}}{1240\,\text{nm}\cdot\text{eV}} = 0.00374\,\text{nm}^{-1} = 37{,}400\,\text{cm}^{-1}$$

8.6. An electron diffraction experiment was performed with a beam of electrons accelerated by a potential difference of 10 keV. What was the wavelength of the electron beam in nm?

We can use the de Broglie equation; take the mass of an electron as 0.922×10^{-30} kg. The velocity of the electron is found by equating its kinetic energy, $\frac{1}{2}mv^2$, to the 10 keV loss of electric potential energy.

$$\tfrac{1}{2}mv^2 = (10^4\,\text{eV})(1.602\times10^{-19}\,\text{J/eV})$$
$$= 1.602\times10^{-15}\,\text{J} = 1.602\times10^{-15}\,\text{kg}\cdot\text{m}^2\cdot\text{s}^{-2}$$

and
$$v = \left(\frac{2\times1.602\times10^{-15}\,\text{kg}\cdot\text{m}^2\cdot\text{s}^{-2}}{0.911\times10^{-30}\,\text{kg}}\right)^{1/2} = (35.17\times10^{14})^{1/2}\,\text{m/s} = 5.93\times10^{7}\,\text{m/s}$$

Now, the de Broglie equation gives us

$$\lambda = \frac{h}{mv} = \frac{6.63\times10^{-34}\,\text{J}\cdot\text{s}}{(0.911\times10^{-30}\,\text{kg})(5.93\times10^{7}\,\text{m/s})}$$
$$\lambda = \frac{1.23\times10^{-11}\,\text{kg}\cdot\text{m}^2\cdot\text{s}^{-1}}{\text{kg}\cdot\text{m}\cdot\text{s}^{-1}} = (1.23\times10^{-11}\,\text{m})(10^{9}\,\text{nm/m}) = 0.0123\,\text{nm}$$

The results calculated above are somewhat in error because of the law of relativity, which becomes more and more relevant as the velocity approaches the speed of light. For instance, for a potential difference of 300 kV, the velocity calculated as above would exceed *c*, an invalid result since no particle can have a velocity greater than the speed of light.

ATOMIC PROPERTIES AND THE PERIODIC LAW

8.7. The Rydberg constant for deuterium (^{2}H or ^{2}D) is 109,707 cm^{-1}. Calculate (*a*) the shortest wavelength in the absorption spectrum of deuterium, (*b*) the ionization energy of deuterium, and (*c*) the radii of the first three Bohr shells (orbits).

(*a*) The shortest-wavelength transition would correspond to the highest frequency and to the highest energy. The transition would be from the lowest energy state (the *ground state*), for which $n = 1$, to the highest, for which $n = \infty$.

$$\tilde{\nu} = R\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) = R = 109{,}707\,\text{cm}^{-1}$$

$$\lambda = \frac{1}{109{,}707\,\text{cm}^{-1}} = (0.91152 \times 10^{-5}\,\text{cm})(10^7\,\text{nm/cm}) = 91.152\,\text{nm}$$

(*b*) The transition calculated in (*a*) is indeed the ionization of the atom in its ground state. From the result of Problem 8.2(*b*),

$$\text{I.E.} = \frac{1239.8\,\text{nm}\cdot\text{eV}}{91.152\,\text{nm}} = 13.601\,\text{eV}$$

This value is slightly greater than the value for ^{1}H.

(*c*) From the equation ($Z = 1$),

$$r = n^2 a_0 = n^2(5.29 \times 10^{-11}\,\text{m})$$

The radii are 1, 4, and 9 times a_0, or 0.529, 2.116, and 4.76 Å. The reduced-mass correction, involving an adjustment of 3 parts in 10^4, is not significant and a_0 for the first Bohr shell of ^{1}H is a good substitution.

8.8. (*a*) Neglecting reduced-mass effects, what optical transition in the He$^+$ spectrum would have the same wavelength as the first Lyman transition of hydrogen ($n = 2$ to $n = 1$)? (*b*) What is the second ionization energy of He? (*c*) What is the radius of the first Bohr orbit for He$^+$?

(*a*) He$^+$ has only one electron. It is classified as a hydrogen-like species with $Z = 2$, and the Bohr equations may be applied. From the equation

$$\tilde{\nu} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

the first Lyman transition for hydrogen would be given by

$$\tilde{\nu} = R\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

The assumption regarding reduced-mass effects is equivalent to considering R for He$^+$ the same as for ^{1}H. The Z^2-term can just be compensated by increasing n_1 and n_2 by a factor of 2 each.

$$\bar{\nu} = R(2^2)\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

The transition in question is then the transition from $n = 4$ to $n = 2$.

(*b*) The second ionization energy for He is the same as the first ionization energy for He$^+$, and the Bohr equations may be applied to the ground state of He$^+$ for which $Z = 2$ and $n = 1$.

$$\tilde{\nu} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = R(2)^2\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) = 4R$$

The result is 4 times the result for deuterium in Problem 9.7. Since $\tilde{\nu}$ is proportional to energy, the ionization energy will likewise be 4 times that for deuterium.

$$\text{I.E.}(\text{He}^+) = 4 \times \text{I.E.}(^2\text{H}) = 4 \times 13.6\,\text{eV} = 54.4\,\text{eV}$$

(*c*)

$$r = \frac{n^2 a_0}{Z} = \frac{0.529\text{Å}}{2} = 0.264\ \text{Å}$$

8.9. (*a*) Write the electron configurations for the ground states of N, Ar, Fe, Fe^{2+}, and Pr^{3+}. (*b*) How many unpaired electrons would there be in each of these isolated particles?

(*a*) The atomic number of N is 7. The first shell (orbit) will contain its maximum of 2 electrons, the next 5 electrons will be in the second shell, 2 filling the lower-energy *s* subshell (orbital) and the remaining 3 electrons filling the *p* subshell. A common notation is

$$1s^2 2s^2 2p^3 \qquad \text{or} \qquad [\text{He}]2s^2 2p^3$$

The second notation forms shows only those electrons beyond those in the noble gas (Group VIIIA or 18) found before the element in question and identifies that element in square brackets.

The atomic number of Ar is 18, which results in the filling of shells 1 through 3 (K, L, and M).

$$1s^2 2s^2 2p^6 3s^2 3p^6$$

The atomic number of Fe is 26. Beyond the electron configuration of argon, the order of filling is 4*s*, then 3*d*, until 26 electrons are assigned (8 beyond argon).

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2 \qquad \text{or} \qquad [\text{Ar}]3d^6 4s^2$$

The iron(II) ion, Fe^{2+}, contains two fewer electrons than the iron atom. Although 4*s* is of lower energy than 3*d* for atomic numbers 19 and 20 (K and Ca), this order reverses for higher nuclear charges. In general, the electrons most easily lost from any atom are those with the largest principal quantum number.

$$[\text{Ar}]3d^6$$

Pr^{3+} has 56 electrons, 3 fewer than the Pr atom (atomic number 59). The order of filling of those elements in the period following Xe is $6s^2$, then one 5*d* electron, then the whole 4*f* subshell, then the rest of the 5*d* subshell followed by the 6*p* subshell. There are frequent replacements of the first 5*d* assignment with an additional 4*f*, or one of the 6*s* with an additional 5*d*, but these irregularities are of no consequence in the assignment of electrons in Pr^{3+}. The 3 electron removed from the neutral atom to form the ion follow the general rule of removal first from the outermost shell (highest *n*) and then from the next-to-outermost (next highest *n*); in this case, the 6*s* electrons are removed first and no 5*d* electrons would remain even if there were one in the neutral atom.

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^2 5s^2 5p^6 \qquad \text{or} \qquad [\text{Xe}]4f^2$$

(*b*) Complete subshells have no unpaired electrons; it is necessary to examine only the electrons past a noble gas core.

For N, the 2*p* is the only incomplete subshell. Following Hund's rule, the three electrons in this subshell will singly occupy the three available subshells. There will be three unpaired electrons.

Argon has no incomplete subshells and, therefore, no unpaired electrons.

Fe has six 3*d* electrons in the only unfilled subshell. The maximum unpairing occurs with double occupancy of one of the available *d* subshells and single occupancy of the remaining four. There will be 4 unpaired electrons.

Fe^{2+} also has 4 unpaired electrons for the same reason as Fe.

Pr^{3+} has 2 unpaired electrons that are in two of the seven 4*f* subshells.

8.10. Nickel's electron configuration is $[\text{Ar}]3d^8 4s^2$. How can we account for the fact that the configuration of the next element, Cu, is $[\text{Ar}]3d^{10} 4s^1$?

In the hypothetical procedure of making up the electronic complement of Cu by adding one electron to the configuration of the providing element, Ni, we might have expected only a ninth 3*d* electron. For atomic number 19, the 3*d* subshell is decidedly of higher energy than is 4*s*; then potassium has a single 4*s* electron and no 3*d* electron. After the 3*d* subshell begins to fill with Sc, atomic number 21 (4*s* filled), the addition of each succeeding 3*d* electron is accompanied by a lowering of the average energy of the 3*d* level. This is because each succeeding element has an increased nuclear charge which is only partially screened from a test 3*d* electron by the additional electron in the same subshell. The energy of the 3*d* subshell decreases gradually as the subshell undergoes filling and drops below the level of the 4*s* toward the end of the transition series.

Another factor is that the configuration $3d^{10}4s^1$ has a spherically symmetrical distribution of electron density, a stabilizing arrangement characteristic of all filled or half-filled subshells. On the other hand, the configuration $3d^9 4s^2$ has a “hole” (a missing electron) in the $3d$ subshell, destroying the symmetry and any extra stabilization.

8.11. The ionization energies of Li and K are 5.4 and 4.3 eV. What can we predict for the I.E. of Na?

The first I.E. of Na should be intermediate between that of Li and K; it can be determined by a simple average of the two values. That average is 4.9 eV, which is reasonably close to the 5.1 eV observed.

8.12. The first ionization energies of Li, Be, and C are 5.4, 9.3, and 11.3 eV. What can be predicted for the ionization energies of B and N?

There is a general increasing trend in I.E. with increasing atomic number in a given period. This is true of the values we have here, but there is a larger increase between Li and Be than between Be and C. The filling of the $2s$ subshell gives Be a greater stability than would be suggested by a smooth progression across the periodic table. The next element, B, would have an I.E. that represents a balancing of two oppositely directed factors: an increase for Be because of the increased Z (nuclear charge increase) and a decrease because a new subshell is beginning to be filled in the case of B (between Be and C). We could guess that the I.E. for B would be less than that for Be—that is the case. The observed I.E. for B is 8.3 eV.

The increase in going from $Z = 5$ to $Z = 6$ is 3.0 eV. We could expect the increase in going to N ($Z = 7$) to be similar, bringing the I.E. of N to about 14.3 eV. Because of the extra stability of the half-filled p subshell, the I.E. is even greater. A value of 14.5 eV is observed.

8.13. In the ionic compound KF, the K^+ and F^- ions are found to have practically identical radii, about 0.134 nm. What can be predicted about the relative covalent radii of K and F?

The covalent radius of K should be much greater than 0.134 nm and that of F much smaller, since atomic cations are smaller than their parent atoms, while atomic ions are larger than their parents. The observed covalent radii of K and F are 0.20 and 0.06 nm.

8.14. The single covalent radius of P is 0.11 nm. What is the prediction for the single covalent radius of Cl?

P and Cl are members of the same period. Cl should have a smaller radius in keeping with the usual trend across the period. The experimental value is 0.10 nm.

8.15. The first I.E. for Li is 5.4 eV and the electron affinity of Cl is 3.61 eV. Compute ΔH (kJ/mol) for the reaction carried out at such low pressures that the resulting ions do not combine with each other.

$$\mathrm{Li}(g) + \mathrm{Cl}(g) \rightarrow \mathrm{Li}^+(g) + \mathrm{Cl}^-(g)$$

The overall reaction may be expressed as two partial reactions:

$$\begin{array}{lll} (1) & \mathrm{Li}(g) \rightarrow \mathrm{Li}^+(g) + e^-(g) & \Delta E = N_A(\text{I.E.}) \\ (2) & \mathrm{Cl}(g) + e^-(g) \rightarrow \mathrm{Cl}^-(g) & \Delta E = N_A(-\text{E.A.}) \end{array}$$

where e^- stands for an electron. Although ΔH for each of the above partial reactions differs slightly from ΔE (by the term $p\Delta V$), the ΔH of the overall reaction is the sum of the two ΔE’s (the overall volume change is zero). Since the values of I.E. and E.A. are given on a per-atom basis, the factor 6.02×10^{23} atoms/mol is required to obtain ΔH on the conventional per-mol basis.

$$\begin{aligned} \Delta H(\text{total reaction}) &= \Delta E_{(1)} + \Delta E_{(2)} = N_A(\text{I.E.} - \text{E.A.}) \\ &= (6.02 \times 10^{23})(1.8\ \text{eV})(1.60 \times 10^{-19}\ \text{J/eV}) = 170\ \text{kJ} \end{aligned}$$

Supplementary Problems

ENERGY RELATIONSHIPS

8.16. What is the wavelength in meters of the radiation from (*a*) a low-range TV station broadcasting at a frequency of 55 MHz, (*b*) an AM radio station at 610 kHz, and (*c*) a microwave oven operating at 14.6 GHz?

Ans. (*a*) 5.5 m; (*b*) 492 m; (*c*) 0.0205 m

8.17. The critical wavelength for producing the photoelectric effect in tungsten is 260 nm. (*a*) What is the energy of a quantum at this wavelength in joules and in electron volts? (*b*) What wavelength would be necessary to produce photoelectrons from tungsten having twice the kinetic energy of those produced at 220 nm?

Ans. (*a*) $7.65 \times 10^{-19}\ \text{J} = 4.77\ \text{eV}$; (*b*) 191 nm

8.18. In a measurement of the quantum efficiency of photosynthesis in green plants, it was found that 8 quanta of red light at 685 nm were needed to evolve one molecule of O_2. The average energy storage in the photosynthetic process is 469 kJ per mole of O_2 evolved. What is the energy conversion efficiency?

Ans. 33.5%

8.19. O_2 undergoes photochemical dissociation into one normal oxygen atom and one oxygen atom 1.967 eV more energetic than normal. The dissociation of O_2 into two normal oxygen atoms is known to require 498 kJ/mol O_2. What is the maximum wavelength effective for O_2's photochemical dissociation?

Ans. 174 nm

8.20. Acriflavine is a dye that, when dissolved in water, has its maximum light absorption at 453 nm, and its maximum fluorescence emission at 508 nm. The number of fluorescence quanta averages 53% of the number of quanta absorbed. Using the wavelengths of maximum absorption and emission, what percentage of absorbed energy is emitted as fluorescence?

Ans. 47%

8.21. The prominent yellow line in the spectrum of a sodium vapor lamp has a wavelength of 590 nm. What minimum accelerating potential will excite this line in an electron tube containing Na vapor?

Ans. 2.10 V

8.22. Show by substitution in the formula given in the text ("Interaction of Light with Matter") that a_0, the radius of the first Bohr orbit for hydrogen, is 5.29×10^{-11} m.

8.23. A sample of an unknown compound is exposed to light of wavelength 1080 Å. Nitrogen is found to be given off during the irradiation, hinting that there may have been N≡N bonds in the sample. Calculate the amount of energy (*bond energy*) necessary to break a mole of these bonds.

Ans. 1.1×10^3 kJ/mol

8.24. What accelerating potential is needed to produce an electron beam with an effective wavelength of 0.0256 nm?

Ans. 2.30 kV

8.25. What is the wavelength of a beam of neutrons (1.67×10^{-24} g) that has a velocity of 2.50×10^5 cm/s?

Ans. 1.59×10^{-10} m or 1.59 Å

8.26. In studies of electron spin resonance (esr) the energy differences between spin states are very small, of the order of 1×10^{-4} eV, compared with about 3 eV in visible spectroscopy. What wavelength of radiation is required for esr, and which types in Problem 8.16 does it resemble?

Ans. 0.012 m, microwave region

8.27. What accelerating potential must be imparted to a proton beam to give it an effective wavelength of 0.0050 nm?

Ans. 33 V

ATOMIC PROPERTIES AND THE PERIODIC LAW

8.28. All atoms with odd Z values must have at least one unpaired electron. Can an even Z atom have unpaired electrons? If so, give examples from the first three periods.

Ans. Yes; C, O, Si, and S

8.29. Which atoms in the first transition period ($Z = 21 - 30$) are diamagnetic? Give their configurations.

Ans. Only Zn; $[\text{Ar}]3d^{10}4s^2$

8.30. The configuration of Cr differs from that derived by the Aufbau procedure. Deduce the actual configuration and explain the anomaly.

Ans. Cr; $[\mathrm{Ar}]3d^5 4s^1$. Aufbau would give $3d^4 4s^2$, so an *s* shifts to *d* to gain the stability of the half-filled subshell. Note that the actual configuration has complete spherical symmetry.

8.31. The configurations of negative ions follow the Aufbau rule. Write the electron configurations for H^-, N^{3-}, F^-, and S^{2-}.

Ans. H^- is $1s^2$ or [He]; N^{3-} is [Ne]; F^- is [Ne]; S^{2-} is [Ar]

8.32. The Rydberg constant for Li^{2+} is $109{,}729\,\mathrm{cm}^{-1}$. (*a*) What is the long-wavelength limit in the absorption spectrum of Li^{2+} at ordinary temperatures (all the ions in ground state)? (*b*) What would be the shortest wavelength in the emission line spectrum of Li^{2+} within the visible (400 to 750 nm) region? (*c*) What would be the subshell radius of the ground state of Li^{2+}? (*d*) Li^{2+} has what ionization energy?

Ans. (*a*) 13.5 nm; (*b*) 415.4 nm ($n = 8 \rightarrow n = 5$); (*c*) 0.176 Å; (*d*) 122.4 eV

8.33. Magnesium and aluminum form an alloy used in the automobile, aerospace, and other industries requiring a light-weight, strong material for the construction of parts. (*a*) What is the complete electron configuration of each metal? (*b*) Manganese, nickel, and titanium are also used in the same industries. Provide the electron configurations of these metals. (*c*) Display the complete electron configuration for thallium, a very toxic metal that must be handled with care.

Ans. (*a*) Mg $1s^2 2s^2 2p^6 3s^2$, and Al $1s^2 2s^2 2p^6 3s^2 3p^1$
(*b*) Mn $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$;
Ni $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
Ti $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
(*c*) Tl $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^1$

8.34. The first ionization energy of Li is found experimentally to be 5.363 eV. If the electron in the second shell ($n = 2$) is assumed to move in a central field of an effective nuclear charge, Z_{eff}, consisting of the nucleus and the other electrons, by how many units of charge is the nucleus shielded by the other electrons? Assume that the ionization energy can be calculated from Bohr theory.

Ans. $Z_{\mathrm{eff}} = 1.26$; since the nuclear charge is 3+, the effective shielding by the two 1*s* electrons is 1.74 charge units.

8.35. What are the electron configurations of Ni^{2+}, Re^{3+}, and Ho^{3+}? How many unpaired electron spins are in each of these ions?

Ans. Ni^{2+} is $[\mathrm{Ar}]3d^8$ with 2 unpaired spins; Re^{3+} is $[\mathrm{Xe}]4f^{14}5d^4$ with 4 unpaired spins; Ho^{3+} is $[\mathrm{Xe}]4f^{10}$ with 4 unpaired spins.

8.36. Which shell (letter and *n* value) would be the first to have a *g* subshell? Note that two-thirds of the elements have electrons in that shell and higher. Why, then, are there no *g* electrons?

Ans. O, $n = 5$. In accord with their high *l* value (4), *g* subshells are too high in energy to receive any electrons via the Aufbau principle in known elements in their ground states.

8.37. Predict for the atomic number of the noble gas beyond Rn, if such an element had sufficient stability to be prepared or observed. Assume no *g* subshells are occupied in the preceding elements.

Ans. 118

8.38. All the lanthanides form stable compounds containing the 3+ cation. Of the few other ionic forms known, Ce forms the most stable 4+ series of ionic compounds and Eu the most stable 2+ series. Account for these unusual ionic forms in terms of their electronic configurations.

Ans. Ce^{4+} has the stable electron configuration of the noble gas, Xe. Eu^{2+}, with 61 electrons, could have the configuration $[\mathrm{Xe}]4f^7$, with the added stability of a half-filled 4*f* subshell.

8.39. For the gaseous reaction $K + F \rightarrow K^+ + F^-$, ΔH was calculated to be 91 kJ under conditions where the cations and anions were prevented by electrostatic separation from combining. K's ionization energy is 4.34 eV. What is F's electron affinity?

Ans. 3.40 eV

8.40. The ionic radii of S^{2-} and Te^{2-} are 1.84 and 2.21 Å. What would you predict for the ionic radius of Se^{2-} and for P^{3-}?

Ans. Since Se falls in between S and Te, it is expected that an intermediate value is correct; observed value is 1.98 Å. Since P is just to the left of S, a slightly larger value is expected; observed value is 2.12 Å.

8.41. Van der Waals radii for S and Cl are 1.85 and 1.80 Å, respectively. What would you predict for the van der Waals radius of Ar?

Ans. Moving toward the right in the same period, the trend is toward smaller size. The observed value is 1.54 Å.

8.42. The first ionization energy of C is 11.2 eV. Would you expect the first ionization energy of Si to be greater or less than this amount?

Ans. Less, because Si is larger; the observed value is 8.1 eV.

8.43. The first ionization energies of Al, Si, and S are 6.0, 8.1, and 10.3 eV. What would be your prediction for the first ionization energy of P?

Ans. A value of about 9.2 eV for P would be halfway between the values for Si and S, but because of the stability of the half-filled subshell, a significantly high energy might be required to remove an electron from P, perhaps higher than for S; observed value is 10.9 eV.

8.44. Several experimenters have attempted to synthesize super-heavy elements by bombarding atoms of the actinide series with heavy ions. While waiting for confirmation and acceptance of the results, some investigators in the early 1970s referred to elements 104 and 105 as *eka*-hafnium and *eka*-tantalum. Why were these names chosen?

Ans. Mendeleev had used the prefix *eka*- (Sanskrit word for first) to name elements whose existence he predicted, applying the prefix to a known element in the same periodic group as the predicted element. His *eka*-boron, *eka*-aluminum, and *eka*-silicon were later discovered, confirmed, and named scandium, gallium, and germanium. Elements 104 and 105 were predicted to have electronic structures analogous to Hf and Ta.

8.45. Consider the trends within the Periodic Table of the Elements. Suppose we knew (previous experience) that the temperature at which manganese melts (*melting point*) is 1246°C, and that of rhenium is 3186°C. What is the predicted melting point of the synthetic element technetium? Note that these elements are in group VIIB.

Ans. The general rule is that an element will have a physical characteristic between the elements directly above and below (or to the right and left) of that element. Of course, taking an average to the two elements' characteristics and rigidly declaring it to be the characteristic of the element in question is very risky. However, applying the concept, the melting point for technetium should be about 2216°C. The observed is 2157°C, which gives us a prediction reasonably close to the actual.

CHAPTER 9

Chemical Bonding and Molecular Structure

INTRODUCTION

The formulas for chemical compounds are not accidents. NaCl is a compound, but $NaCl_2$ is not. CaF_2 is a compound, but CaF is not. On the other hand, there are elements that form two, or even more, different compounds; Cu_2O and CuO exist and so do N_2O, NO, and NO_2. In the case of ionic compounds, the relative number of positive and negative ions in a formula is governed by establishing a combination that is electrically neutral (overall charge zero). In covalent compounds, structures are formed by establishing covalent bonds (electrons are shared). There is a range of covalent bonds from truly equal sharing of electrons to an extremely unequal sharing.

IONIC COMPOUNDS

Ionic bonding is the term used to indicate that a compound is composed of oppositely charged particles called *ions*. We can determine the charges on the ions by thinking in terms of the electron configuration (electronic structure) of the atoms and comparing them to the noble gas (Group VIIIA) electron configuration. Generally speaking, those metals whose atomic numbers are within 2 or 3 of a noble gas tend to form ionic compounds with nonmetals within 2–3 atomic numbers of a noble gas. The vocabulary associated with ionic compounds identifies the positive ion as the *cation* (**cat**′i′-on) and the negative ion as the *anion* (**an**′i′-on).

EXAMPLE 1 What is the empirical formula for potassium chloride? Potassium loses one electron to achieve argon's electron configuration ($8e^-$ in the outside orbit) and, because of this loss, forms the K^+ cation. Chlorine gains one electron to achieve the argon electron configuration and forms the chloride anion, Cl^-. Since compounds must be neutral, the ratio of one potassium ion to one chloride ion is the empirical formula, KCl (and also is the molecular formula). A note of interest: KCl is often used as a substitute for NaCl for those who cannot tolerate sodium, such as heart patients.

For transition metals, the lanthanides, and the actinides, no such simple rule exists. If we accept the ions' charges as chemical facts, we can still write the empirical formulas for ionic compounds so that the net (overall) charge is zero. If we had Fe^{2+} and O^{2-}, the compound would require a minimum of one of each of the elements for a neutral formula, FeO, whereas Fe^{3+} and O^{2-} would have the formula Fe_2O_3.

The naming of the binary (two participants) compounds is set by using the name of the element from which the cation is derived, e.g., Li^+ is the *lithium ion*. The names of the anions composed of a single element are formed by using the name of the element and changing the word ending to -*ide*, e.g., O^{2-} is the *oxide ion*. When two cations exist for the same element, the accepted procedure is to write the charge *per atom* in Roman numerals within parentheses directly after the name of the metal, e.g., Fe^{2+} is the *iron(II) ion*. Note that there is still some use of the older system of differentiating the two charge states with the use of *-ous* to represent the lower charge and *-ic* for the higher charge. Applying the older system, Fe^{2+} is the *ferrous ion* and Fe^{3+} is the *ferric ion*.

EXAMPLE 2 Name the two oxides of lead, PbO and PbO_2. Because oxide is −2, the lead must be +2 in the first case and +4 in the other. The names are lead(II) oxide and lead(IV) oxide, pronounced "lead two oxide" and "lead four oxide," respectively. In the older system, the Latin names were used, providing us with the names plumbous oxide and plumbic oxide, respectively. Notice that the name in the newer system gives us the charge on the cation, but the older system just tells us which cation has the higher charge or lower charge without giving us the magnitude.

Table 9-1 lists a few of the more commonly encountered polyatomic ions. These ions, their names, and their charges should be memorized.

Although hard-and-fast rules cannot be given, the following guidelines are helpful. Compounds of metals with nonmetal or polyatomic anions tend to be ionic. Compounds of nonmetals with nonmetals tend to be covalent. Physical properties can help classify compounds, also. Being hard, brittle, and having a high melting point indicates ionic compounds. Compounds liquid at room temperature and gases generally are covalent compounds. Your textbook provides you with more complete (and complex) rules for determining the character of a compound, as well as naming them.

The complex oxy-anions are named in a somewhat systematic matter by using *-ate* for the most common or most stable and *-ite* for the ion containing less oxygen. The prefix *per-* is added to an *-ate* name to indicate even more oxygen, and the prefix *hypo-* is added to an *-ite* name to indicate a lower oxygen content than in the *-ite* ion. The system takes a bit of "getting used to," but does work well.

Table 9-1 Common Polyatomic Ions

Ion	Name	Ion	Name
NH_4^+	ammonium	SO_4^{2-}	sulfate
OH^-	hydroxide	SO_3^{2-}	sulfite
CO_3^{2-}	carbonate	HSO_4^-	hydrogen sulfate
HCO_3^-	hydrogen carbonate*	ClO_4^-	perchlorate
CN^-	cyanide	ClO_3^-	chlorate
$C_2H_3O_2^-$**	acetate	ClO_2^-	chlorite
O_2^{2-}	peroxide	ClO^-	hypochlorite
NO_3^-	nitrate	CrO_4^{2-}	chromate
NO_2^-	nitrite	$Cr_2O_7^{2-}$	dichromate
PO_4^{3-}	phosphate	MnO_4^-	permanganate

*A commonly used name is *bicarbonate*. *Bi-* identifies the addition of one hydrogen ion (H^+).

**The organic chemist prefers a different representation, which is CH_3COO^-.

COVALENCE

The covalent force between atoms *sharing* two or more electrons involved in forming a chemical bond is related to *delocalization* of those electrons. The meaning of "delocalization of electrons" is that they are not where they are predicted—in the case of sharing electrons, one electron is originally in orbit about an atom and the other electron is in orbit about a different atom. The delocalization of the two electrons results in their orbiting *both* nuclei, not just one. Think in terms of smearing the electron cloud so that it no longer is located around one nucleus, but surrounds two.

When a covalent bond is formed, the distance between the two nuclei involved becomes much less than if the bond were not formed. As an example, the distance between the hydrogens in H_2 is 74 pm, whereas the sum of the distance of the van der Waals (nonbonding) radii of the two hydrogen atoms is 240 pm.

This bonding of two atoms at close approach is also reflected in energetic considerations. The energy of a bonded pair of atoms is less than the sum of the energies of the separated atoms. The *bond energy* is the magnitude of this energy lowering. From another viewpoint, the bond energy is the amount of energy, ΔE, required to break a chemical bond into two nonbonded fragments. Bond formation is exothermic and bond rupture is endothermic. Covalent bond energies range from about 150 to 550 kJ/mol for single electron-pair bonds formed among elements in the first three periods at normal temperatures.

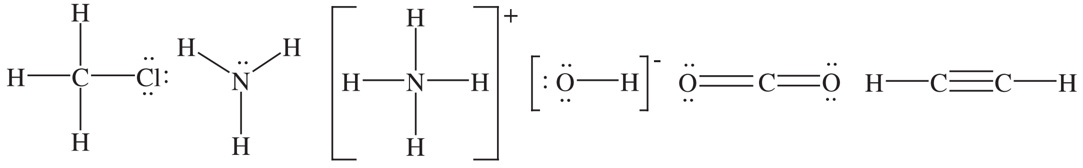
A factor associated with the covalent bonding process is that the spins of the bond-forming electrons, which are unpaired in separate atoms, become paired during the bond formation.

VALENCE-BOND REPRESENTATION

Up to this point, many of the examples provided make use of the *octet rule*. The octet rule states that the stable atom possesses eight valence electrons (the electron configuration of the previous inert gas, most of which have eight valence electrons). Some of the lighter elements, such as hydrogen and lithium, will have helium's electron configuration (two electrons in the outside shell). The electrons do not necessarily have to be in pairs and, further, electrons shared in bonding are both counted for each atom in the bond. Worthy of note is that a single covalent bond consists of a pair of shared electrons, a double bond has two shared pairs, and a triple bond has three shared pairs. Bond distances are usually shorter and bond energies are usually greater for multiple bonds than for single bonds.

Structural formulas, such as those in Fig. 9-1, are typical of the valence electron distributions in covalent molecules and ions. These structures are not meant to indicate actual bond angles, or lengths, in three-dimensional varieties like methyl chloride, ammonia, and the ammonium ion; they merely show the number of bonds connecting the participating atoms. In these *Lewis formulas* (*structures*), a *line* between two atoms represents a *pair* of shared electrons and a *dot* represents an unshared electron. Unshared electrons usually occur in pairs, *lone pairs*, on a single atom. *Two lines* constitute a *double bond*, and *three lines* constitute a *triple bond*. The total number of electrons shown in such a molecular structure is equal to the sum of the numbers of valence electrons in the free atoms: 1 for H, 4 for C, 5 for N, 6 for O, and 7 for Cl. For an ionic structure, one additional electron must be added to this sum for each unit of negative charge on the entire ion, as in OH^-. Conversely, one electron must be subtracted from the sum for each unit of positive charge on the ion, as in the ammonium ion. The number of pairs of electrons shared by an atom is called its *covalence*.

The covalence of hydrogen is always one because it cannot form more than one chemical bond. The covalence of oxygen is almost always two and occasionally one. The covalence of carbon is four in almost all of its stable compounds—there may be single, double, or triple bonds involved, but the total number of bonds is four. Although the octet rule is not a rigid rule for chemical bonding, it is obeyed for C, N, O, and F in almost all their compounds. The octet is exceeded commonly for elements in the third and higher periods.



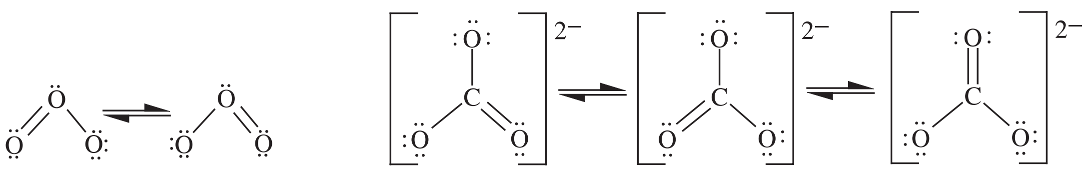
Methyl chloride Ammonia Ammonium ion Hydroxide ion Carbon dioxide Acetylene

Fig. 9-1

Resonance

Sometimes more than one Lewis structure can be written and there is no reason to select one over another—all of the structures must be used to represent the substance correctly. The true structure is said to be a *resonance* hybrid of those Lewis structures.

EXAMPLE 3 Experimentation has shown that the two terminal oxygens in ozone are equivalent, that is, they are equidistant from the central oxygen. If only one of the resonance diagrams in Fig. 9-2(*a*) were written, it would appear that one of the terminal oxygens is bonded more strongly to the central oxygen (double bond) than is the other (single bond) and that the more strongly bonded atom should be closer to the central atom. The hybrid of the two ozone structures gives equal weight to the extra bonding of the two terminal oxygen atoms. Similarly, the three resonance structures of carbonate, Fig. 9-2(*b*), are needed to account for the experimental fact that all three oxygens are equidistant from the central carbon.



(*a*) Ozone (*b*) Carbonate ion

Fig. 9-2

The total bond energy of a substance for which resonance structures are written is greater than would be expected if there were only one formal Lewis structure. This *additional* stabilization is called *resonance energy*. It arises from the same principle that is responsible for covalent bond energy, the delocalization of electrons around the atoms forming the bond. As a result of resonance in ozone, for example, the electrons constituting the second pair of the double bond are delocalized around the three oxygen atoms. The drawing of two or more resonance structures is a way to present a clear picture of the delocalization that may not be clearly presented or even possible with a single sketch.

Formal charge

Although a molecule is electrically neutral, there is a technique for identifying local charges associated with the various parts of the molecule. The algebraic sum of those charges in a molecule, of course, must equal zero. In the case of an ion, there is a net charge which is the algebraic sum of the local charges in the ion. In one method of apportioning charges to an atom in a molecule or polyatomic ion, the shared electrons in a covalent bond are divided equally between the two atoms forming the bond. (Recall that covalent bonds are formed by sharing electrons, one from one member of the bond and one from the other.) Unshared valence electrons within an atom are assigned exclusively to that atom. Each atom is then assigned a *formal charge*, *FC*, which is equal to the number of valence electrons possessed by that atom in the neutral free state *minus* the **total** number of valence electrons assigned to it (unshared e's $+ \frac{1}{2}$ each covalent bonding pair of e's). These charges may be written into the diagram of the structure.

$$FC = (\text{valence electrons}) - (\text{total number of valence electrons assigned})$$

EXAMPLE 4 Figure 9-3 shows a single resonance structure for ozone. Each oxygen is assigned a 6 due to the number of valence electrons present (a Group VIA element—6 electrons).

(1) The central oxygen is assigned just five electrons (two in the unshared pair $+ \frac{1}{2}$ of the three pairs in the bonds); this atom, being one electron short of the complement of six in a free oxygen atom, is assigned +1 ($FC = 6 - 5 = +1$).

(2) The terminal oxygen connected by the single bond is assigned 7 (6 in unshared pairs and 1 from the bond); therefore, $FC = 6 - 7 = -1$.

(3) The doubly bound oxygen on the left is assigned 6 (4 in the unshared pairs plus half of the two shared pairs), providing us with the $FC = 6 - 6 = 0$.

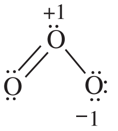


Fig. 9-3

A rough rule useful in predicting one allowable Lewis structure over another is that structures minimize the number of formal charges. Especially to be avoided are formal charges of magnitude greater than 1 and structures in which formal charges of the same sign are located on adjacent atoms.

Dipole moments and electronegativity

There are some experimental procedures that give information about the *actual* distribution of charges within a molecule (as distinct from the arbitrary assignment of formal charges). One such procedure is the measurement of *dipole moment*. An electric dipole is a neutral object that has a positive charge of a magnitude q and a separately located equal, but opposite, negative charge (the charges cancel to neutrality). The extent to which a dipole is aligned in an electric field is dependent on the dipole moment (measurable), which is defined as the product of q and the distance, d, separating the (+) and (−) charges.

In a covalent diatomic molecule the dipole member would be expected to be zero if the bonding electrons were shared truly equally by the two atoms. This is the case in molecules which are of the type X_2 (H_2, N_2, etc.), where two identical atoms are bonded. In the more general type, XY, two different kinds of atoms are bonded (C—H, N=O, etc.), and a dipole moment is usually observed. This is explained by imagining that one of the atoms, Y, has a greater attraction for the shared electrons in the bond than does X. Y is said to have a greater *electronegativity* than X. Electronegativity correlates with other atomic properties; in general, atoms with high ionization energies and/or high electron affinities tend to have high electronegativities. The most electronegative elements in order of decreasing electronegativity are $F > O > N \cong Cl$. Metals are less electronegative than nonmetals. Of note is that carbon is only slightly more electronegative than hydrogen, especially when considering organic molecules.

Hybrid orbitals

The assignment of electrons to the various atomic orbitals (Chapter 8) concerned the electron distribution in the *ground state* (the state having the lowest energy) of an isolated *free* atom. From the following ground-state configurations of elements in the second period except fluorine (can you recall why?), one might predict that the maximum covalence of an element would be equal to the number of unpaired electrons. This would be assumed since an unpaired electron from each of the bonding atoms participates in the covalent bond formation, as described above.

B	$[He]2s^2 2p^1$	or	$[He]2s^{\uparrow\downarrow}2p_x^{\uparrow}$
C	$[He]2s^2 2p^2$	or	$[He]2s^{\uparrow\downarrow}2p_x^{\uparrow}2p_y^{\uparrow}$
N	$[He]2s^2 2p^3$	or	$[He]2s^{\uparrow\downarrow}2p_x^{\uparrow}2p_y^{\uparrow}2p_z^{\uparrow}$
O	$[He]2s^2 2p^4$	or	$[He]2s^{\uparrow\downarrow}2p_x^{\uparrow\downarrow}2p_y^{\uparrow}2p_z^{\uparrow}$

Noticing where the unpaired electrons are located, the maximum covalences of B, C, N, and O should then be 1, 2, 3, and 2, respectively. These predictions account for most of the known compounds and complex ions of nitrogen (e.g., NH_3, NO_3^-) and of oxygen (e.g., H_2O, CH_3OH, HOOH), but not for the commonly observed trivalence (+3) of B (e.g., BI_3), or the tetravalence (±4) of carbon (e.g., CH_4, CCl_4, CH_3OH).

Let us take a second look at the electron configurations above and attempt an explanation for the charge (oxidation number, valence) of +3 for boron, as in BI_3, just mentioned. The electronegativities of these two elements are very close, implying that the bond between them is, in fact, covalent. Since there are to be three pairs of shared electrons, but the electron configuration provided, $[\mathrm{He}]2s^{\uparrow\downarrow}2p_x^{\uparrow}$, only allows one covalent bond to form, there must have been another electron configuration before all three bonds formed. Since the 2*s* and 2*p* subshells (orbitals) are in the same shell (orbit) and their energy levels are reasonably close, the application of sufficient energy to the 2*s* electrons will result in one of the electrons being boosted out of the next *empty* subshell, $2p_x$, resulting in three unpaired electrons.

$$[\mathrm{He}]2s^{\uparrow\downarrow}2p_x^{\uparrow} \qquad \text{becomes} \qquad [\mathrm{He}]2s^{\uparrow}2p_x^{\uparrow}2p_y^{\uparrow}$$

Your textbook tells you that the arrows represent the opposite characteristics of electrons, ↑↓ represents a pair of electrons, but ↑ is an unpaired electron. Notice that the 2*s* electron that is boosted to the $2p_y$ subshell reversed its characteristics, as indicated by the downward arrow in 2*s* becoming an upward arrow in the $2p_t$ subshell. Some energy is required to form this *hybrid orbital* and, more loosely, *bond hybridization*, as the electron is boosted from a lower energy level to a higher one; also, some energy is used to reverse the electron's characteristics.

The above explanation accounts for the number of covalent bonds formed by boron and carbon, but not for the equivalence of these bonds. The difference in spatial character of *s* and *p* orbitals (Fig. 8-3) and their energies might suggest differences in the bonds they formed, as measured by bond energy, bond distance, or bond angles. Experiment shows that all three bonds in BF_3 are equivalent, that the angles between any two bonds are the same, and that the three fluorine atoms lie at the corners of an equilateral triangle with the boron atom in the center. Similarly, in CH_4 all four bonds are equivalent, the angles between any two bonds are the same, and the four hydrogen atoms lie at the corners of a regular tetrahedron (Fig. 9-4) with the carbon atom at the center.

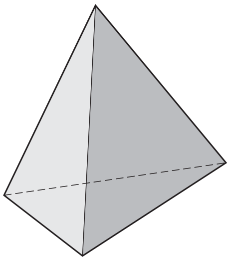


Fig. 9-4

The equivalence of the bonds in BF_3, CH_4, and similar compounds was first explained by Linus Pauling. To accommodate the surrounding atoms, *s* and *p* orbitals of a given atom may mix with each other, or *hybridize*. The mathematical formulations of the *hybrid orbitals* are simple linear combinations of the mathematical formulations of the separate *s* and *p* orbitals. The geometrical description of each hybrid orbital is a kind of superposition of the mappings of the separate *s* and *p* orbitals. Pauling showed that one *s* and three *p* orbitals are hybridized to give maximum concentration of the electron probability distribution along some particular direction (to best form a bond along this direction); the four resulting so-called sp^3 hybrid orbitals indeed point to the corners of a regular tetrahedron. The angle of $109°289'$ is made by any two bonds (lines) connecting the center of a regular tetrahedron with atoms at the corners (Problem 9.18). This is the observed situation in CH_4, CCl_4, SiF_4, and many compounds of the Group IVA elements.

A similar hybridization of one *s* with two *p* orbitals leads to a set of sp^2 hybrid orbitals which have their maximum concentrations along a set of lines in one plane forming angles of 120° with each other. This is the observed situation in BF_3. The angles are close to 120 in C_2H_4, in which each of the two carbon atoms forms a set of sp^2 hybrid orbitals, as in Fig. 9-5. The first of two other important types of hybrid orbitals are the *sp* type in which the two orbitals point in directions leading to a 180° bond angle (Fig. 9-6). The other hybridization results in the d^2sp^3 type in which the six orbitals point to the corners of a regular octahedron (Fig. 9-7), the situation in SF_6 and many coordination compounds.

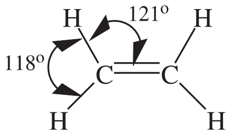


Fig. 9-5

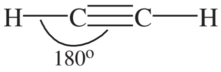


Fig. 9-6

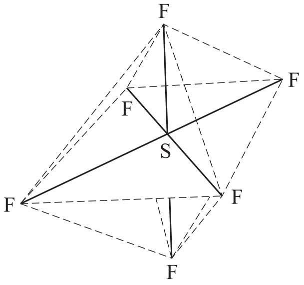


Fig. 9-7

MOLECULAR-ORBITAL REPRESENTATION

The valence electrons in Lewis structures are described as being either unshared electrons localized on particular atoms or shared electrons assigned to bonds linking particular pairs of atoms. An alternative representation handles the electrons by assigning them to *molecular orbitals* (MOs) appropriate to the molecule as a whole. Just as an atomic orbital is the mathematical solution of a Schrödinger equation describing the probability distribution of the various positions that an electron having a given set of quantum number may occupy around the atomic nucleus, so a molecular orbital describes the distribution of positions in a molecule available to an electron having a given set of quantum number. Molecular orbitals may be approximated by writing mathematical combinations of the atomic orbitals of the constituent atoms or they may be pictured, at least in qualitative terms, as geometrical combinations of the contributing atomic orbitals. The rules governing the use of molecular orbitals are:

1. The total number of molecular orbitals (MOs) equals the sum of the number of atomic orbitals (AOs) of the constituent atoms.
2. Each orbital can hold 0, 1, or 2 electrons, corresponding to the possibility of two different directions of electron spin and the application of the Pauli principle.
3. When several MOs of equal or almost equal energy exist, electrons tend to fill those orbitals so as to maximize the number of unpaired electron spins. The more nearly equal the energy levels, the greater this tendency (*Hund's rule*).
4. The directions in space describing the orientation of the orbitals, although arbitrary in the case of the free atom (Fig. 8-3), are related to the positions of neighboring atoms in the case of molecules or complex ions.
5. A molecular orbital is most likely to be composed of AOs of similar energy levels.
6. In diatomic molecules, or more generally in localized two-center bonds, orbitals of two atoms that may be combined to form an MO are those that have the same symmetry about the axis between the two atomic centers in the bond. This rule does not extend to constructing MOs that extend over three or more atoms; more complicated rules would be necessary.
7. A two-centered orbital with high electron probability in the region between the nuclei is a *bonding* orbital. A stable chemical bond exists when the number of electrons in bonding orbitals exceeds the number in antibonding orbitals.

The direction properties of molecular orbitals are governed by quantum numbers analogous to the atomic quantum number l and m_l. Greek letters are used in molecular orbital notation to designate increasing values of the l-type quantum number, σ, π, δ, etc., analogous to the Latin letters s, p, d, etc., for atomic orbitals. Only σ and π orbitals will be considered in this book. There are two kinds of σ orbitals, bonding and antibonding (Fig. 9-8). An antibonding orbital is designated with a superscript asterisk applied to the Greek letter, as σ^*, π^*, etc. A bonding orbital has a region of electron overlap (high probability) between the bonded atoms and has a lower energy than either of the component AOs. An antibonding orbital has a nodal plane (region of zero probability) between the bonding atoms and is perpendicular to the bond axis; its energy is greater than that of either constituent AO.

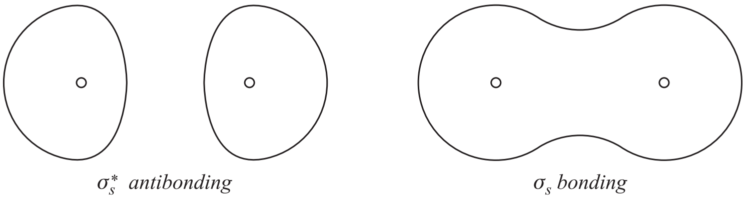


Fig. 9-8

If the bond axis is designated by x, σ bonds can be formed by combining any two of the following atomic orbitals, each of which has a region of high electron probability lying along the x axis and is cylindrically symmetrical about it: s, p_x, $d_{x^2-y^2}$, or hybrid orbitals pointing along the x axis. If the bond axis is z, σ orbitals may be formed from s, p_z, d_{z^2}, or appropriate hybrids. If the bond axis is y, the component atomic orbitals for σ orbitals are s, p_y, $d_{x^2-y^2}$, or appropriate hybrids.

A π orbital related to a bond in the x direction is characterized by having a zero value at all points along the x axis. π_y orbitals, having their maximum probabilities in the $+y$ and $-y$ directions (that is, above and below the xz plane), may be formed from p_y atomic orbitals. Similarly, π_z orbitals having their maximum probabilities above and below the xy plane may be formed from p_z AOs, π orbitals may also be bonding or antibonding (Fig. 9-9). A d_{xy} orbital may combine with a p_y orbital, or a d_{xz} with a p_z to form π orbitals.

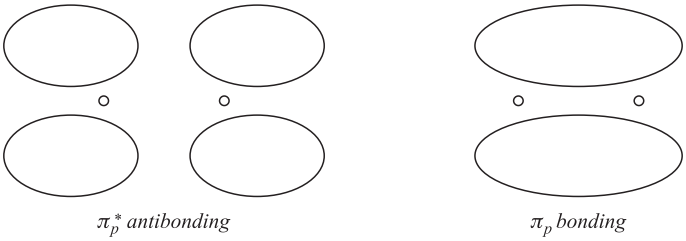


Fig. 9-9

Nonbonding AOs are those which do not interact with orbitals of other atoms because:

1. The two atoms are too far apart for good orbital overlap (e.g., the case of nonadjacent atoms).
2. The energy of the nonbonding orbital is not close to that of any orbital on the adjacent atom (e.g., the 3s orbital of Cl is of much lower energy than the 1s orbital of H in HCl).
3. The nonbonding orbital is in an inner shell and would not overlap with an orbital even of the neighboring atom (e.g., the K electrons in F_2).
4. The nonbonding orbital does not match its symmetry with any available orbital of the adjacent atom (e.g., the 3p_y of Cl does not have a symmetry match with the 1s of H in HCl, where x is the bonding direction and the 2p_y orbital of H is too high in energy to enter the picture).

A nonbonding orbital has the same energy as in the free atom. Electrons occupying nonbonding orbitals correspond to the unshared electrons in Lewis structures.

A buildup principle analogous to that for atoms exists for molecules. The order of filling MOs from the valence shells in the case of *homonuclear* diatomic molecules where x is the bond axis is

$$\sigma_s < \sigma_s^* < \pi_y = \pi_z < \sigma_{p_x} < \pi_y^* = \pi_z^* < \sigma_{p_x}^*$$

The ordering may change for *heteronuclear* diatomic molecules and for homonuclear molecules at the point where this complete set of orbitals is about half-filled.

The *bond order* in a diatomic molecule is defined as one-half the difference between the number of electrons in bonding orbitals and the number of antibonding orbitals. The factor one-half preserves the concept of the electron pair and makes the bond order correspond to the multiplicity in the valence-bond formulation: one for a single bond, two for a double bond, and three for a triple bond. Fractional bond orders are allowed, but are not within the scope of this discussion.

π BONDING AND MULTICENTER π BONDS

Ethylene

Ethylene, C_2H_4, has a basic framework established by combining five two-centered bonding σ orbitals, four of which are made from a 1*s* orbital on each hydrogen and an sp^2 orbital on a carbon. The remaining σ orbital is made from one sp^2 orbital on each of the carbons. The combinations of these two-centered σ orbitals are bonding MOs that extend over the whole molecular framework. These extended MOs, represented by the lightly shaded regions of Fig. 9-10, may be referred to as σ-type because their electron density is concentrated mainly along the axes connecting pairs of adjacent atoms.

If the plane of each $H_2C{-}C$ group is designated as the *xy* plane, the p_x and p_y AOs are used to form the sp^2 hybrid orbitals. The p_z orbitals on the two carbons (the darkly shaded regions of Fig. 9-10) are then available for forming π_z orbitals, as indicated by the lines between the darkly shaded orbitals in Fig. 9-10 representing the overlap of orbitals. After filling the five σ-type bonding orbitals, the remaining electron pair (of the total of 12 valence electrons on the two carbons and four hydrogens) goes into the π_z orbital. The two carbons are bonded partly by the electrons in the σ-type framework, constituting the equivalent of a single bond between the two carbons (plus the equivalent of a single bond connecting each of the hydrogens to its adjacent carbon), and partly by the pair of π electrons forming the second part of the double bond indicated in Fig. 9-5. The π bond, which is rigid, prevents rotation about the $C{=}C$ axis and constrains all six atoms in C_2H_4 to the same plane.

Acetylene

In acetylene, C_2H_2, the σ-type skeleton of three bonding orbitals (the lightly shaded regions in Fig. 9-11) is formed from the 1*s* orbitals on the hydrogen atoms and the hybrid *sp* orbitals on the carbon atoms. The p_x AOs are used to form the hybrid orbitals which point along the bonding *x* direction and the remaining *p* orbitals are free to form the π_y and π_z orbitals, represented by the lines joining the darkly shaded regions of Fig. 9-11. The ten valence electrons (one from each hydrogen and four from each carbon) fill the three σ-type orbitals and π_y and π_z orbitals. The carbons are held together by the equivalent of a triple bond (one σ bond and two π bonds), as indicated in Fig. 9-6.

Ozone

In ozone, O_3, the atoms are held together in the first instance by a σ-type framework in the *xy* plane of the molecule represented by the lightly shaded regions of Fig. 9-12. The electron density is concentrated mainly along the axes connecting pairs of nearest-neighbor oxygen atoms. The p_z orbitals of all three oxygen atoms have the symmetry with respect to the plane of the molecule and can combine to form π orbitals. The p_z orbital of the central atom overlaps with the p_z orbitals of both terminal oxygen atoms. As a result, a π bonding orbital and a π^* antibonding orbital extend over all three atoms in the molecule. Further, a π nonbonding orbital involves the two terminal atoms. The electrons in ozone occupy the π bonding orbital, enveloping all three nuclei, with equal probability on the two sides of the molecule. This representation is an alternative to resonance. It was conceptualized in the attempt to conform to the octet rule. The π nonbonding orbital is also occupied in ozone. The occupied π bonding orbital is represented by the lines joining the darkly shaded regions of Fig. 9-12.

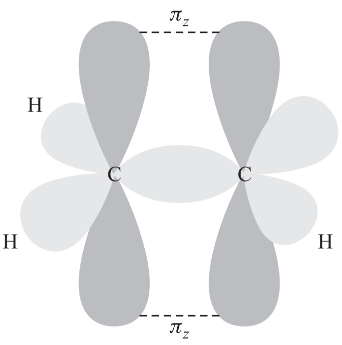


Fig. 9-10

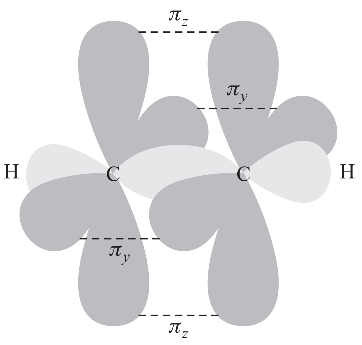


Fig. 9-11

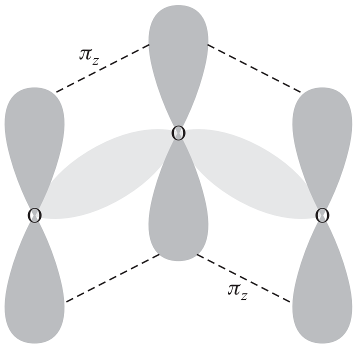


Fig. 9-12

A note

Multicentered π orbitals are involved in the molecular-orbital representation of most structures for which resonance must be invoked in the valence-bond representation. In a long chain of atoms bonded within a planar configuration, such as the plant pigment carotene, $C_{40}H_{56}$, or in planar ring compounds, like naphthalene, $C_{10}H_8$, each π orbital extends over many carbon atoms, all those in the basic molecular plane, since the overlap of the p_z orbital of any nonterminal carbon with those of its two or three neighbors allows for the buildup of long chains or rings of extensively overlapping electron probability distributions.

SHAPES OF MOLECULES

Bond lengths

Bond lengths between a given pair of atoms are approximately constant from compound to compound if the nature of the bond (single, double, or triple) is the same. If it is assumed that the length of a single covalent bond is the sum of the *covalent radii* of the two bonding atoms, then quick and fairly reliable estimates of bond lengths can be obtained from readily available information, such as in Table 9-2.

Table 9-2 Single-Bond Covalent Radii

Carbon	77 pm	Oxygen	66 pm
Silicon	117 pm	Sulfur	104 pm
Nitrogen	70 pm	Fluorine	64 pm
Phosphorus	110 pm	Chlorine	99 pm
Antimony	141 pm	Iodine	133 pm

From the precisely measured lengths 154 pm, 133 pm and 120 pm for $H_3C{-}CH_3$, $H_2C{=}CH_2$, and $HC{\equiv}CH$, respectively, we can conclude that the bonds become shorter in the progression from a single bond to a double bond to a triple bond. A rule of thumb has been developed to allow a 21 pm shortening for any double bond and a 34 pm shortening for any triple bond, assuming the bonds are located between the same atoms. In the case of resonance or multicenter π orbitals, a bond length is intermediate between the values it would have in the separate resonance structures. This concept is also true if the bond is between the values it would have in the absence of π bonding and in the presence of a localized two-centered π bond. Some applications of this rule are shown in Table 9-3.

VSEPR bond angles

Starting with the Lewis structure, it is possible to predict fairly accurately the bond angles in a molecule. The *VSEPR* method (Valence Shell Electron Pair Repulsion) focuses on a central atom and counts the number

Table 9-3

Substance	Bond	Predicted Length	Observed Length
CH_3Cl	C—Cl	$r_C + r_{Cl} = 77 + 99 = 176\,\text{pm}$	177 pm
$(CH_3)_2O$	C—O	$r_C + r_O = 77 + 66 = 143\,\text{pm}$	143 pm
H_2CO	C═O	$r_C + r_O - 21 = 143 - 21 = 122\,\text{pm}$	122 pm
ICN	C≡N	$r_C + r_N - 34 = 77 + 70 - 34 = 113\,\text{pm}$	116 pm

of atoms bonded to it plus the number of unshared pairs. Multiple bonds count the same as single bonds. This characteristic VSEPR number is the number of orbitals (each occupied by an electron pair) that must emanate from the central atoms. The angles between them are determined by the principle that the electron pairs will repel each other. The VSEPR method is a simple technique that does not require explicit identification of the orbitals. Invoking the hybrid orbital technique results in the same angles, but in a more formal manner linked to the mathematical treatments of bonding. VSEPR numbers, corresponding to angles, and hybrid orbital sets are listed in Table 9-4.

Table 9-4

VSEPR Number	Nominal Bond Angles	Hybrid Orbital Set
2	180°	*sp*
3	120°	sp^2
4	109°28′	sp^3
5	90°, 120°, 180°	dsp^3
6	90°, 180°	d^2sp^3

Deviations from the angles arise from unshared pairs, which repel more strongly than shared pairs. For example, the VSEPR number is 4 for CH_4 and $:NH_3$. The H—C—H angle in CH_4 is a perfect tetrahedral angle (109°28′), but the H—N—H bond angle in $:NH_3$ is compressed to about 107° by the unshared pair. The VSEPR for water is also 4. Water's oxygen has two unshared pairs compressing the HOH angle to 104.5°.

Double bonds also contribute extra repulsion compressing adjacent bond angles slightly, as shown in Fig. 9-5. Deviations arise if the various atoms around the central atom are very different in size.

COORDINATION COMPOUNDS

The electrons of an electron-pair bond need not be contributed by both of the bonding atoms, as is demonstrated in the formation of the ammonium ion by the addition of a proton to ammonia. The Lewis structures for these two entities are shown in Fig. 9-13; recall that H^+ has no electrons. Such a bond is often called a <u>coordinate</u> *covalent bond*, but is essentially no different from any other covalent bond. The special name indicates that one of the members of the bond brings to the process of bonding any electrons. In this particular case, once the bond has formed, it becomes indistinguishable from the other three N—H bonds in the molecule with the structure being a regular tetrahedron.

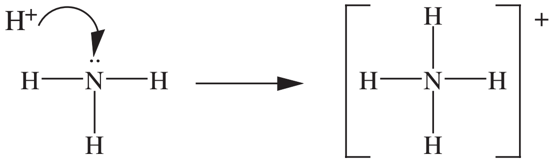


Fig. 9-13

Coordinate covalent bonding is a common type of bonding in coordination compounds, in which a central metal atom or ion is bonded to one or more neutral or ionic *ligands*. A typical ligand, such as NH_3, Cl^-, or CO, has an unshared electron pair that forms the coordinate covalent bond by interacting with the unfilled orbitals of the central metal. The overall charge of a complex ion is the algebraic sum of the charge of the central metal and the charges of the ligands.

A number of rules have been adopted internationally for the naming of coordination compounds:

1. If the compound itself is ionic, the cation is named first.
2. A complex ion or nonionic molecule carries the name of the central metal last, with its oxidation state (charge per atom) in Roman numerals (or 0) enclosed in parentheses. (A detailed discussion of oxidation state is provided in Chapter 11.)
3. Ligands that are anions are named with the suffix *-o*, as in *chloro*, *oxalato*, *cyano*.
4. The number of ligands of a given type is indicated by a Greek prefix, like *mono-* (often omitted), *di-*, *tri-*, *tetra-*, *penta-*, *hexa-*.
5. If the name of a ligand contains a Greek prefix, the number of ligands is indicated by such prefixes as *bis-*, *tris-*, *tetrakis-*, for 2, 3, or 4, respectively, and the name of the ligand is enclosed in parentheses.
6. When the complex ion is an anion, the Latin name of the metal is used with the suffix *-ate*.
7. Some neutral ligands are given special names—*ammine* for NH_3, *aqua* for H_2O, *carbonyl* for CO.
8. When several ligands occur in the same complex, they are named in alphabetical order (ignore any numerical prefixes).

EXAMPLE 5 Names of compounds containing complex ions:

$[Co(NH_3)_6](NO_3)_3$	Hexaamminecobalt(III) nitrate
$Ni(CO)_4$	Tetracarbonyl nickel(0)
$K[Ag(CN)_2]$	Potassium dicyanoargentate(I)
$[Cr(NH_3)_4Cl_2]Cl$	Tetraaminedichlorochromium(III) chloride
$[Co(NH_2C_2H_4NH_3)_3]Br$*	Tris(ethylenediamine)cobalt(III) bromide

*Often abbreviated as $[Co(en)_3]Br_3$.

Structure, properties, and bonding

In many coordination compounds, the ligands are arranged around the central metal in regular geometrical forms, such as the octahedron, the tetrahedron, or the square. In the formulas listed above, the brackets define the complex made up of the central metal and its ligands. These brackets are often omitted where there is no problem determining the nature of the complex. Many of the compounds of complexes are colored. Some are paramagnetic because of the presence of unpaired electrons, while others with the same metal atom are not paramagnetic. The molecular-orbital energy-level diagram, Fig. 9-14, is the key to the explanation the properties. The use of the derivation is important in the solving of problems. Here we shall consider only the six-coordinated octahedral complexes.

The hybridization on a metal atom leading to octahedral bonding is d^2sp^3. If the bonding axes are x, y, and z, the two d orbitals that are used for the hybridization are those that point along one or more of these axes, d_{z^2} and $d_{x^2-y^2}$ (Fig. 8-3). Each of the resulting six hybrid orbitals mixes with an orbital directed along a bonding axis in the ligand, such as a p or a tetrahedral hybrid, to form σ or σ^* molecular orbitals. Each bonding σ orbital is occupied by a pair of electrons.

The full set of molecular orbitals for the complex may be constructed from the following atomic orbitals: all five d orbitals of the next-to-outermost shell of the metal, the s and three p orbitals of the metal's outer shell, and one orbital from each of the six ligands pointed along a bond axis (such as a p or a hybrid orbital). The total number

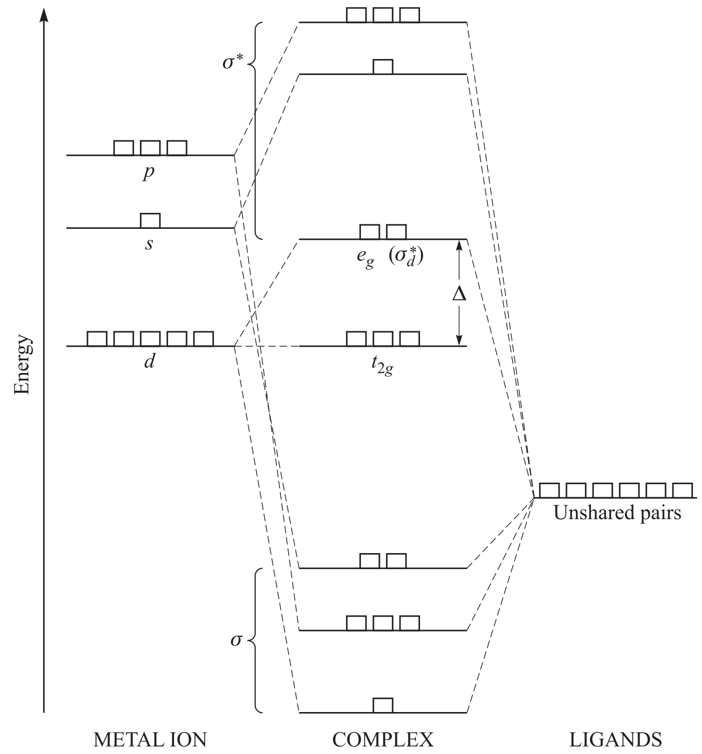


Fig. 9-14

of participating atomic orbitals is 15; the total number of orbitals remaining after molecular-orbital formation must still be 15. The electrons to be accommodated in these orbitals include the six previously unshared pairs provided by the six ligands for bond formation to the metal plus the valence electrons of the metal (the number depending on the oxidation state).

Figure 9-14 displays a molecular-orbital diagram with the metal's atomic orbitals shown on the left and the ligand's on the right. A more complicated diagram would be needed if the ligands also had π orbitals that participate in the bonding to the metal. The actual energy spacing will depend on the particular case, but the relative ordering of the $(n - 1)d$, ns, and np metal orbitals (where n is the principal quantum number of the outermost shell) in general. Also, it is common for the ligand's orbitals to be at lower energy than the metal's orbitals. Note that, of the nine metal orbitals, only six contribute to primary bonding in the complex. These six are the same ones that can be hybridized to form the octahedral hybrids pointing along the $\pm x$, $\pm y$, and $\pm z$ directions, namely, the s, the three p, and the d_{x^2}, and $d_{x^2-y^2}$. The six metal orbitals contributing to bonding mix with the six ligand orbitals to form six σ-type bonding and six σ^*-type antibonding molecular orbitals that are delocalized over the whole complex. The bonding molecular orbitals have lower energies than the ligand's orbitals and the antibonding have higher energies, as is usual. Also as usual, the lower the energy of a bonding orbital, the higher is its corresponding antibonding orbital. The three remaining metal d orbitals, not having σ character with respect to bond directions, remain nonbonding and their energy is unchanged to a first approximation. Several consequences can be seen from this diagram:

1. The 12 electrons supplied by the ligands can be thought to occupy and fill the six bonding σ-type orbitals.
2. The next-lowest-lying orbitals, available for the valence electrons supplied by the metal, are the three nonbonding orbitals, d_{xy}, d_{xz}, and d_{yz} orbitals, which do not point toward the ligands.
3. Of the σ^*-type antibonding orbitals, the lowest-lying are the two whose metal components are d_{x^2} and $d_{x^2-y^2}$, designated as σ_d^*. The energy difference between this level and the nonbonding level is denoted as Δ.

(The symbol for this energy difference is not standard; various textbooks use X, $10Dq$, or Δ_0.) The σ_d^* and the nonbonding orbitals are referred to, respectively, as e_g and t_{2g}.

4. The first three valence electrons of the metal will occupy the t_{2g} orbitals.
5. The next two valence electrons of the metal could occupy the t_{2g} or the e_g orbitals, depending on whether Δ is respectively greater than or less than the energy increase associated with pairing two electrons in the same orbital, in violation of rule 1 under "Magnetic Properties" in Chapter 8. If the t_{2g} orbitals are preferentially filled, the complexes tend to have a low spin and the d^3 and d^6 configurations are stabilizing, in accordance with the features of filled or half-filled equal-energy orbitals. If the e_g orbitals are filled before the t_{2g} orbitals are double occupied, the complexes tend to have high spin and the d^5 and d^{10} are stabilizing configurations.
6. The weak electron transitions responsible for the color of coordination complexes are correlated with the t_{2g} to e_g transition of energy Δ. The origin of the strong transitions responsible for the deep colors of some complexes of metals in high oxidation states, like the permanganate and the chromate ions, has a different explanation not covered here.

With regard to the options in rule 5, CN^-, CO, and NO_2^- are *strong-field* ligands that tend to increase Δ and promote low-spin complexes; OH^- and Cl^- are *weak-field* ligands that lead to smaller values of Δ and high-spin complexes. A more complete listing of ligands in order of their field strength is known as the *spectrochemical series*.

ISOMERISM

Quite a few molecules and ions have the same chemical formula (numbers and kinds of atoms), but have different three-dimensional shapes and/or the atoms are assembled in different manners. These substances are referred to as being *isomers* and may differ in their physical properties (melting point, boiling point, density, color, etc.) and their chemical properties. There are three categories of isomers described below.

Structural isomerism

One way of describing a chemical compound or ion is to list for each atom the numbers of each kind of atom connected to it by covalent bonds. Isomers which differ in these listings are *structural isomers*.

EXAMPLE 6 Figure 9-15 depicts the two structures that can be drawn for butane, C_4H_{10}, that conform to the octet rule for carbon and hydrogen. In *n*-butane, two of the carbons are bonded to one carbon each and two are bonded to two each. In *iso*-butane, three of the carbons are bonded to one carbon each and the fourth to three carbons. *n*-Butane melts at –135°C and boils at –0°C, while *iso*-butane melts at –145°C and boils at –10°C.

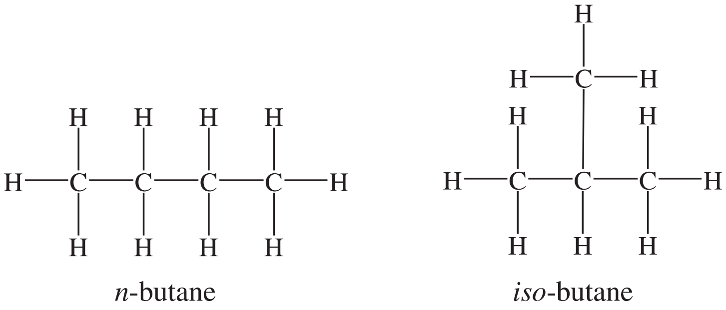


Fig. 9-15

In the case of *n*-butane, within any one molecule there is a continuous, practically unrestricted, rotation of the atoms about any C—C bond, so that all structures on paper differ only by the angular position of an atom or group of atoms linked by a single bond and are really the same, as shown in Fig. 9-16. These diagrams are all representations of the same substance, *n*-butane. In each, we can number the carbon atoms 1 to 4 as we move from one end of the molecule's carbon skeleton to the other. We see that the kinds of neighbors of a given numbered carbon atom are the same in all three sketches.

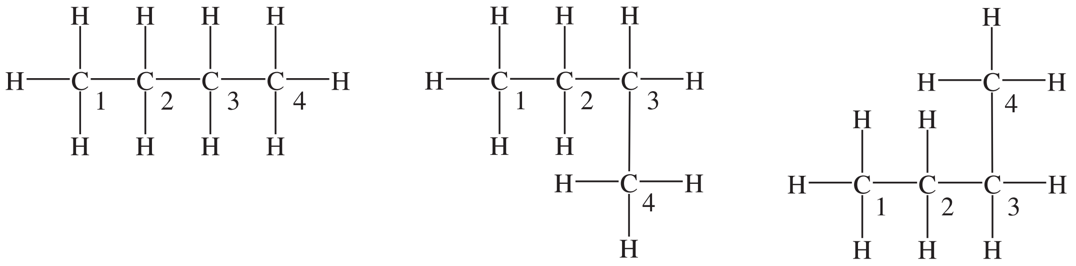


Fig. 9-16

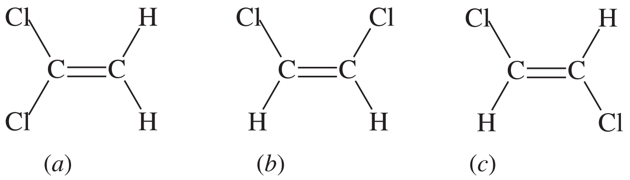
Structural isomers also exist for some coordination compounds. One example is a set of compounds in which a ligand in one isomer may occupy a position outside the coordination sphere in another isomer, such as $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$. These two compounds are structural isomers, each recognizable by its own color and complete set of distinctive properties.

Geometrical isomerism

In some isomers the listing of bonded atoms around each atom is the same, but the compounds differ because at least two atoms, bonded to the same or to adjacent atoms but not to each other, are at different distances in several forms. Such isomers are referred to as *geometrical isomers*.

An important set of geometrical isomers occurs in compounds containing a carbon-carbon double bond. The double bond does not allow for a rotation because it is rigid, which also keeps the atoms bonded to the doubly bonded carbons coplanar (in the same plane). As a result, there are different positions available across the double bond, above it, and below, as shown in Example 7.

EXAMPLE 7 In Fig. 9-17 molecules (*a*) and (*b*) are *structural isomers* of each other, as are (*a*) and (*c*). These relationships are noted because the chlorines are located on **different carbons**; however, (*b*) and (*c*) have the chlorines located on the same carbons.

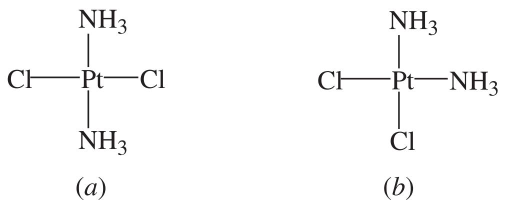


(*a*) (*b*) (*c*)

Fig. 9-17

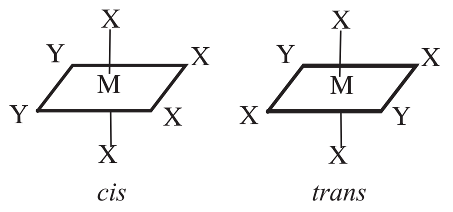
A second isomerism is shown in the case of the (*b*) and (*c*). Notice that the chlorines are on **the same carbons** in the two compounds, but differ in their locations—in (*b*) the chlorines are on the same side of the double bond and (*c*) shows the chlorines are on opposite sides of the double bond. These relationships exist because there is no rotation allowed about a double bond. These are called *geometrical isomers*.

EXAMPLE 8 Geometrical isomerism in compounds with square symmetry is illustrated in Fig. 9-18. Because of the rigidity of the square planar arrangement in the Pt, N, and Cl atoms there are two distinct forms. Notice that the chlorines in (*a*) are opposite each other, but the chlorines in (*b*) are adjacent. This is because the four locations around the central metal are different, but if the structure had been tetrahedral, the locations of the atoms would not have been different and there would be no isomerism.



(*a*) (*b*)

Fig. 9-18



cis *trans*

Fig. 9-19

Identical adjacent atoms are said to be *cis*, as in Fig. 9-17(*b*) and Fig. 9-18(*b*). When opposite each other, identical atoms are called *trans*, as in Fig. 9-17(*c*) and Fig. 9-18(*a*).

In octahedral complexes, structures of type MX_4Y_2 may exist as geometrical isomers. The two Y atoms (or groups) can occupy either adjacent sites, as in Fig. 9-19(*a*), or may occupy opposites sites, as in Fig. 9-19(*b*). Only two isomers exist in this case because there only two different distances between corners of a regular octahedron. The *cis* and *trans* forms of $Pt(NH_3)_2Cl_4$ are isomers of this type. Possibilities for geometrical isomerism occur for other octahedral formula types, like MX_3Y_3, or complexes with more than two different kinds of ligands.

Optical isomerism

Optical isomerism is the existence of molecules that are mirror images of each other (not superimposable); this means that there will be pairs of isomers. Among the important category of optical isomers are compounds containing four different groups singly bonded to a given carbon atom (Fig. 9-20) and octahedral complexes with three different kinds of ligands or with several multivalent ligands (Fig. 9-21).

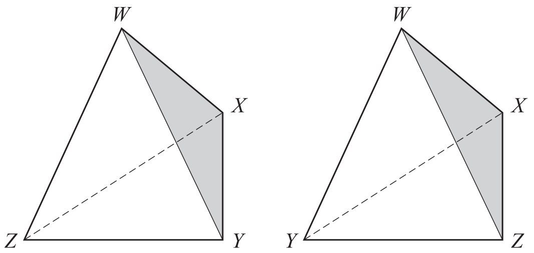


Fig. 9-20

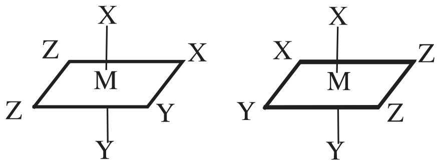


Fig. 9-21

BONDING IN METALS

Molecular orbital (MO) theory has been used to explain the bonding in metallic crystals, such as pure sodium or pure aluminum. Each MO, instead of dealing with a few atoms in a typical molecule, must cover the entire crystal (might be 10^{20} or more atoms!). Following the rule that the number of MOs must equal the number of atomic orbitals (AOs) combined, this many MOs must be so close on an energy level diagram that they form a continuous band of energies. Because of this factor, the theory is known as *band theory*.

Let us take a look at a piece of sodium metal. Of the 11 electrons, the 10 forming the neon core are localized around each Na nucleus, leaving one electron per atom to fill the MOs that are throughout the crystal. If there were *N* atoms in the crystal, *N* MOs could be formed by use of one 3*s* orbital from each. Although these MOs have varying amounts of bonding and nonbonding character, their energies form a continuum within the 3*s* band.

In metals beyond Group IA, the picture becomes more complicated as both the *s* and *p* orbitals are used to form the band of MOs, which then contains many more orbitals than the number of electron pairs available. The criterion for electrical conductivity, a property associated with metals, is that the energy band be only partially filled.

A simple alternative model, consistent with band theory, is the *electron sea* concept illustrated in Fig. 9-22 for sodium. The circles represent the sodium ions which occupy regular lattice positions (the second and fourth lines of atoms are in a plane below the first and third). The eleventh electron from each atom is broadly delocalized so that the space between sodium ions is filled with an "electron sea" of sufficient density to keep the crystal electrically neutral. The massive ions vibrate about the nominal positions in the electron sea, which holds them in place something like cherries in a bowl of gelatin. This model successfully accounts for the unusual properties of metals, such as the electrical conductivity and mechanical toughness. In many metals, particularly the transition elements, the picture is more complicated, with some electrons participating in local bonding in addition to the delocalized electrons.

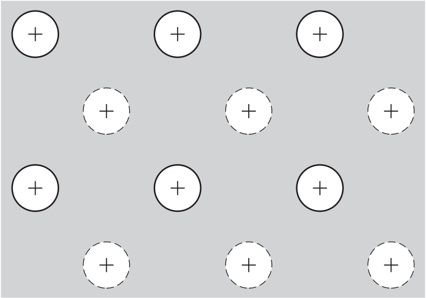


Fig. 9-22

Solved Problems

FORMULAS

9.1. Write the formulas for the following ionic compounds: (*a*) barium oxide; (*b*) aluminum chloride; (*c*) magnesium phosphate.

(*a*) Barium displays a charge of $+2$ as an ion and the charge of an oxide ion is -2. It takes one each of the ions to provide the zero charge of a compound; the formula is BaO.

(*b*) Since aluminum's charge is $+3$, it will take three chloride ions at -1 each; therefore, $AlCl_{3.}$.

(*c*) The charges on the ions are $+2$ for Mg and -3 for phosphate. We are to use the lowest number with 2 and 3 as common factors, which is 6. That means using 3 magnesium ions and 2 phosphate ions, which provides us with the formula $Mg_3(PO_4)_2$.

9.2. Name the following compounds: (*a*) Mg_3P_2; (*b*) $Hg_2(NO_3)_2$; (*c*) NH_4TcO_4.

(*a*) Since binary compounds are named on the basis of the ions involved, this compound is *magnesium phosphide*. Recall that a negative ion composed of a single element has the word ending *-ide*, explaining the naming of P^{3+}.

(*b*) The naming of (Hg_2) requires that we calculate the charge on each mercury ion. Since the total charge on $(NO_3)_2$ is -2 and there are two mercury ions, then each mercury ion must be $+1$. The name of the compound is *mercury(I) nitrate* (*mercurous nitrate*).

(*c*) Since the charge on the ammonium ion is $+1$, the other ion must be -1. A look at the periodic table tells us that Tc is in the same group as Mn; Mn forms MnO_4^- (permanganate), implying that the ion TcO_4^- should be handled in the same manner. The name of the compound is *ammonium pertechnetate*.

9.3. Determine the charges of the complex ions written in bold italics:

(*a*) $\mathrm{Na_2}\boldsymbol{MnO_4}$ (*b*) $\mathrm{H_4}[\boldsymbol{Fe(CN)_6}]$ (*c*) $\mathrm{NaCd_2}\boldsymbol{P_3O_{10}}$ (*d*) $\mathrm{Na_2}\boldsymbol{B_4O_7}$
(*e*) $\mathrm{Ca_3}(\boldsymbol{CoF_6})_2$ (*f*) $\mathrm{Mg_3}(\boldsymbol{BO_3})_2$ (*g*) $\boldsymbol{UO_2}\mathrm{Cl_2}$ (*h*) $(\boldsymbol{SbO})_2\mathrm{SO_4}$

(*a*) Since two sodium ions have a $+2$ total charge, then MnO_4 must be -2.

(*b*) The ion in brackets must balance the charge of four H^+'s; it must be -4.

(*c*) The ion must balance the charge of one Na^+ and two Cd^{2+} ions (total $+5$). Then, the ion is -5.

(*d*) Since there are two sodium ions (total $+2$), the charge on the complex ion must be -2.

(*e*) Three calcium ions provides $+6$, total. Each of the two complex ions must supply -3.

(*f*) The three Mg^{2+} ions ($+6$, total) tells us that each complex displays a -3.

(*g*) The charge of the complex ion must balance two Cl^- ions and, therefore, is $+2$.

(*h*) A single sulfate has a charge of -2. Then, each of the two complex ions must be $+1$.

9.4. The formula of calcium pyrophosphate is $Ca_2P_2O_7$. Determine the formulas of sodium pyrophosphate and iron(III) pyrophosphate (ferric pyrophosphate).

Because the pyrophosphate ion forms a compound with two calcium ions totaling $+4$, the charge on pyrophosphate must be -4. The compounds requested must be $Na_4P_2O_7$ and $Fe_4(P_2O_7)_3$.

9.5. Write the octet structural formulas for (*a*) CH_4O; (*b*) C_2H_3F; (*c*) azide ion, N_3^-.

(*a*) Rather than using the valence electrons, let us consider the number of bonds typically formed. Each hydrogen can form only one chemical bond. This means that no hydrogen can be between two other atoms. Carbon can form four chemical bonds and oxygen can form two chemical bonds. The only structure that will work is Fig. 9-23.

(*b*) Knowing that carbon will bond to carbon with one, two, or three bonds, look at Fig. 9-24 and verify that this is the only possible structure.

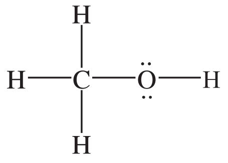


Fig. 9-23

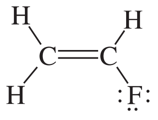
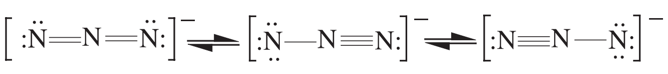


Fig. 9-24

(*c*) The total number of available valence electrons in the azide ion is 16 (5 in each of the 3 free N atoms plus 1 arising from the net ionic charge of -1). From this information, it can be seen that a linear structure without multiple bonds is not possible (Fig. 9-25), because there is no way to utilize all of the electrons. However, multiple bonds between the atoms are possible allowing for more than one possible layout to satisfy this set of circumstances, as shown in Fig. 9-26.

Incorrect structure

Fig. 9-25



(*a*) (*b*) (*c*)

Correct structures

Fig. 9-26

Two resonance structures for the azide ion are shown with the triple bond [Fig. 9-26(*b*) and (*c*)], because the two terminal nitrogen atoms are the same (look at it as a 180° rotation of the molecule in space). Interestingly, a different

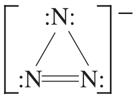


Fig. 9-27

structure can be proposed that is based on a three-member ring (Fig. 9-27). The problem with this structure is that the 60° angles required to close the ring place too much stress on the bonds for the structure to be stable and, therefore, is not a possible choice.

9.6. Experimentally, the azide ion is found to be linear with each adjacent nitrogen-nitrogen distance equal to 116 pm. (*a*) Evaluate the formal charge at each nitrogen in each of the three linear octet structures shown in Fig. 9-26. (*b*) Predict the relative importance of the three resonance structures.

(*a*) In structure (*a*) of Fig. 9-26 the central N is assigned $\frac{1}{2}$ of the four shared pairs, or four electrons. This number is one less than the number of valence electrons in a free N atom; this atom has a formal charge of $+1$. Each terminal N is assigned four unshared electrons plus $\frac{1}{2}$ of the two shared pairs, or a total of six electrons. The formal charge is -1. The net charge of the ion, -1, is the sum $2(-1)+1$.

In structures (*b*) and (*c*) of Fig. 9-26 the central N again has four assigned electrons with a resulting formal charge of $+1$. The terminal N with the triple bond has 2 plus $\frac{1}{2}$ of 3 pairs (a total of 5) with a formal charge of 0. The singly bonded terminal N has 6 plus $\frac{1}{2}$ of 1 pair (total = 7) with a formal charge of -2. The net charge of the ion, -1, is the sum of $+1$ and -2.

(*b*) Structure (*a*) is the most important because it has no formal charge of magnitude greater than 1. For structure (*a*) the N—N bond distance is predicted to be $(70+70)$ minus the double-bond shortening of 21 pm, or 119 pm. The observed bond length is 116 pm.

9.7. The sulfate ion is tetrahedral with four equal S—O distances of 149 pm. Draw a reasonable structural formula consistent with these facts.

Each of the five atoms involved belong to Group VIA, which tells us there are 30 electrons ($6e^-$ for each atom). Further, there are two additional electrons for the net ion charge of -2. It is possible to place the 32 valence electrons in an octet structure having only single bonds. There are two objections to this structure (Fig. 9-28). The first is that the predicted bond distance, $r_S + r_O = 104 + 66 = 170$ pm, is much too high. Secondly, the calculated formal charge on the sulfur, $+2$, is rather high. Regardless, this structure appears widely in textbooks. The reasoning is that the short bond length is the result of the strong attraction between the $+2$ sulfur and -1 oxygens (formal charges).

A structure like that in Fig. 9-29 places zero formal charge on the sulfur and -1 on each of the singly bonded oxygens. The shrinkage in bond length due to double-bond formation helps to account for the low observed bond distance (149 instead of 170 pm, calculated). Other resonance structures (making a total of six) with alternate locations of the double bonds are, of course, implied. Structures like this, with an expanded valence level beyond the octet, are generally considered to involve *d* orbitals of the central atom. This is the reason that second-period elements (C, N, O, F) do not form compounds requiring more than eight valence electrons per atom (the $2d$ subshell simply does not exist).

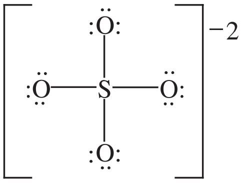


Fig. 9-28

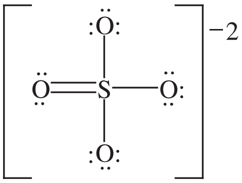


Fig. 9-29

9.8. Draw all the octet resonance structures of (*a*) benzene, C_6H_6, and (*b*) naphthalene, $C_{10}H_8$. Benzene is known to have a hexagonal symmetry, and the carbon framework of naphthalene consists of two fused hexagons in the same plane.

(*a*) There is only one structure that will satisfy the requirement of electron pairing and the dictates of the octet rule. That structure is a ring composed of carbons bonded to carbons forming a hexagon. Each of the carbons is bonded to 1 hydrogen. The remaining bonds between carbons are placed so that alternate bonds are double bonds. Figure 9-30 shows the two resonance structures possible in this arrangement of atoms and bonds.

Figure 9-31 displays a shorthand notation for the benzene ring (Fig. 9-30) where each of the points represents a carbon with associated hydrogen(s). Note that the alternating double bonds are indicated. This structure tells us that we are dealing with *aromatic* compounds. Aromatic compounds are characterized by hydrocarbons forming rings with single bonds between carbons in the ring alternating with double bonds between carbons.

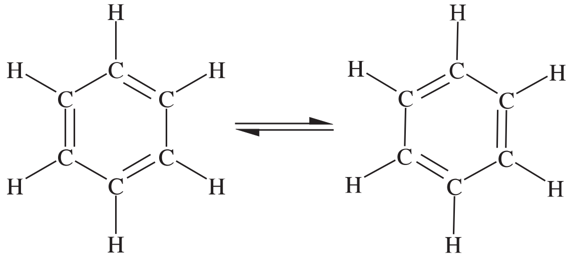


Fig. 9-30

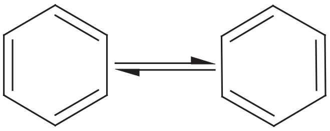


Fig. 9-31

(*b*) As shown in Fig. 9-32, the two carbons at the fusion of the rings reach their covalence of four without bonding to hydrogen. The shorthand notation is provided in Fig. 9-33. As with other notations of this type, there is a C—H bond at each of the locations not indicating four bonds per carbon.

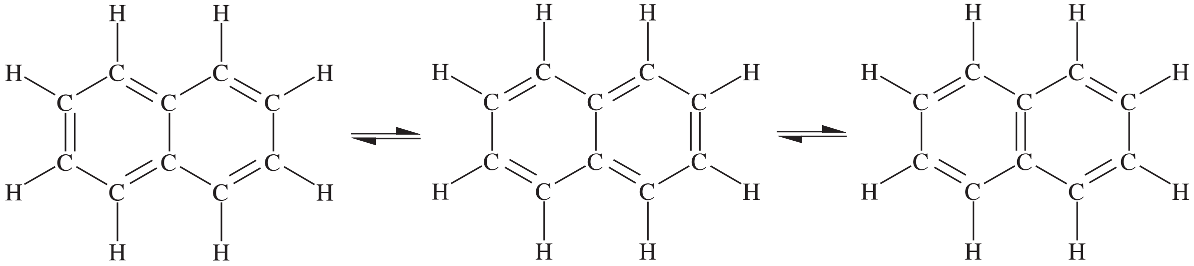


Fig. 9-32

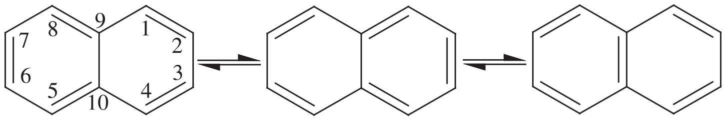


Fig. 9-33

There is another commonly used form of shorthand notation used to show the structure benzene, naphthalene, and other aromatic compounds. That notation involves indicating that the electrons that form the second bond between carbons are not fixed between two specific carbons, but are free to move within the ring. The notation for these *delocalized* electrons is a circle within the ring structure, as shown in Fig. 9-34.

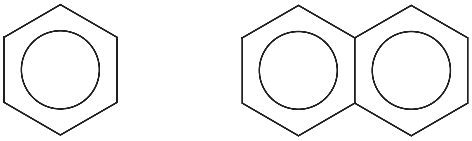


Fig. 9-34

BONDING PROPERTIES

9.9. From the data in Problem 7.41, express the H—H bond energy in kJ/mol.

The bond energy is the energy needed to dissociate gaseous H_2 into separate atoms.

$$H_2 \rightarrow 2H$$

ΔH for this reaction is twice ΔH_f for 1 mol of H.

$$\Delta H = 2(218\,\text{kJ/mol}) = 436\,\text{kJ/mol}$$

9.10. Does Table 7-1 give sufficient data for the evaluation of Br—Br bond energy?

No; the energy of Br is given in the table with respect to the standard state for Br_2, which is the liquid state, not the gaseous state. The bond energy is the energy required to dissociate individual Br_2 molecules (gaseous) into individual Br atoms.

9.11. The enthalpies of hydrogenation of ethylene (C_2H_4) and benzene (C_6H_6) have been measured where all reactants and products are gases. Estimate the resonance energy of benzene.

$$\begin{aligned} &C_2H_4 + H_2 \rightarrow C_2H_6 &\qquad \Delta H = -137\,\text{kJ} \\ &C_6H_6 + 3H_2 \rightarrow C_6H_{12} &\qquad \Delta H = -206\,\text{kJ} \end{aligned}$$

If C_6H_6 had three isolated carbon to carbon bonds, ΔH of hydrogenation would be close to three times ΔH of hydrogenation of C_2H_4, with one double bond (−411 kJ/mol). The fact that benzene's hydrogenation is less exothermic by the calculation, $411 - 206 = 205$ kJ/mol, means that benzene has been stabilized by resonance to the extent of 205 kJ/mol.

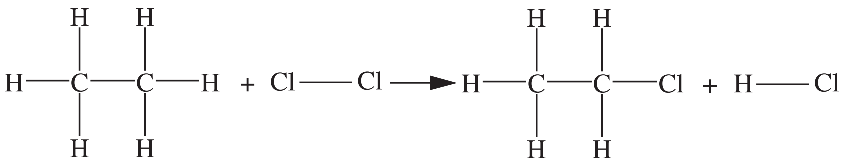
9.12. Estimate ΔH for the reaction:

$$C_2H_6(g) + Cl_2(g) \rightarrow C_2H_5Cl(g) + HCl(g)$$

The following are the average bond energies in kJ/mol:

C—C	C—H	Cl—Cl	C—Cl	H—Cl
348	414	242	327	431

Since we are provided bond energies with which to work this problem, we must first identify all bonds involved and whether they are broken or established during the reaction.



Bonds broken		*Bonds formed*	
C—H	414	C—C	327
Cl—Cl	242	H—Cl	431

Note that bond breaking is endothermic ($+\Delta H$) and bond formation is exothermic ($-\Delta H$) ΔH for the reaction is calculated by the algebraic summation ($+ 414 + 242 - 327 - 431 = -102\,\text{kJ}$):

$$\begin{aligned} \text{from the bond energies} &= -102\,\text{kJ/mol} \qquad \text{(estimated)} \\ \text{from the } \Delta H_f^\circ \text{ values} &= -113\,\text{kJ/mol} \qquad \text{(exact)} \end{aligned}$$

There is a difference between the two calculations. Bond energies are calculated from the energies of the specific bond found in many different compounds (an average). The calculations for heats of formation are for the particular molecule under consideration (the entire molecule). In reality, the energy required to break a bond is dependent on the location of that bond in a specific molecule because the bond energy for it is determined by the environment in which the bond is located. In other words, the bond energy depends not only on the specific bond, but on the influences of the bonds and atoms in the surroundings provided by the molecule in which that bond is found.

9.13. The dipole moment (μ) of LiH is $1.964 \times 10^{-29}\ \text{C} \cdot \text{m}$, and the interatomic distance between Li and H in this molecule is 159.6 pm. Approximately what is the percent ionic character in LiH?

Let us calculate the dipole moment of a hypothetical, 100% ionized Li^+H^- ion pair with a separation of 159.6 pm, that is, assuming a point charge at each nucleus.

$$\begin{aligned} \mu\ \text{(hypothetical)} &= \text{(1 electronic charge)} \times \text{(separation)} \\ &= (1.602 \times 10^{-19}\,\text{C})(1.596 \times 10^{-10}\,\text{m}) = 2.557 \times 10^{-29}\,\text{C} \cdot \text{m} \end{aligned}$$

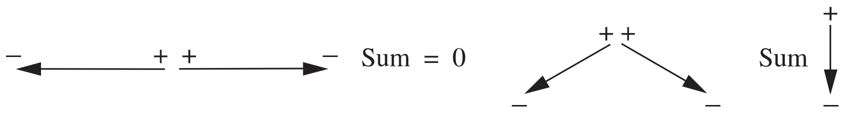
The approximate *percent ionic character* equals 100% times the fraction determined by the actual dipole moment divided by the hypothetical dipole moment.

$$\text{Percent ionic character} = 100\% \times \frac{1.964 \times 10^{-29}\,\text{C} \cdot \text{m}}{2.557 \times 10^{-29}\,\text{C} \cdot \text{m}} = 76.8\%\ \text{ionic}$$

9.14. The dipole moments of SO_2 and CO_2 are $5.37 \times 10^{-30}\ \text{C} \cdot \text{m}$ and zero, respectively. What can be said of the shapes of the two molecules?

Oxygen is considerably more electronegative than either sulfur or carbon. Each sulfur-oxygen and carbon-oxygen bond should be polar with a net negative charge resides on the oxygen.

Since CO_2 has no net dipole moment, the two C—O bond moments must exactly cancel. This can occur only if the two bonds are in a straight line, as in Fig. 9-35(*a*). (The net moment of the molecule is the vector sum of the bond moments.) The existence of a dipole moment in SO_2 must mean that the molecule is not linear, but bent, as in Fig. 9-35(*b*).



(*a*) (*b*)

Fig. 9-35

9.15. Using molecular-orbital considerations, account for the fact that oxygen gas is paramagnetic. What is the bond order in O_2?

The oxygen atom has the $1s^2 2s^2 2p^4$ configuration in the ground state. Aside from the first orbit electrons of the two atoms in O_2, which are so deeply imbedded in their respective atoms as to not overlap with other electrons, the remaining 12 electrons (6 from each atom) will fill the lowest of the available molecular orbitals as shown in Fig. 9-36. The bond axis is the x-axis. The electron configuration of O_2 is: $[\mathrm{He}]\sigma_s^2\sigma_s^{*2}\sigma_{px}^2\pi_{y,z}^4\pi_y^{*1}\pi_z^{*1}$.

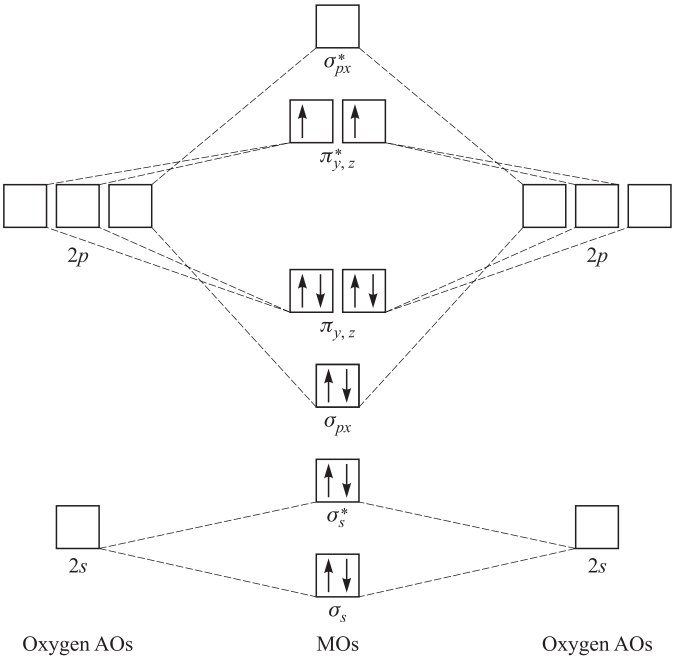


Fig. 9-36 Electrons are indicated by arrows, orbitals by squares, first orbit electrons are omitted. *Note*: The above energy level diagram is not relevant to the molecules B_2 and C_2, in which the order of the σ_{px} and $\pi_{y,z}$ levels is reversed.

The last two electrons went into the antibonding equi-energetic π^* orbitals, one into π_y^* and one into π_z^*, so as to maximize electron spin in accordance with Hund's rule. These two unpaired electrons tell us that the molecule is paramagnetic. (BO, bonding orbitals; ABO, antibonding orbitals.)

$$\text{Bond order} = \frac{(\text{number of electrons in BO}) - (\text{number of electrons in ABO})}{2} = \frac{8-4}{2} = 2$$

9.16. Explain the observations that the bond length in N_2^+ is 2 pm greater than in N_2, while the bond length in NO^+ is 9 pm less than in NO.

The electron configurations are written for the four molecules according to the buildup principle.

N_2	$[\mathrm{He}]\sigma_s^2\sigma_s^{*2}\sigma_{p_x}^2\pi_{y,z}^4$
N_2^+	$[\mathrm{He}]\sigma_s^2\sigma_s^{*2}\sigma_{p_x}^2\pi_{y,z}^3$
NO	$[\mathrm{He}]\sigma_s^2\sigma_s^{*2}\sigma_{p_x}^2\pi_{y,z}^4\pi_{y,z}^{*1}$
NO^+	$[\mathrm{He}]\ \sigma_s^2\sigma_s^{*2}\sigma_{p_x}^2\pi_{y,z}^4$

The computed bond orders are 3 for N_2 and $2\frac{1}{2}$ for N_2^+. N_2, therefore, has a stronger bond and should have the shorter bond length. The computed bond orders are $2\frac{1}{2}$ for NO and 3 for NO^+. The NO^+ cation has the stronger bond and should have the shorter bond length. In contrast to the ionization of N_2, which involves the loss of an electron in the *bonding* orbital, the ionization of NO involves the loss of an electron in an *antibonding* orbital.

9.17. Two substances having the same molecular formula, C_4H_8O, were examined in the gaseous state by electron diffraction. The carbon-oxygen distance was found to be 143 pm in compound A and 124 pm in compound B. What can you conclude about the structures of these two compounds?

In compound A the carbon-oxygen distance is the sum of the single-bond covalent radii of carbon and oxygen, indicating a single bond (77 pm + 66 pm = 143 pm).

(*a*) (*b*)

Fig. 9-37

Then, the oxygen cannot be terminal. One such structure is the heterocyclic compound tetrahydrofuran [Fig. 9-37(*a*)].

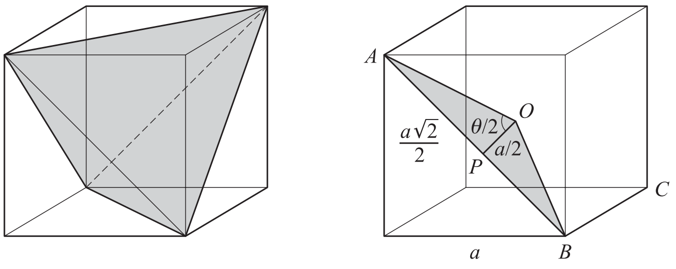
In compound B, the carbon-oxygen distance is close to that predicted for a double bond, 122 pm. Then, the oxygen must be terminal. A structure that conforms to these data is 2-butanone [Fig. 9-37(*b*)].

SHAPES OF MOLECULES

9.18. Verify the value $\Theta = 109°28'$ for the central angles in a regular tetrahedron.

A simple way of constructing a regular tetrahedron is to select alternating corners of a cube and to connect each of the selected corners with each of the other three, as in Fig. 9-38(*a*). Figure 9-38(*b*) shows triangle *OAB*, determined by the center of the cube, *O*, which is also the center of the tetrahedron, and two corners of the tetrahedron, *A* and *B*. If *P* is the midpoint of *AB*, we see from right triangle *OPA* that the mathematical relationship is as follows:

$$\tan\frac{\Theta}{2} = \frac{\overline{AP}}{\overline{OP}} = \frac{a\sqrt{2}/2}{a/2} = \sqrt{2} \qquad \frac{\Theta}{2} = 54°44' \qquad \Theta = 109°28'$$



(*a*) (*b*)

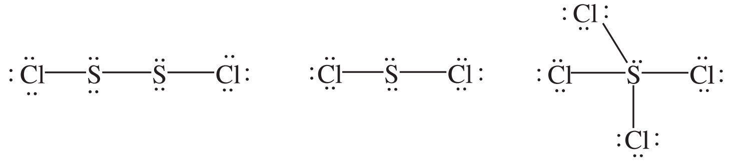
Fig. 9-38

9.19. The C—C single-bond distance is 154 pm. What is the distance between the terminal carbons in propane, C_3H_8? Assume that the four bonds of any carbon atom are pointed toward the corners of a regular tetrahedron.

With reference to Fig. 9-38(*b*), two terminal carbons can be thought of as lying at *A* and *B* with the central atom at *O*. Then,

$$\overline{AB} = \overline{2AP} = 2\left(\overline{AO}\,\sin\frac{\Theta}{2}\right) = 2(154\,\text{pm})(\sin 54°44') = 251\,\text{pm}$$

9.20. Sulfur and chlorine combine in various proportions forming S_2Cl_2, SCl_2, and SCl_4. Draw the Lewis structures of these molecules and, using VSEPR, predict their shapes.



(*a*) (*b*) (*c*)

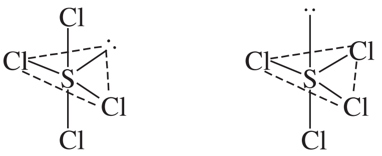
Fig. 9-39

In S_2Cl_2, Fig. 9-39(*a*), each S has a VSEPR number of 4 so that each ClSS bond angle is about 109.5° (probably somewhat less because of extra repulsion from the unshared pairs on each sulfur), and the molecule cannot be linear (straight). There is free rotation around the S—S bond so that there is no fixed conformation of the molecule.

In SCl_2, Fig. 9-39(*b*), the S atom has a VSEPR number of 4, also. The Cl—S—Cl angle is a little less than 109° and the molecule is angular (bent).

In SCl_4, Fig. 9-39(*c*), the VSEPR number is 5, but one of the positions has an unshared electron pair. That must be one of the trigonal positions in the trigonal pyramid, Fig. 9-40(*a*), in which there are two shared-unshared angles of 90°, rather than an axial position (*b*), which has three shared-unshared angles of 90°.

The stick figure corresponding to Fig. 9-40(*a*) has been called a “see-saw” or a “saw-horse” in which the axial ClSCl group represents a horizontal beam. *Note:* The unshared pair bends the ClSCl slightly.



(*a*) (*b*)

Fig. 9-40

9.21. What are the O—N—O bond angles in the nitrate, NO_3^{1-}, and nitrite, NO_2^{1-}, ions?

Only one Lewis structure for each ion needs to be drawn to deduce the VSEPR number, which is 3 in both cases for the central N. (In NO_3^{1-} there are three σ-bonded neighbors and no unshared pairs and in NO_2^{1-} there are two neighbors and one unshared pair, as shown in Fig. 9-41.) The nominal bond angle is 120°, exactly what is found in nitrate since resonance makes all the angles equal. The nitrite ion is a different story because the unshared pair repels the bonding pairs more than they repel each other, forcing them closer to each other. We would expect a slightly smaller angle than 120°; it turns out to be 115°.

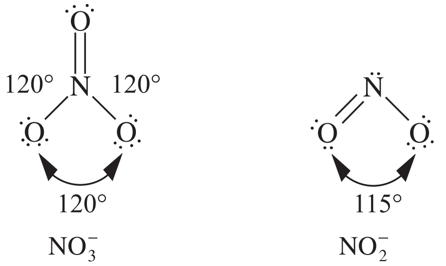


Fig. 9-41

9.22. The $POCl_3$ molecule has the shape of an irregular tetrahedron with the P atom located centrally. The Cl—P—Cl bond angle is found to be 103.5°. Give a qualitative explanation for the deviation of this structure from a regular tetrahedron.

The VSEPR number for the P atom is 4, so that the nominal bond angles are $109°28'$. However, the Lewis structure for $POCl_3$ shows a double bond between P and O. (P is allowed to exceed the octet because of the availability of $3d$ orbitals.) The increased electron density in the P═O bond would make the repulsion between the P═O bond and the P—Cl bond greater than between two P—Cl bonds. The Cl—P—Cl angle is lowered and the Cl—P═O angle increased.

9.23. PCl_5 has the shape of a trigonal bipyramid (Fig. 9-42) and IF_5 has the shape of a square pyramid (Fig. 9-43). Account for the difference.

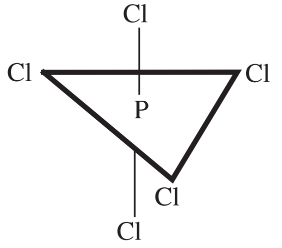


Fig. 9-42

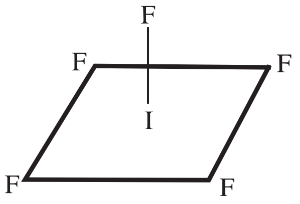


Fig. 9-43

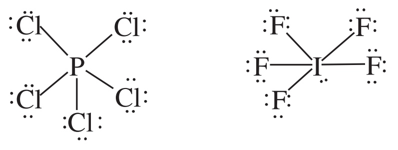


Fig. 9-44

The Lewis structures of the singly bonded compounds (Fig. 9-44) reveal a VSEPR number of 5 in PCl_5, for which the trigonal bipyramid structure with 90°, 120°, and 180° angles is predicted (Table 9-4). However, the unshared pair on the iodine raises its VSEPR number to 6 so that the nominal bond angles are 90°. The square pyramid structure of IF_5 may be thought of as an octahedron (Fig. 9-7) with the unshared pair pointing to the corner below the indicated horizontal plane. Because of the repulsion of the unshared pair, the iodine atom is expected to be slightly below the base plane of the pyramid.

9.24. Which of the four C—C bond types in naphthalene (Fig. 9-33) is predicted to be the shortest?

The four different kinds of carbon-carbon bonds are represented by 1-2, 1-9, 2-3, and 9-10. (*Every other carbon-carbon bond is equivalent to one of these four. For example, 6-7 is equivalent to 2-3, 7-8 is equivalent to 1-2, etc.*) The bond with the greatest double-bond character should be the shortest. Among the three resonance structures shown in Fig. 9-33, the frequency of double bonds for the various bond types is as follows: 2 in *1–2* [in (*a*) and (*c*)], 1 in *1–9* [in (*b*)], 1 in *2–3* [in (*b*)], and 1 in *9–10* [in (*c*)]. Bond *1–2* is expected to have the greatest double-bond character and to be the shortest. This prediction is found to be true experimentally. The above four bonds are found to have lengths of 136.5, 142.5, 140.4, and 139.3 pm, respectively.

Note that the method of counting the number of resonance structures containing a double bond between a given pair of carbon atoms is very crude and cannot distinguish among the last three of the listed bond types, each of which shows a double bond in only one resonance structure. Even within the framework of the limited resonance theory, it would be necessary to know the relative weighting of each of the two equivalent structures (*a*) and (*b*) with the nonequivalent structure (*c*).

9.25. What is the shape of the triple iodide ion, I_3^-?

The Lewis structure reveals a VSEPR number of 5 for the central iodine atom, two bonded neighbors and three unshared pairs. To determine which corners of the trigonal bipyramid are occupied by the terminal iodine atoms, find the arrangement which maximizes the angles between the unshared pairs. The preferred arrangement, Fig. 9-45(*a*), must be the one in which the unshared pairs are all at 120° because any other alternative [Fig. 9-45(*b*) and (*c*)] would have two sets of pairs at 90°. Therefore, the two terminal iodine atoms must occupy the axial positions (180° to each other), making the molecule linear.

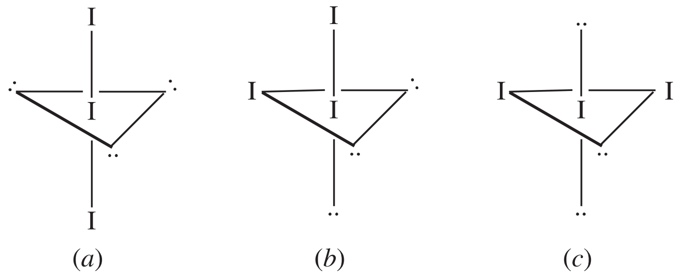

(*a*) (*b*) (*c*)

Fig. 9-45

COORDINATION COMPOUNDS

9.26. Soluble compounds of the complex ion $[Co(NH_3)_3]^{3+}$ have a maximum absorption of visible light at 437 nm. (*a*) What is the value of Δ for this complex ion; express the answer in cm^{-1}. (*b*) What is the color of this ion in solution? (*c*) How many unpaired electrons would you expect this ion to have if it is considered low-spin, and how many if it is considered high-spin?

(*a*)
$$\Delta = \left(\frac{1}{437\,\text{nm}}\right)\left(\frac{10^9\,\text{nm}}{10^2\,\text{cm}}\right) = 22{,}900\,\text{cm}^{-1}$$

(*b*) The color depends not only on the wavelengths of the absorption maximum, but also on the shape of the whole absorption band and on the color sensitivity of the human eye. Because of these factors, the prediction of the color from the data is not absolute; however, a decent prediction can be made. The absorption, which peaks in the blue-violet region of the spectrum, would be expected to cover most of the blue region and part of the green. The prediction of the ion's color in solution is complementary (the opposite) of the light absorbed and expected to be yellow.

(*c*) The electron configuration of Co^{3+} is $[Ar]3d^6$. The spin is due to unpaired *d* electrons. For low spin, the six *d* electrons would all be paired in the three t_{2g} orbitals, and the spin would be zero. For high spin, the two e_g molecular orbitals would be available as well (see Fig. 9-14). Four of the available orbitals would be half filled (1 electron each) and one would be filled (1 pair of electrons) in order to maintain the maximum number of unpaired electrons, four in this case. The Δ value is large enough to rule out high spin and the ion is diamagnetic.

9.27. Predict the magnetic properties of (*a*) $[Rh(NH_3)_6]^{3+}$ and (*b*) $[CoF_6]^{3-}$.

(*a*) This problem can be approached by comparison with Problem 9.26. For analogous complexes of two different members of the same group in the periodic table, Δ increases with increasing atomic number. Since Δ for $[Co(NH_3)_3]^{3+}$ is already so high that the ion is low-spin, $[Rh(NH_3)_6]^{3+}$ is certainly low-spin and diamagnetic (observed $\Delta = 34{,}000\,\text{cm}^{-1}$; therefore, diamagnetic).

(*b*) F^- is a weak-field ligand, tending to form complexes with a low Δ value, so that the ion is expected to be high-spin with four unpaired and parallel electron spins [compare with Problem 9-26(*c*)]. The measured Δ is $13{,}000\,\text{cm}^{-1}$, a low figure, and the ion is paramagnetic.

ISOMERISM

9.28. Write all the structural isomeric formulas for C_4H_9Cl.

The molecular composition resembles butane, C_4H_9, except that one of the hydrogens is replaced by a chlorine. Figure 9-15 is a good starting place because butane's two carbon skeletons are shown.

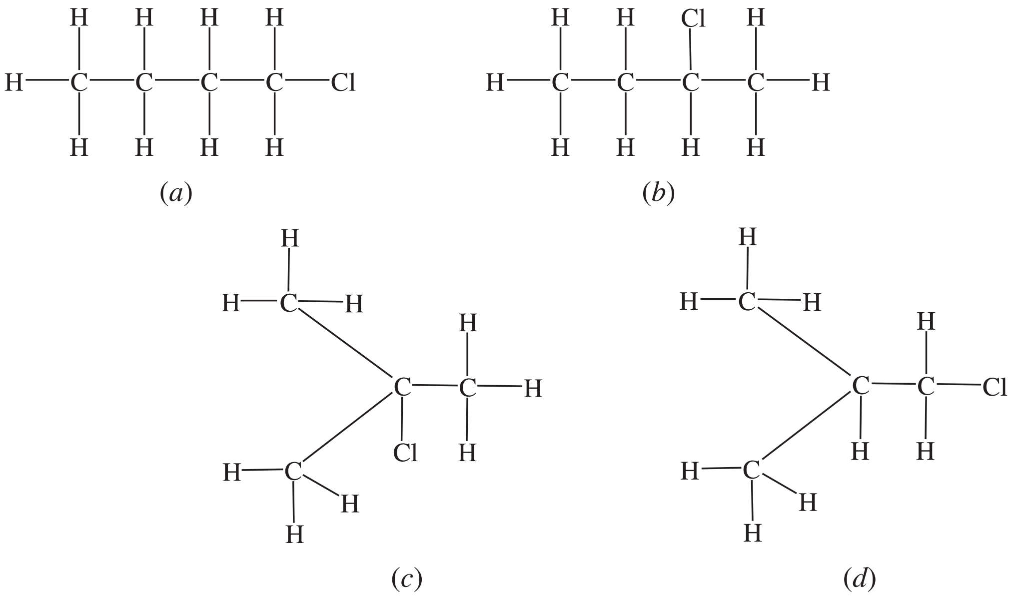


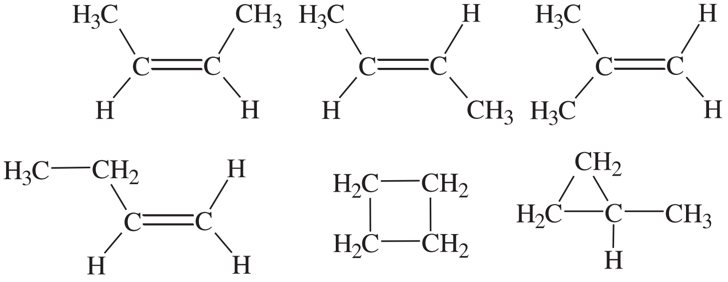
Fig. 9-46

Note that the two terminal (end) carbons of *n*-butane [Fig. 9-46(*a*) and (*b*)] are identical and that the two interior carbons are also identical. If a chlorine were to be substituted on the left carbon, it would be the same as substituting on the right if we were to rotate the molecule 180° and we would still have (*a*). The same concept is true of the interior carbons; substituting as in (*b*) or substituting at the left, interior carbon yields the same molecule on rotation.

In *iso*-butane [Fig. 9-46(*c*) and (*d*)] one isomer (*c*) has the Cl on the central carbon and there is only one other isomer (*d*) because the three terminal carbons are identical. A point worth noting is that all of the C to C bonds are single bonds; this means that, since there is free rotation about a single bond, all of the hydrogens bonded to a particular carbon are identical. Because of this factor, replacing one H on a carbon with a Cl is the same as replacing any other.

9.29. Write formulas for all the structural and geometrical isomers of C_4H_8.

If the four carbons are in a row, there must be one double bond in order to satisfy the requirement that each carbon have four chemical bonds. The double bond occurs either in the center of the molecule or toward an end. If in the center, two geometrical isomers occur with different positions of the terminal carbons relative to the double bond. In the latter case, two structural isomers occur differing in the extent of the branching within the carbon skeleton. Additional possibilities are ring structures.



9.30. Which of the isomeric C_4H_9Cl from Fig. 9-46 would you expect to be optically active?

Compound (*b*) is the only one which would exist in optically active isomeric forms because it is the only one which has a carbon atom bonded to four different groups (the C bonded to the Cl). All other carbons have either two hydrogens or two methyl groups ($-CH_3$).

9.31. How many geometrical isomers could $[Rh(py)_3Cl_3]$ have? The abbreviation *py* is for the ligand pyridine.

One of the two possibilities, Fig. 9-47(*a*), has the three chlorines occupying bonding positions *cis* (adjacent) to each other on one face of the octahedron and the three pyridines on the opposite face. The other possibility, Fig. 9-47(*b*), indicates that there are two of the chlorines *trans* (opposite) to each other and two of the pyridines are also *trans* to each other.

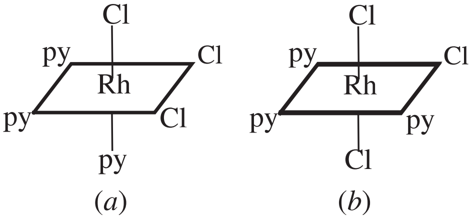


Fig. 9-47

9.32. Some ligands are multifunctional, that is, they have two or more atoms that can bind to the central metal atom or ion. Each binding site occupies a different corner on the coordination surface. Ethylenediamine (abbreviated *en*) is such a ligand. The two binding atoms are nitrogens and the two binding sites must be *cis* to each other because of the shape and size of the *en*. How many geometrical isomers of $[Cr(en)_2Cl_2]^+$ should exist and which isomer(s) might display optical activity?

Two geometrical isomers exist, *cis* and *trans* (Fig. 9-48). Each *en* can be represented by an arc terminating at the two binding sites. By drawing other arrangements of arcs while preserving positions of the chlorines, one can see that (*b*) is a distinct mirror image of (*a*); however, the mirror image of (*c*) is the exact same structure as (*c*). In other words, only the *cis* isomers can be optically active.

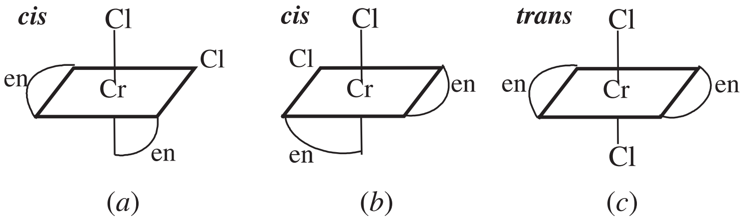


Fig. 9-48

BONDING IN METALS

9.33. Explain why metals are usually lustrous (mirror-like).

In the band model there is a continuum of empty energy levels, rather than discrete energy levels. This situation allows light quanta of all energies within a wide range of wavelengths to be absorbed equally, then the energized electrons will re-emit the light when they fall back into their ground-state orbitals. This is the mechanism for reflection of light of all frequencies, which we call "luster."

9.34. Predict how the Group II metals differ from Group I in density, melting point, and mechanical strength.

In any given period, the Group II ions are smaller and may then approach each other more closely. At the same time, twice as many electrons are present in the electron sea. The closer approach and the much greater electrostatic interactions between the 2+ ions and the sea of high negative charge density lead to greater density and much greater bonding energy, which in turn leads to a much higher melting point and greater hardness. Actually, going from Group I to Group II increases the density by a factor of about 2 and raises the melting point by hundreds of degrees.

9.35. Metals feel cool to the touch compared with other materials because they are very good conductors of heat. How can we explain this unusual thermal conductivity?

In most material, heat is conducted by atom-to-atom transfer of vibrational motion from the hot end to the cooler end. In metals, the thermal energy is transferred primarily by the motion of the electron sea's free electrons, which are very mobile.

Supplementary Problems

FORMULAS

9.36. Determine the charges on the groups written in bold italics, as the chloride in Na***Cl***.
(*a*) Ca$\boldsymbol{C_2O_4}$; (*b*) Ca($\boldsymbol{C_7H_5O_3}$)$_2$ · 2H$_2$O; (*c*) Mg$_3$($\boldsymbol{AsO_3}$)$_2$; (*d*) ***MoO***Cl$_3$; (*e*) $\boldsymbol{CrO_2}$F$_2$; (*f*) $\boldsymbol{PuO_2}$Br; (*g*) (***PaO***)$_2$S$_3$

Ans. (*a*) −2; (*b*) −1; (*c*) −3; (*d*) +3; (*e*) +2; (*f*) +1; (*g*) +3

9.37. Heavy metal compounds tend to be toxic and require careful handling; some of those are compounds of lead, thallium, mercury, and barium. Provide the formulas of these heavy metal bromides, sulfides, nitrides, and carbonates. The more common oxidation numbers of the metals having more than one are Pb^{2+}, Tl^{+}, Hg^{2+}.

Ans. $PbBr_2$, PbS, Pb_3N_2, $PbCO_3$ TlBr, Tl_2S, Tl_3N, Tl_2CO_3
$HgBr_2$, HgS, Hg_3N_2, $HgCO_3$ $BaBr_2$, BaS, Ba_3N_2, $BaCO_3$

9.38. Write the formulas for the following ionic compounds: (*a*) lithium hydride; (*b*) calcium bromate; (*c*) chromium(II) oxide; (*d*) thorium(IV) perchlorate; (*e*) nickel phosphate; (*f*) zinc sulfate.

Ans. (*a*) LiH; (*b*) $Ca(BrO_3)_2$; (*c*) CrO; (*d*) $Th(ClO_4)_4$; (*e*) $Ni_3(PO_4)_2$; (*f*) $ZnSO_4$

9.39. Write the chemical formulas for (*a*) gold(III) nitrate, cobalt(II) nitrate, bismuth(V) nitrate, radium nitrate, tin(IV) nitrate, and arsenic(III) nitrate. (*b*) Write the sulfite compounds.

Ans. (*a*) $Au(NO_3)_3$, $Co(NO_3)_2$, $Bi(NO_3)_5$, $Ra(NO_3)_2$, $Sn(NO_3)_4$, $As(NO_3)_3$
(*b*) $Au_2(SO_3)_3$, $CoSO_3$, $Bi_2(SO_3)_5$, $RaSO_3$, $Sn(SO_3)_2$, $As_2(SO_3)_3$

9.40. Name the following compounds: (*a*) $Al(NO_3)_3$; (*b*) $Al(NO_2)_3$; (*c*) AlN; (*d*) $Al_2(SO_4)_3$; (*e*) $Al_2(SO_3)_3$; (*f*) Al_2S_3; (*g*) Sb_2S_3; (*h*) Sb_2S_5

Ans. (*a*) aluminum nitrate; (*b*) aluminum nitrite; (*c*) aluminum nitride; (*d*) aluminum sulfate; (*e*) aluminum sulfite; (*f*) aluminum sulfide; (*g*) antimony(III) sulfide ; (*h*) antimony(IV) sulfide.

9.41. Write the chemical formulas for (*a*) cupric sulfide; (*b*) stannous fluoride; (*c*) plumbous chloride; (*d*) ferric iodide; (*e*) auric nitrate; (*f*) mercuric sulfide.

Ans. (*a*) CuS; (*b*) SnF_2; (*c*) $PbCl_2$; (*d*) FeI_3; (*e*) $Au(NO_3)_3$; (*f*) HgS

9.42. Name the following compounds: (*a*) $Mg(IO)_2$; (*b*) $Fe_2(SO_4)_3$; (*c*) $CaMnO_4$; (*d*) $KReO_4$; (*e*) $CaWO_4$; (*f*) $CoCO_3$

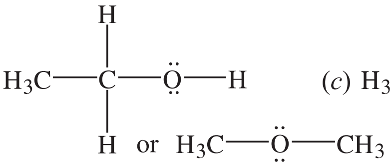
Ans. (*a*) Magnesium hypoiodite; (*b*) iron(III) sulfate or ferric sulfate; (*c*) calcium manganate; (*d*) potassium perrhenate; (*e*) calcium tungstate; (*f*) cobalt(II) carbonate

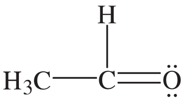
9.43. The formula for potassium arsenate is K_3AsO_4. The formula for potassium ferrocyanide, systematically called potassium hexacyanoferrate(II), is $K_4Fe(CN)_6$. Write the formulas for (*a*) calcium arsenate; (*b*) iron(III) arsenate; (*c*) barium ferrocyanide; (*d*) aluminum ferrocyanide.

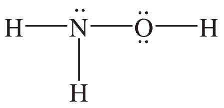
Ans. (*a*) $Ca_3(AsO_4)_2$; (*b*) $FeAsO_4$; (*c*) $Ba_2Fe(CN)_6$; (*d*) $Al_4[Fe(CN)_6]_3$

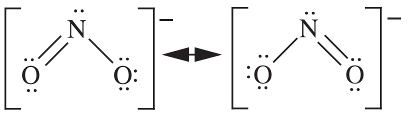
9.44. Draw Lewis structures for each of the following: (*a*) C_2HCl; (*b*) C_2H_6O; (*c*) C_2H_4O; (*d*) NH_3O; (*e*) NO_2^- (both O's terminal); (*f*) N_2O_4 (all O's terminal); (*g*) OF_2

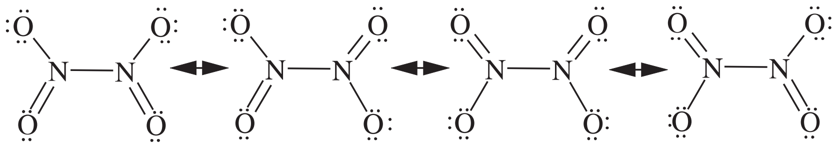
(*a*) 

(*b*) 

(*c*) 

(*d*) 

(*e*) 

(*f*) 

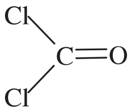
(*g*) 

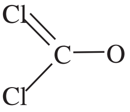
Ans. Note that not all have resonance structures.

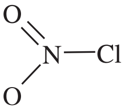
9.45. Complete the following structures by adding unshared electron pairs where necessary. Then evaluate the formal charges.

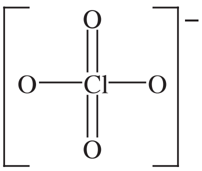
(*a*) $N\equiv C-C\equiv N$ (*b*) $N=C=C=N$ (*c*) $Cl-C\equiv N$

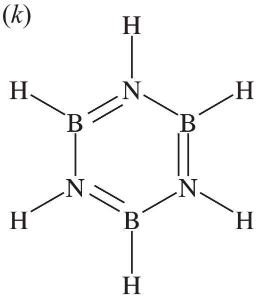
(*d*) $Cl=C=N$ (*e*) $N=N=O$ (*f*) $N\equiv N-O$

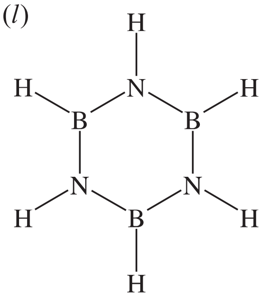
(*g*) 

(*h*) 

(*i*) 

(*j*) 

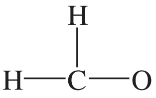
(*k*) 

(*l*) 

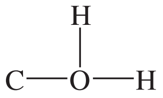
Ans. (*a*) all zero; (*b*) +1 on one N (which does not have an octet), −1 on the other; (*c*) all zero; (*d*) +1 on Cl, −1 on N; (*e*) −1 on terminal N, +1 on central N; (*f*) +1 on central N, −1 on O; (*g*) all zero; (*h*) +1 on doubly bonded Cl, −1 on O; (*i*) +1 on N, −1 on singly bonded O; (*j*) +1 on Cl, −1 on singly bonded O; (*k*) +1 on each N, −1 on each B; (*l*) all zero

9.46. Given that the formula for formaldehyde is CH_2O, one could draw three Lewis structures starting with the skeletons:

$H-C-O-H$



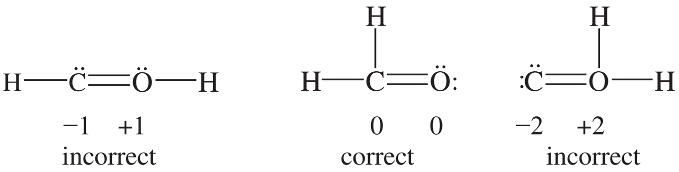
$H-\overset{\overset{\displaystyle H}{|}}{C}-O$



$C-\overset{\overset{\displaystyle H}{|}}{O}-H$

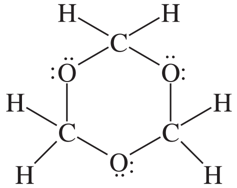
There are 12 valence electrons of which six are used in each of the above skeletons. Use the other six to complete the octets about C and O; determine the formal charges; and decide which structure is correct.

Ans.

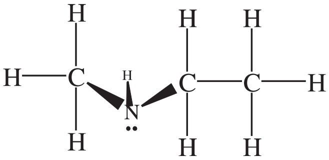


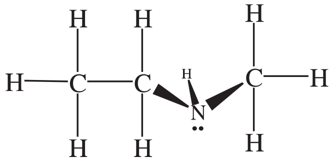
9.47. Three molecules of formaldehyde can condense into one cyclic molecule. Draw the Lewis structure of the molecule. *Hint*: The C and O atoms alternate.

Ans.



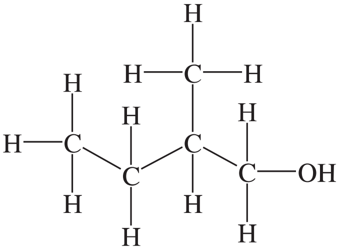
9.48. Are these two structures isomers? If not, why not? If they are isomers, what is the classification of the isomerism?



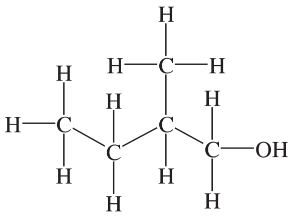


Ans. No. The right structure is the left structure rotated 180°.

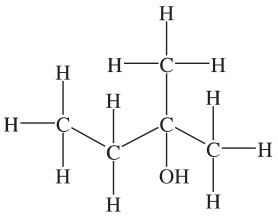
9.49. What are the isomers of this compound holding the carbon skeleton stable?



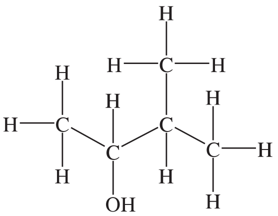
Ans. There are five sketches including the above structure repeated in the list below. Note that changing positions for the OH on each of the carbons does not always provide us with different isomers; (*e*) and (*e*) are the same structure!



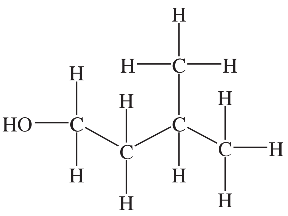
(*a*)



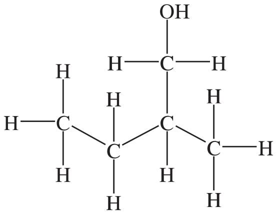
(*b*)



(*c*)



(*d*)



(*e*)

9.50. Of the isomers of the compound in the previous question, which is/are optically active?

Ans. Only those carbons with four different groups attached allow for optical activity; there are no structures that qualify, except for (*c*).

BONDING PROPERTIES

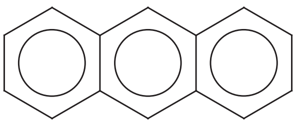
9.51. The chlorine-oxygen bond distance in ClO_4^- is 144 pm. What do you conclude about the valence-bond structures for this ion?

Ans. Since the Cl—O single-bond length estimated from Table 9-2 is 165 pm, there must be considerable double-bond character in the bonds.

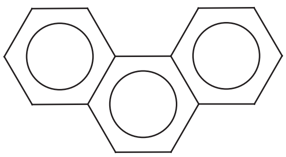
9.52. The VSEPR number for phosphorus is 4 for PH_3. However, the bond angles noted are not $109°28'$, the tetrahedral angle. Explain.

Ans. The unshared pair of electrons on the phosphorus tends to compress the angle.

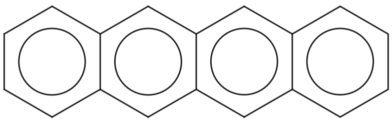
9.53. Considering *only* double bonds between adjacent carbons, how many resonance structures can be written for each of the following aromatic hydrocarbons?



(*a*) Anthracene



(*b*) Phenanthrene



(*c*) Naphthacene

Ans. (*a*) 4; (*b*) 5; (*c*) 5

9.54. The structure of 1,3-butadiene is often written as $H_2C{=}CH{-}CH{=}CH_2$. The distance between the central carbon atoms is 146 pm. Comment on the adequacy of the assigned structure.

Ans. The expected bond length is $77 + 77 = 154$ pm for a purely single bond. There must be non-octet resonance structures involving double bonding between the central carbons, such as

$$^{+}CH_2{-}CH{=}CH{-}\ddot{C}H_2^{-}$$

9.55. The average C—C bond energy is 347 kJ/mol. What do you predict for the Si—Si single-bond energy and why?

Ans. Because Si is a much bigger atom than C, there will be less orbital overlap (less electron sharing) and probably less than 300 kJ/mol bond energy.

9.56. The average C—Cl bond energy is 330 kJ/mol. What do you predict for the C—N single-bond energy and why?

Ans. The chlorine atom is significantly larger than the nitrogen and has a much larger nuclear charge, leading us to conclude that the C—N bond energy is most likely less than 330 kJ/mol. The reported average C—N bond energy is 300 kJ/mol.

9.57. (*a*) What are the bond orders for CN^-, CN, and CN^+? (*b*) Which of these species should have the shortest bond length?

Ans. (*a*) CN^-, 3; CN, $2\frac{1}{2}$; CN^+, 2; (*b*) CN^-

9.58. Other than oxygen, O_2, which homonuclear diatomic molecule(s) of second period elements should be paramagnetic?

Ans. Boron, B_2

9.59. Assuming the elements in the second period can form homonuclear diatomic molecules, which diatomic molecules should have zero bond order?

Ans. Be_2, Ne_2

9.60. Dipole moments are sometimes expressed in *debyes*, where

$$1 \text{ debye} = 10^{-18} \text{ (esu of charge)} \times \text{cm}$$

The electrostatic unit (esu) of charge is defined by $1 \text{ C} = 2.998 \times 10^9$ esu. What is the value of 1 debye in SI units?

Ans. $3.336 \times 10^{-30} \text{ C} \cdot \text{m}$

9.61. Where in space are the six electrons in benzene, normally drawn as a ring inside a hexagon?

Ans. The six electrons occupy molecular orbitals, which are made by combining *p*-orbitals that are perpendicular to the plane of the molecule. The electron density can be shown by two identical circular clouds, one above and one below the plane of the molecule.

9.62. If a hydrogen were to be removed from benzene and were to be substituted by a chlorine (or any other entity with a single bond), where would the chlorine be located with respect to the plane of the molecule?

Ans. It would be either above or below the plane of the molecule, but definitely not in the plane of the molecule. The bond is formed using a *p*-orbital and that limits the choice to above or below the plane of the molecule.

9.63. The dipole moment of HBr is $2.6 \times 10^{-30} \text{ C} \cdot \text{m}$ and the interatomic spacing is 141 pm. What is the percent ionic character of HBr?

Ans. 11.5%

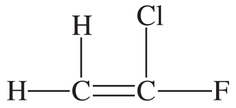
9.64. The dipole moments of NH_3, AsH_3, and BF_3 are $(4.97, 0.60, \text{and } 0.00) \times 10^{-30} \text{ C} \cdot \text{m}$, respectively. What can be concluded about the shapes of these molecules?

Ans. NH_3 and AsH_3 are both pyramidal and BF_3 is planar. From the dipole moments alone, nothing can be concluded about the relative flatness of the NH_3 and AsH_3 pyramids because the electronegativities of nitrogen and arsenic are different.

9.65. The As—Cl bond distance in $AsCl_3$ is 217 pm. Estimate the single-bond radius of As.

Ans. 118 pm

9.66. Predict the bond length between carbon and fluorine in 1-chloro-1-fluoroetheylene (refer to Table 9-2) and predict if there is likely to be variation from your calculations.



Ans. The predicted bond length is 141 pm; however, the presence of the C═C and the chlorine will tend to affect this prediction. Fluorine and chlorine are quite electronegative (compared with carbon), forming negative centers that tend to repel.

9.67. The carbon-carbon double-bond energy in C_2H_4 is 615 kJ/mol and the carbon-carbon single-bond energy in C_2H_6 is 347 kJ/mol. Why is the double-bond energy appreciably less than twice the single-bond energy?

Ans. The σ orbital has greater electron overlap between the atoms because its component atomic orbitals are directed toward each other, whereas the component p orbitals making up the π orbital are directed perpendicularly to the internuclear axis and have only side-to-side overlap.

9.68. Estimate ΔH for the reaction:

$$C_2H_5Cl(g) \rightarrow HCl(g) + C_2H_4(g)$$

given the following bond energies in kJ/mol:

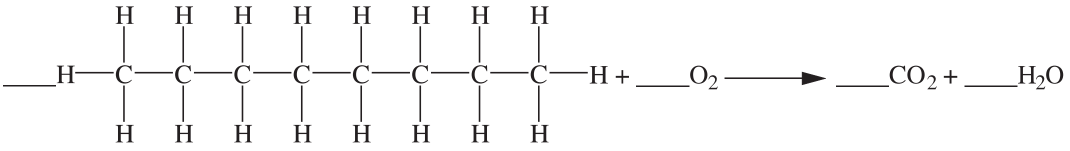
C—C	C—H	Cl—Cl	C—Cl	H—Cl	C═C
346	413	242	339	432	602

Ans. −64 kJ

9.69. Estimate the bond energy of the F—F bond given that ΔH_f° of HF(g) is −271 kJ/mol. The bond energies are H—F, 565 kJ/mol, and H—H, 435 kJ/mol.

Ans. 153 kJ/mol

9.70. Using bond energies, calculate the energy involved in the burning of 1 mol octane, one of the components of gasoline (balance reaction first).



$$\_\_\_\_\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H} + \_\_\_\_O_2 \longrightarrow \_\_\_\_CO_2 + \_\_\_\_H_2O$$

The bond energies (kJ/mol) are: C—C (346), C—H (413), C═O (732), C—O (358), O═O (498), and H—O (463).

Ans. −3965 kJ/mol octane (exothermic reaction)

9.71. Ethanol, C_2H_5OH, is in the spirits that caramelize the sugar on the top of crème brûlée. Calculate the amount of energy involved in the combustion of one mole of ethanol using the bond energies in Problem 9.70.

Ans. −980 kJ/mol C_2H_5OH (exothermic reaction)

SHAPES OF MOLECULES

9.72. The platinum-chlorine distance has been found to be 232 pm in several crystalline compounds. If this value applies to both of the compounds in Fig. 9-18, what is the Cl—Cl distance in (*a*) structure (*a*); (*b*) structure (*b*)?

Ans. (*a*) 464 pm, (*b*) 328 pm

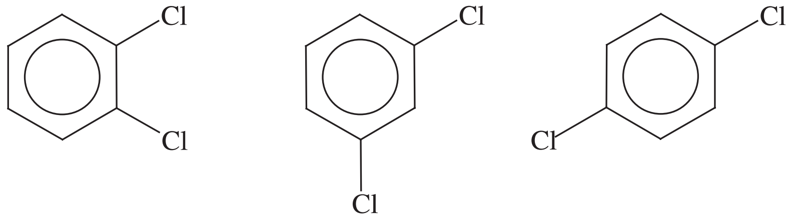
9.73. What is the length of a polymer molecule containing 1001 carbon atoms singly bonded in a line if the molecule could be stretched to its maximum length consistent with maintenance of the normal tetrahedral angle within any C—C—C group?

Ans. 126 nm or 1260 Å

9.74. A plant virus was examined by the electron microscope and was found to consist of uniform cylindrical particles 15.0 nm in diameter and 300 nm long. The virus has a specific volume of $0.73\ \mathrm{cm^3/g}$. If the virus particle is considered to be one molecule, what is its molar mass?

Ans. 4.4×10^7 g/mol

9.75. Assuming the covalent radii in the C—Cl bond are additive, what would be the Cl—Cl distance in each of the three dichlorobenzenes (Fig. 9-49)? Assume that the ring is a regular hexagon and that each C—Cl bond lies on a line through the center of the hexagon. The distance between adjacent carbons is 140 pm.



(*a*) (*b*) (*c*)

Fig. 9-49

Ans. (*a*) 316 pm; (*b*) 547 pm; (*c*) 632 pm

9.76. Estimate the length and width of the carbon skeleton of anthracene, Problem 9-53(*a*). Assume hexagonal rings with equal C—C distances of 140 pm.

Ans. 730 pm long and 280 pm wide

9.77. BBr_3 is a symmetrical planar molecule with all B—Br bonds lying at 120° to each other. The distance between Br atoms is found to be 324 pm. From this fact and given that the covalent radius of Br is 114 pm, estimate the covalent radius of boron. Assume all bonds are single bonds.

Ans. 73 pm

9.78. What is the VSEPR number for the central atoms in each of the following species? (*Hint*: Draw the Lewis structures first.) (*a*) SO_2; (*b*) SO_3; (*c*) SO_3^{2-}; (*d*) SO_4^{2-}; (*e*) SF_6; (*f*) S_3^{2-}

Ans. (*a*) 3; (*b*) 3; (*c*) 4; (*d*) 4; (*e*) 6; (*f*) 4

9.79. What are the bond angles in each of the species in Problem 9.78?

Ans. (*a*) slightly less than 120°; (*b*) 120°; (*c*) slightly less than 109°28′; (*d*) 109°28′; (*e*) 90°; (*f*) slightly less than 109°28′

9.80. Provide the VSEPR number, the general shape, and the bond angles for each of the following species: (*a*) XeF_4; (*b*) XeO_3; (*c*) XeF_2

Ans. (*a*) VSEPR number 6, square planar, 90°; (*b*) VSEPR number 4, trigonal pyramid with one unshared pair at the apex, slightly less than 109°28′; (*c*) VSEPR number 5, linear, 180°

9.81. Which of these molecules or ions is/are straight (i.e., all bond angles 180°)? (*a*) OF_2; (*b*) HCN; (*c*) H_2S; (*d*) CO_2; (*e*) IF_2^-

Ans. (*b*), (*d*), and (*e*)

9.82. Which of the these molecules or ions is/are bent? (*a*) $BeCl_2$; (*b*) HOCl; (*c*) HO_2^-; (*d*) NH_2^-; (*e*) N_3^-

Ans. (*b*), (*c*), and (*d*)

9.83. Which of these molecules or ions is/are flat (all atoms in the same plane)? (*a*) BF_3; (*b*) XeO_4; (*c*) NO_3^-; (*d*) C_2H_2; (*e*) HN_3

Ans. (*a*); (*c*); (*d*); (*e*); (*d*) is perfectly linear; (*e*) is bent at the H end

9.84. Which of these molecules or ions is expected to have a dipole moment? (*a*) CH_2Cl_2; (*b*) *cis*-$C_2H_2Cl_2$; (*c*) *trans*-$C_2H_2Cl_2$; (*d*) CH_2CCl_2; (*e*) SF_4; (*f*) XeF_4; (*g*) C_2F_4; (*h*) H_2SO_4; (*i*) NH_4^+; (*j*) N_2H_4; (*k*) NCl_3

Ans. (*a*); (*b*); (*d*); (*e*); (*h*); (*k*)

9.85. Disregarding any hydrogen atoms, which of these molecules or ions is/are expected to be flat? (*a*) $CH_3CHCHCl$; (*b*) HNO_3; (*c*) $H_2PO_4^-$; (*d*) $SOCl_2$; (*e*) C_6H_5OH

Ans. (*a*), (*b*), and (*e*)

COORDINATION COMPOUNDS

9.86. Name the following compounds (en = ethylenediamine, py = pyridine):
(*a*) $[Co(NH_3)_5Br]SO_4$ (*b*) $[Cr(en)_2Cl_2]Cl$ (*c*) $[Pt(py)_4][PtCl_4]$
(*d*) $K_2[NiF_6]$ (*e*) $K_3[Fe(CN)_5CO]$ (*f*) $CsTeF_5$

Ans. (*a*) pentaamminebromocobalt(III) sulfate

(*b*) dichlorobis(ethylenediamine)chromium(III) chloride

(*c*) tetrapyridineplatinum(II) tetrachloroplatinate(II)

(*d*) potassium hexafluoronickelate(IV)

(*e*) potassium carbonylpentacyanoferrate(II)

(*f*) cesium pentafluorotellurate(IV)

9.87. Write the formulas for the named compounds using square brackets to enclose the complex ion.
(*a*) triamminebromoplatinum(II) nitrate; (*b*) dichlorobis(ethylenediamine)cobalt(II) monohydrate;
(*c*) pentamminesulfatocobalt(III) bromide; (*d*) potassium hexafluoroplantinate(IV);
(*e*) tetraaquadibromochromium(III) chloride; (*f*) ammonium heptafluorozirconate(IV)

Ans. (*a*) $[Pt(NH_3)_3Br]NO_3$; (*b*) $[Co(en)_2Cl_2] \cdot H_2O$; (*c*) $[Co(NH_3)_5SO_4]Br$ (*d*) $K_2[PtF_6]$;
(*e*) $[Cr(H_2O)_4Br_2]Cl$; (*f*) $(NH_4)_3[ZrF_7]$

9.88. Considering that Δ for $IrCl_6^{3-}$ is 27,600 cm^{-1}, (*a*) What is the wavelength of maximum absorption? (*b*) What do you predict for the magnetic behavior of this ion?

Ans. (*a*) 362 nm; (*b*) diamagnetic

9.89. (*a*) What is the maximum number of unpaired electrons which a high-spin octahedral complex of the first transition series could possess in the ground state? (*b*) Which first transition elements could show this maximum? Provide the oxidation states.

Ans. (*a*) 5; (*b*) Mn(II) and Fe(III)

9.90. If the metal of the first transition series has a d^n configuration (in its relevant oxidation state) and forms an octahedral complex, for what values of *i* could magnetic properties alone distinguish between strong-field and weak-field ligands?

Ans. 4, 5, 6, 7

9.91. Both $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ appear colorless in dilute solutions. The former ion is low-spin and the latter is high-spin. (*a*) How many unpaired electrons are in each of these ions? (*b*) In view of the apparent significant difference in their Δ values, why should both ions be colorless?

Ans. (*a*) 0 in $[Fe(CN)_6]^{4-}$, 4 in $[Fe(H_2O)_6]^{2+}$, (*b*) Δ for $[Fe(CN)_6]^{4-}$ is so large that the absorption peak is in the ultraviolet; Δ for $[Fe(H_2O)_6]^{2+}$ is so small that its absorption peak is in the infrared. Both of these ions produce solutions that absorb practically no visible light.

9.92. The hexaaquairon(III) ion is practically colorless. Its solutions become red when NCS^- is added. Explain. (Compare with Problem 9.91.)

Ans. Water is not a strong-field ligand (Problem 9.91). NCS^- has vacant π^* orbitals that overlap the t_{2g} orbitals of the metal and so can accept electron density from the metal. This “back-bonding” increases the strength of the metal-ligand bond and lowers the t_{2g} energy level, making NCS^- a strong-field ligand. These ligands cause an increase in Δ; this produces a lowering of the wavelength of maximum *d*-*d* absorption from the near-infrared well into the visible region (into the blue-green).

ISOMERISM

9.93. How many structural isomers can be drawn for each of these compounds? (*a*) C_5H_{12}; (*b*) C_3H_7Cl; (*c*) $C_3H_6Cl_2$; (*d*) $C_4H_8Cl_2$; (*e*) $C_5H_{11}Cl$; (*f*) C_6H_{14}; (*g*) C_7H_{16}

Ans. (*a*) 3 (*b*) 2; (*c*) 4; (*d*) 9; (*e*) 8; (*f*) 5; (*g*) 9

9.94. Among the paraffin hydrocarbons (C_nH_{2n+2}, where *n* is a whole number), what is the empirical formula of the compound of lowest molar mass which could demonstrate optical activity in at least one of its structural isomers?

Ans. C_7H_{16}

9.95. How many structural and geometrical isomers can be written for the following without counting ring compounds: (*a*) C_3H_5Cl; (*b*) $C_3H_4Cl_2$; (*c*) C_4H_7Cl; (*d*) C_5H_{10}?

Ans. (*a*) 4; (*b*) 7; (*c*) 11; (*d*) 6

9.96. For the square coplanar complex $[Pt(NH_3)(NH_2OH)py(NO_2]^+$, how many geometrical isomers are possible? Describe them.

Ans. There are three isomers. Any one ligand can be *trans* to any of the other three; the two ligands not *trans* to the first have their positions automatically fixed as *trans* to each other.

9.97. Predict whether $[Ir(en)_3]^{3+}$ should exhibit optical isomerism. If so, prove by diagrams that the two optical isomers are not simple rotational aspects of the same compound.

Ans. There are two optical isomers, which are represented in Fig. 9-50.

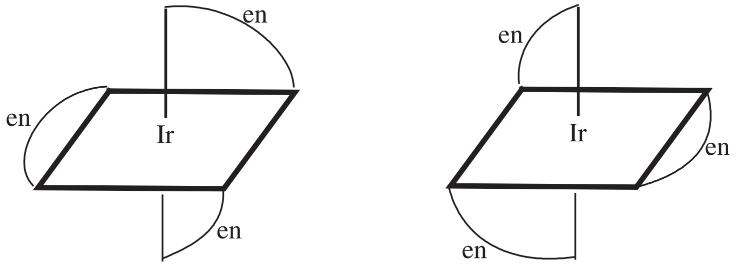


Fig. 9-50

9.98. How many isomers are there with the formula $[M(en)XY_3]$, where M is the central metal, en is the bidentate ligand ethylenediamine, and X and Y are monodentate ligands? Explain how they differ.

Ans. There are two geometric isomers. One of the isomers has two of the Y's *trans* to each other. In the second isomer, all the Y's are *cis*.

BONDING IN METALS

9.99. In silicon there is a gap in energy between the band of bonding MOs and the band of an equal number of antibonding MOs, all derived from the 3*s* and 3*p* atomic orbitals. Is silicon a metal electrical conductor? Explain.

Ans. No. In a crystal of *N* atoms there will be 4*N* MOs, 2*N*of them bonding. The 4*N* valence electrons will just fill these 2*N* bonding MOs, but metallic conductivity requires that the band be only partially filled.

9.100. How does a rise in temperature affect the electrical conductivity of a metal? Explain.

Ans. A rise in temperature lowers the conductivity because vigorous atomic motion disrupts the long-range order of the lattice which obstructs the MOs that are throughout the whole crystal.

9.101. Most metals are ductile and malleable, in contrast to the brittleness of most other solids. Account for these properties in terms of the electron-sea model.

Ans. Since the atoms are rather far apart and the electron sea offers little resistance to deformation, it does not require much energy to cause one layer of atoms to slide past another. Because of this factor the crystal is deformed rather than being shattered by an external stress.

CHAPTER 10

Solids and Liquids

INTRODUCTION

Solids are substances that tend to have a definite shape indicating an extremely well-organized and regular structure (*crystalline structure*). The crystalline structure is studied through various means, including the use of x-rays. These studies are used to make predictions relating to the stability of the structure when under stress, the changes that occur with the addition of other substances, and the prediction of the characteristics of other crystalline substances.

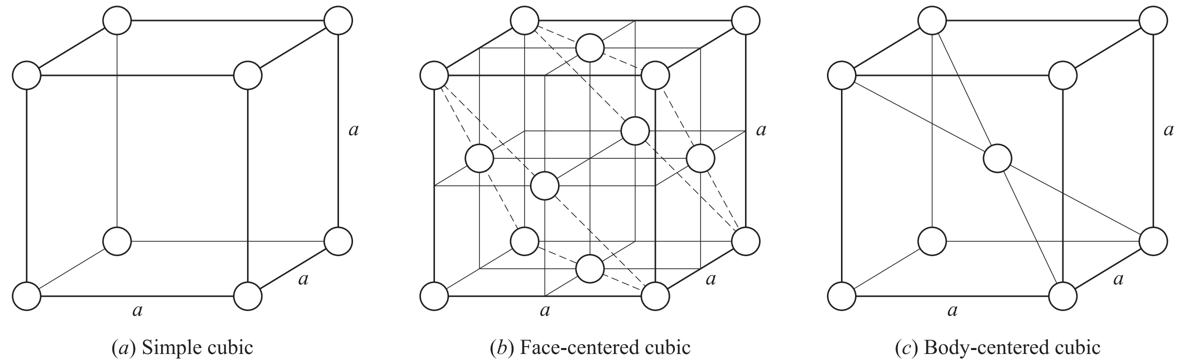
CRYSTALS

The arrangement of the simpler particles in a crystalline array is called a *lattice*. Every lattice is a three-dimensional stacking of identical building blocks called *unit cells*. The properties of a crystal, including its overall symmetry, can be understood in terms of the unit cell. Each different unit cell (14 of them) can fill in space by being arranged adjacent to an identical unit with others placed above, below, and in the other adjacent positions (think of stacking boxes in a warehouse). Figure 10-1 contains sketches of three unit cells for your inspection; these are the only unit cells we discuss in detail in this book.

The unit cells in Fig. 10-1 are the only ones having cubic symmetry. The lattice points (corners of the cubes and centers of the edges or faces) represent the *centers* of the atoms or ions occupying the lattice. The atoms or ions by themselves are not points (displayed as circles), but are three-dimensional objects which usually are in contact with each other. The representations of these objects in Fig. 10-1 are purposely out of scale (shrunken) for simplicity. The length of the cube edge is designated by *a*. A crystal having any of these three lattices can be thought of as a three-dimensional stack of unit cell cubes, packed face-to-face so that the space occupied by the crystal is completely filled.

The crystal classes that are less symmetrical than the cubic have unit cells that may be thought of as more or less distorted cubes, the opposite faces of which are parallel to each other. Such shapes are generally known as *parallelipiped*. Crystals with hexagonal symmetry, like snow or ice, have unit cells that are prisms with a vertical axis perpendicular to a rhombus-shaped base, the equal edges of which are at 60° and 120° with respect to each other. A typical hexagonal unit cell is shown in Fig. 10-2. The letters designate the length of each of the edges. Although this doesn't look like a hexagonal prism, three unit cells joined adjacent to each other will produce the structure.

Keeping in mind that a crystal is composed of many of its unit cells and assuming there is no contamination, the density of a crystal can be computed from the properties of the unit cell. It is necessary to apportion the mass of the crystal among the various unit cells, and then to divide the mass apportioned to one unit cell by the volume of the unit cell. In computing the mass of a unit cell, it is important to assign to the cell only that fraction of



(*a*) Simple cubic (*b*) Face-centered cubic (*c*) Body-centered cubic

Fig. 10-1 Unit cells of symmetry.

an atom which lies completely in that cell. If an atom is shared by cells, the portion of the atom in each unit is credited to that unit cell.

If a unit cell is cubic, we see from Fig. 10-3, since a corner atom is shared by eight unit cells, that

$$\begin{aligned}\text{Mass per unit cell} = {} & \frac{1}{8}(\text{mass of atoms, like } A\text{, on corners of the unit cell}) \\ & + \frac{1}{4}(\text{mass of noncorner atoms, like } C\text{, on the unit cell edges}) \\ & + \frac{1}{2}(\text{mass of nonedge atoms, like } B\text{, on the faces of the unit cell}) \\ & + (\text{mass of interior atoms, like } G\text{, within the unit cell})\end{aligned}$$

Note that the formula holds whether or not all the atoms belong to the same species and also holds for noncubic cells.

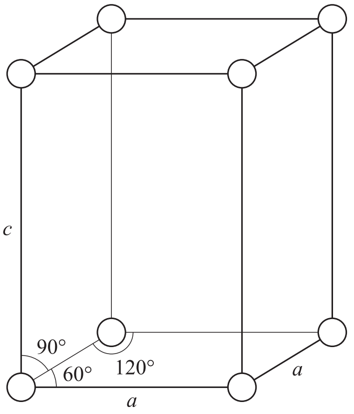


Fig. 10-2 A hexagonal unit cell.

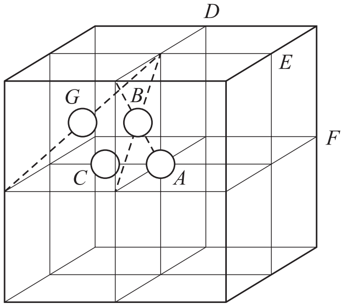


Fig. 10-3 Stack of eight cubic unit cells.

Coordination number

The *coordination number* of an atom in a crystal is the number of nearest-neighbor atoms. The coordination number is constant for a given lattice [see Problems 10.1(*b*) and 10.14(*d*)].

Close packing

Two simple lattice structures allow a high degree of packing of the atoms in a crystal. The first is called a *close-packed* structure. It is a structure in which identical spheres (the atoms) occupy the greatest fraction of the total space. It can be achieved by packing on top of each other two-dimensional close-packed layers. In each of the layers, every sphere is surrounded by a regular hexagonal arrangement of six other spheres, as in Fig. 10-4. In the figure, the large circles represent the spheres in one such layer. The squares surround the *centers* of spheres in the adjoining superimposed layer. If the third and every odd-numbered layer is made up of spheres directly over the spheres in the first layer and if every even-numbered layer is made up of spheres directly over the spheres in the second layer, the structure is a *hexagonal close-packed* structure. The corresponding unit cell for the centers of the spheres is given in Problem 10-15.

In the case of the second structure allowing a high degree of packing, if the structure is a regular alternation of three kinds of layers, the third being made up of spheres whose centers are enclosed by small circles in Fig. 10-4, the structure is a *cubic close-packed* structure. The unit cell of this structure is the face-centered cubic. The close-packed layers are perpendicular to a body diagonal of the unit cell [see the dashed triangles in Fig. 10-1(*b*)].

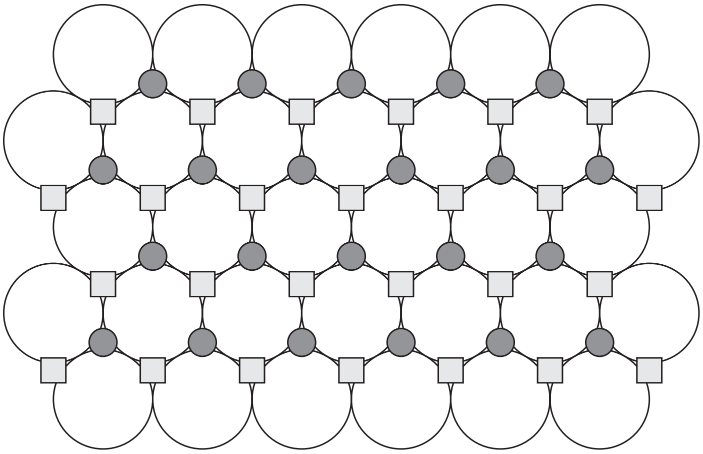


Fig. 10-4

Both the hexagonal close-packed and cubic close-packed lattices have the same 74 percent filling of space by spheres in contact [see Problem 10.1(*d*)], and the two lattices also have the same coordination number, which is 12.

There are commonly void spaces (*holes*) in a crystal that can sometimes admit foreign particles of a smaller size than the hole. An understanding of the geometry of these holes becomes an important consideration as characteristics of the crystal will be affected when a foreign substance is introduced. In the cubic close-packed structure, the two major types of holes are the *tetrahedral* and the *octahedral* holes. In Fig. 10-1(*b*), tetrahedral holes are in the centers of the indicated minicubes of side *a*/2. Each tetrahedral hole has four nearest-neighbor occupied sites. The octahedral holes are in the body center and on the centers of the edges of the indicated unit cell. Each octahedral hole has six nearest-neighbor occupied sites.

CRYSTAL FORCES

The strength of the forces holding crystalline substances together varies considerably. In *molecular crystals*, such as CO_2 and benzene (both nonpolar, both in the solid state), each molecule is almost independent of all the others and retains practically the same internal geometry (bond lengths and angles) that it has in the gaseous or liquid state. These crystals are held together by van der Waals forces, a very weak intermolecular attractive force. The melting and boiling points for these substances are never very high as compared to the substances described next.

For substances that can undergo hydrogen bonding, the intermolecular forces in the crystal can be great enough to impose a noticeable change in the molecular geometry. *Hydrogen bonding* is the attraction between the positive charge-carrying hydrogen of a polar bond in one molecule (or part of a molecule) and the negative charge-carrying atom of a polar bond of another molecule (or part of the same molecule—a common condition in proteins). The most important polar bonds that allow hydrogen bonding are those between hydrogen and the most electronegative element: fluorine, oxygen, nitrogen, and chlorine. Water is an example of extensive hydrogen bonding; the angle between the two O—H bonds in the vapor is about 105°, but equals the tetrahedral $109°28'$ in the crystal conforming with the crystalline spatial requirements, rather than the molecular arrangement.

In *metals*, a special type of crystalline force comes into play which is characterized by a largely nondirectional nature. Fixed bond angles do not play a major role in metals and the more stable crystal structures for most elementary metals are those with the densest packing. Important exceptions are the Group IA metals and iron, which have the body-centered cubic structure. In the *covalent crystals*, like diamond or silicon carbide, the crystal is held together by a three-dimensional network of covalent bonds, the mutual angles of which are determined largely by the covalent bonding requirements of the individual atoms.

IONIC RADII

The attractive forces operating in *ionic crystals* are mostly electrostatic in nature, the classical attraction between oppositely charged particles. To avoid the repulsion between similarly charged particles, ionic substances crystallize in structures in which a positive and a negative ion can come within touching distance, while ions of like charge are kept away from each other. In fact, the dimensions of most simple purely ionic crystals can be understood by assuming an ionic radius (Chapter 9) for each ion that is valid for all compounds of that ion and taking the smallest cation-anion separation to be the sum of the ionic radii of the cation and anion. Radii for some elementary ions are listed in Table 10-1.

Table 10-1 Ionic Radii

Ion	Radius/pm	Ion	Radius/pm
Li^+	60	Cd^{2+}	97
Na^+	95	Ni^{2+}	69
K^+	133	Al^{3+}	50
Cs^+	169	H^-	208
Ag^+	126	F^-	136
Mg^{2+}	65	Cl^-	181
Ca^{2+}	99	Br^-	195
Sr^{2+}	113	I^-	216
Ba^{2+}	135	O^{2-}	140
Zn^{2+}	74	S^{2-}	184

FORCES IN LIQUIDS

The forces that bind atoms, ions, and molecules in liquids are the same as in those that result in solids. The difference is that the strengths of these forces are not sufficient to hold the particles in as rigid a structure as is seen in the solid state. Although, just above the melting point, these forces are insufficient to restrain the atoms, ions, or molecules to their lattice positions, in most cases they are strong enough to prevent vaporization.

Liquid metals and salts, especially those that are ionic, are not common except in industrial technology and occur at much higher temperatures than normally encountered. Since the internal forces are so strong, the temperatures required for melting are high and the temperature range for the liquid state is very great as compared with the melting points for covalent substances.

Most familiar liquids consist of molecular substances (water, alcohols, benzene, bromine, etc.) which freeze into molecular solids. The molecules are bound to their neighbors by weak forces, the strongest of which, by far, are hydrogen bonds. Others are known collectively as van der Waals forces. All atoms and molecules are attracted to one another. If a molecule has a permanent dipole moment (Chapter 9), dipole-dipole attraction makes a significant contribution to the weak force. But even in the absence of permanent dipoles, weak forces known as London forces exist. London forces are due to the presence of transient dipoles of very short duration, as explained by Fritz London. Generally, the greater the atomic number of the atoms in contact, the greater the area of contact and the greater the London forces between molecules.

The strength of the weak forces is revealed by the volatility of a substance—the greater the intermolecular attractive forces, the higher the boiling point. An example is Group VIIIA, the noble gases (inert gases). These elements display a steady increase in boiling point as the atomic number increases due to the increase in London forces. Additionally, comparing $SiCl_4$ (B.P. 57.6°C) to PCl_3 (B.P. 75.5°C, we see the contribution of the dipole-dipole attractions in the latter case. The contributions of dipole-dipole attractions and hydrogen bonding are very important in comparing organic compounds, as illustrated by C_2H_6 (ethane's B.P. −89°C, London forces only), CH_3F (methyl fluoride's B.P. −78°C, dipole), and CH_3OH (methyl alcohol's B.P. 65°C, H bonding). Among the compounds of formula C_nH_{2n+2} the straight-chain compound always has a boiling point higher than any of its branched chair isomers because of the increased area of contact of such a molecule with its surroundings.

Solved Problems

CRYSTAL DIMENSIONS

10.1. Metallic gold crystallizes in the face-centered cubic lattice. The length of the cubic unit cell [Fig. 10-1(*b*)] is $a = 407.0\,\text{pm}$. (*a*) What is the closest distance between gold atoms? (*b*) How many "nearest-neighbors" does each gold atom have at the distance calculated in (*a*)? (*c*) What is the density of gold? (*d*) Prove that the *packing factor* for gold, the fraction of the total volume occupied by the atoms themselves, is 0.74.

(*a*) Consider the corner gold atom in Fig. 10-1(*b*). The closest distance to another corner atom is *a*. The distance to an atom at the center of a face is one-half the diagonal of that face, as follows:

$$\frac{1}{2}(a\sqrt{2}) = \frac{a}{\sqrt{2}}$$

and, by substitution, the closest distance between atoms is

$$\frac{407.0\,\text{pm}}{\sqrt{2}} = 287.8\,\text{pm}$$

(*b*) The problem is to find how many face-centers are equidistant from a corner atom. Point *A* in Fig. 10-3 may be taken as the reference corner atoms. In that same figure, *B* is one of the face-center points at the nearest distance to *A*. In the plane *ABD* in the figure there are three other points equally close to *A*: the centers of the squares in the upper right, lower left, and lower right quadrants of the plane, measured around *A*. Plane *ACE*, parallel to the plane of the paper, also has points in the centers of each of the squares in the four quadrants around *A*. Additionally, plane *ACF*, perpendicular to the plane of the paper, has points in the centers of each of the squares in the four quadrants around *A*. Adding them up, there are 12 nearest-neighbors in all, the number expected for a close-packed structure.

The same result would have been obtained by counting the nearest-neighbors around *B*, a face-centered point.

(*c*) Let us use m for the mass of a single gold atom and the atomic mass of 197.0 g/mol Au. For the face-centered cubic structure, with 8 corners and 6 face-centers,

$$\text{Mass per unit cell} = \frac{1}{8}(8m) + \frac{1}{2}(6m) = 4m$$

and
$$m = \left(197.0\,\frac{\text{g}}{\text{mol}}\right)\left(\frac{1\text{ mol}}{6.022\times 10^{23}\text{atoms}}\right) = 3.27\times 10^{-22}\text{ g/atom}$$

then
$$\text{Density} = \frac{4m}{a^3} = \frac{4(3.27\times 10^{-22})}{(4.07\ \times 10^{-8}\text{ cm})^3} = 19.4\text{ g/cm}^3$$

The reverse of this type of calculation can be used for a precise determination of Avogadro's number, provided the lattice dimensions, the density, and the atomic mass are known precisely.

(*d*) Since the atoms at closest distance are in contact in a close-packed structure, the closest distance between centers calculated in (*a*), $a/\sqrt{2}$, must equal the sum of the radii of the two spherical atoms, $2r$. Going one step further, $r = a/\sqrt{2}/2 = a/2^{3/2}$. From (*c*), there are four gold atoms per unit cell. Then,

$$\text{Volume of 4 gold atoms} = 4\left(\frac{4}{3}\pi r^3\right) = 4\left(\frac{4}{3}\pi\right)\left(\frac{a}{2^{3/2}}\right)^3 = \frac{\pi a^3}{3\sqrt{2}}$$

and
$$\text{Packing fraction} = \frac{\text{volume of 4 gold atoms}}{\text{volume of unit cell}} = \frac{\pi a^3/3\sqrt{2}}{a^3} = \frac{\pi}{3\sqrt{2}} = 0.7405$$

Note that the parameter a for the gold unit cell canceled and that the result holds for any cubic close-packed structure. The *metallic* radius calculated above, $r = a/2^{3/2} = 143.9$ pm, is different from both an ionic radius and a covalent radius.

10.2. Show that the tetrahedral and octahedral holes in gold are appropriately named. Find the closest distance between an impurity atom and a gold atom if the impurity atom occupies (*a*) a tetrahedral hole, (*b*) an octahedral hole. How many holes of each type are there per gold atom?

(*a*) Examine Fig. 10-1(*b*) and imagine a hole in the center of the upper left front minicube. This hole is equidistant from the four occupied corners of the minicube, the common distance being half a body diagonal of the minicube, or

$$\frac{1}{2}\sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2} = \frac{a\sqrt{3}}{4}$$

These four occupied corners define a regular tetrahedron (see Problem 9.18) with the center of the tetrahedron being the point equidistant from the corners, which we showed as the location of the hole. This justifies the name "tetrahedral hole." As the unit cell contains 8 tetrahedral holes, one in each minicube, and 4 gold atoms (Problem 10.1), there are $8 \div 4 = 2$ tetrahedral holes per gold atom.

(*b*) Now, consider the hole at the center of the unit cell of Fig. 10-1(*b*). This hole is equidistant from the centers of all six faces of the unit cell, all of which are the nearest occupied sites to the hole. These six points are the vertices of an eight-faced figure; the faces are congruent equilateral triangles (whose edges are face diagonals of the minicube). Such a figure is a regular octahedron and the hole is at its center; "octahedral hole" is correct.

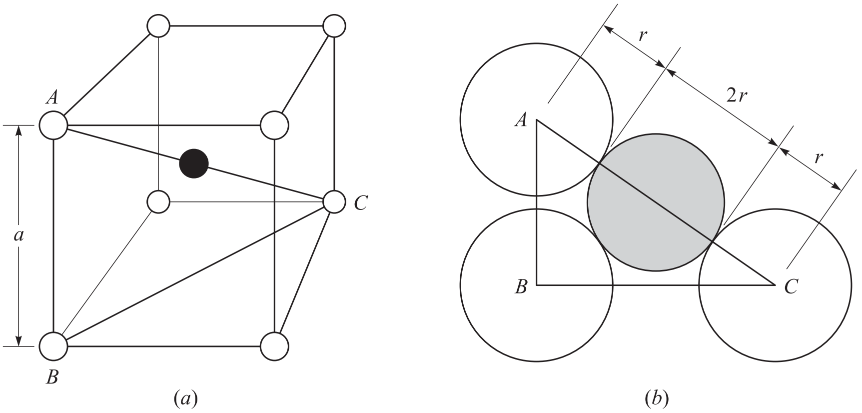
The distance between the hole and the nearest-neighbor atom is $a/2$. A similar proof can be made for an octahedral hole on the center of an edge of the unit cell in Fig. 10-1(*b*) if we note that the actual crystal lattice consists of a three-dimensional stack of unit cells, as in Fig. 10-3. Each such edge-center hole is shared by four unit cells and there are 12 edges in a cube, so that the number of octahedral holes per unit cell is

$$1 + \frac{1}{4}(12) = 4$$

The ratio of octahedral holes to gold atoms is 4:4, or 1:1, which can be simply stated as 1.

There are competing advantages of tetrahedral and octahedral holes for housing impurities or second components of an alloy. If the crystal forces, whatever their nature, depend mostly on interactions between nearest-neighbors, the octahedral hole has the advantage of having more nearest-neighbors with which it interacts (6 instead of 4). However, the tetrahedral hole has a shorter near-neighbor distance ($a\sqrt{\frac{3}{4}} = 0.433a$, as opposed to $0.500a$), giving it the advantage of a greater potential interaction with any one host atom. An octahedral hole, with its larger nearest-neighbor distance, can accommodate a larger impurity or alloying atom than can a tetrahedral hole, without straining the host lattice.

10.3. CsCl crystallizes in a cubic structure that has a Cl^- at each corner and a Cs^+ at the center of the unit cell. Use the ionic radii listed in Table 10.1 to predict the lattice constant, a, and compare with the value of a calculated from the observed density of CsCl, 3.97 g/cm^3.



(*a*) (*b*)

Fig. 10-5

Figure 10-5(*a*) shows a schematic view of the unit cell where the shaded circles are the Cs^+ cation and the unshaded circles represent Cl^-. The circles are made small with respect to the unit cell length, a, in order to show more clearly the locations of the various ions. Figure 10-5(*b*) is a more realistic representation of the right triangle *ABC* showing anion-cation-anion contact along the diagonal *AC*.

Let us assume that the closest Cs^+-to-Cl^- distance is the sum of the ionic radius of Cs^+ and Cl^-, which is $169 + 181 = 350\,\text{pm}$. This distance is one-half the cube diagonal, or $a\sqrt{3}/2$. Then

$$\frac{a\sqrt{3}}{2} = 350\,\text{pm} \qquad \text{or} \qquad a = \frac{2(350\,\text{pm})}{\sqrt{3}} = 404\,\text{pm}$$

The density can be used to calculate a if we count the number of ions of each type per unit cell. The number of assigned Cl^- ions per unit cell is one-eighth of the number of corner Cl^- ions, or $\frac{1}{8}(8) = 1$.

The only Cs^+ in the unit cell is the center Cs^+, so that the assigned number of cesium ions is also 1. (This type of assignment of ions or atoms in a compound must always agree with the empirical formula of the compound, as the 1:1 ratio does in this case.) The assigned mass per unit cell is that of 1 formula unit of CsCl by

$$\frac{132.9 + 35.5}{6.02 \times 10^{23}}\,\text{g} = 2.797 \times 10^{-22}\,\text{g}$$

$$\text{Volume of unit cell} = a^3 = \frac{\text{mass}}{\text{density}} = \frac{2.797 \times 10^{-22}\,\text{g}}{3.97\,\text{g/cm}^3} = 70.4 \times 10^{-24}\,\text{cm}^3$$

then,

$$a = \sqrt[3]{70.4 \times 10^{-24}\,\text{cm}^3} = 4.13 \times 10^{-8}\,\text{cm} = 413\,\text{Å}$$

This value, based on the experimental density, is to be considered the more reliable, since it is based on a measured property of CsCl, while the ionic radii are based on averages over many different compounds. Unit cell dimensions can be measured accurately by x-ray diffraction and from them the theoretical density can be calculated. The measured density is usually lower because most samples that are large enough to measure are not perfect single crystals and contain empty spaces in the form of grain boundaries and various crystalline imperfections.

The CsCl structure is *not* described as body-centered, since the particle occupying the center is different from the particles occupying the corners of the unit cell. There are two ways of describing the structure. One way is to say that Cs^+ occupies the central holes of the Cl^- simple cubic lattice. Another way is to say that the structure is made up of two interpenetrating simple cubic lattices, one made up of Cl^- and one of Cs^+. The Cs^+ lattice is displaced from the Cl^- lattice along the direction of the unit cell diagonal by one-half the length of the unit cell diagonal.

10.4. The CsCl structure (Fig. 10-5) is observed in alkali halides only when the radius of the cation is sufficiently large to keep its eight nearest-neighbor anions from touching. What minimum value for the ratio of the cation-to-anion radii, r_+/r_-, is needed to prevent this contact?

In the CsCl structure, the nearest cation-anion distance occurs along the diagonal of the unit cell cube, while the nearest anion-anion distance occurs along a unit cell edge. This relationship is shown in Fig. 10-5(*b*). In the figure,

$$\overline{AB} = a \qquad \overline{BC} = a\sqrt{2} \qquad \overline{AC} = a\sqrt{3}$$

If we assume anion-cation contact along AC, then $\overline{AC} = 2(r_+ + r_-) = a\sqrt{3}$. In the limiting case, where the anions touch along the edge of the unit cell, $2r_- = a$. Dividing the former equation by the latter,

$$\frac{r_+}{r_-} + 1 = \sqrt{3} \qquad \text{or} \qquad \frac{r_+}{r_-} = \sqrt{3} - 1 = 0.732$$

If the ratio were less than this critical value, anions would touch (increasing repulsive forces). Also, the cation and anion would be separated (decreasing attractive forces). Both effects would tend to make the structure unstable.

10.5. Ice crystallizes in a hexagonal lattice. At the low temperature at which the structure was determined, the lattice constants were $a = 453$ pm and $c = 741$ pm (Fig. 10-2). How many water molecules are contained in a unit cell?

The volume, V, of the unit cell in Fig. 10-2 is

$$V = (\text{area of rhombus base}) \times (\text{height } c)$$

$$V = (a^2 \sin 60^\circ)c = (453\,\text{pm})^2(0.866)(741\,\text{pm}) = 132 \times 10^6\,\text{pm}^3 = 132 \times 10^{-24}\,\text{cm}^3$$

Although the density of ice at the experimental temperature is not stated, it could not be very different from the value at 0°C, which is $0.92\,\text{g/cm}^3$.

$$\text{Mass of unit cell} = V \times \text{Density} = (132 \times 10^{-24}\,\text{cm}^3)(0.92\,\text{g/cm}^3)(6.02 \times 10^{23}\,\text{u/g}) = 73\,\text{u}$$

This is close to 4 times the molecular mass of water; we conclude that there are four molecules of water per unit cell. The discrepancy between 73 u and the actual mass of four molecules, 72 u, is undoubtedly due to the uncertainty in the density at the experimental temperature.

10.6. $BaTiO_3$ crystallizes in the perovskite structure. This structure may be described as a barium-oxygen face-centered cubic lattice, with barium ions occupying the corners of the unit cell, oxide ions occupying the face-centers, and titanium ions occupying the centers of the unit cells. (*a*) If titanium is described as occupying holes in the Ba-O lattice, what type of hole does it occupy? (*b*) What fraction of the holes of this type does it occupy? (*c*) Suggest a reason why it occupies those holes of this type but not the other holes of the same type?

(*a*) These are octahedral holes.

(*b*) The octahedral holes at the centers of the unit cells constitute just one-fourth of all the octahedral holes in a face-centered cubic lattice (see Problem 10.2).

(*c*) An octahedral hole at the center of a unit cell has six nearest-neighbor oxide ions and is occupied by a titanium ion. The other octahedral holes are located at the centers of the edges of the unit cell and have six nearest-neighbors each, as is the case with any octahedral hole. However, two of the six neighbors are barium ions (at the unit-cell corners terminating in a given edge) and four are oxide ions. The proximity of two cations, Ba^{2+} and Ti^{4+}, would be electrostatically unfavorable.

CRYSTAL FORCES

10.7. The melting point of quartz, a crystalline form of SiO_2, is 1610°C, and the sublimation point of CO_2 is −79°C. How similar do you expect the crystal structures of these two substances to be?

The big difference in melting points suggests a difference in type of crystal binding. The intermolecular forces in solid CO_2 must be very low to be overcome by a low-temperature sublimation. CO_2 is actually a molecular lattice held together only by the weak van der Waals forces between discrete CO_2 molecules. SiO_2 is a covalent lattice with a three-dimensional network of bonds; each silicon atom is bonded tetrahedrally to four oxygen atoms and each oxygen is bonded to two silicon atoms.

10.8. In the hexagonal ice structure (Fig. 10-6 shows the position of the oxygen atoms), each oxygen is coordinated tetrahedrally with four other oxygens. There is an intervening hydrogen between adjoining oxygen atoms. The ΔH of sublimation of ice at 0°C is 51.0 kJ/mol H_2O. It has been estimated by comparison with non-hydrogen-bonded solids having intermolecular van der Waals forces similar to those in ice that the ΔH of sublimation would be only 15.5 kJ/mol if ice were not hydrogen-bonded. Estimate the strength of the hydrogen bond in ice from these data.

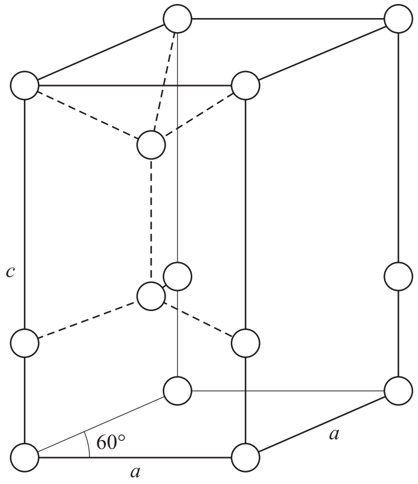


Fig. 10-6

The excess of ΔH of sublimation above that of a non-hydrogen-bonded solid can be attributed to hydrogen bonds.

$$\Delta H_{\text{excess}} = 51.0 - 15.5 = 35.5\,\text{kJ/mol}$$

Each H_2O is hydrogen-bonded to four other water molecules through O—H—O linkages (indicated in Fig. 10-6 only for the two interior molecules). Each such hydrogen-bonded linkage is shared by two water molecules (to which the two oxygen atoms belong). Our conclusion is that on the average, each water can be assigned 4 halves, or 2 hydrogen bonds.

$$\Delta H_{\text{hydrogen bond}} = \frac{35.5\,\text{kJ/mol H}_2\text{O}}{2\,\text{mol hydrogen bonds/mol H}_2\text{O}} = 17.8\,\text{kJ/mol hydrogen bond}$$

Then, from Fig. 10-6,

$$8\left(\frac{1}{8}\right)+4\left(\frac{1}{4}\right)+2=4$$

Four water molecules are assigned to the unit cell, agreeing with the result from Problem 10.5.

10.9. Which would have the higher melting point, (*a*) V or Ca, (*b*) MgO or KCl? Explain.

(*a*) Vanadium is expected to have a much greater charge density in the electron sea since it has three 3*d* electrons in addition to the two 4*s* electrons to contribute; calcium only has two electrons in the outside orbit. Further, the ionic cores, being smaller, will be closer together. As a result of these factors, the crystal forces will be greater in vanadium than calcium. The actual melting points are 1890°C for vanadium and 845°C for calcium. The relative closeness of the cores is indicated by the densities, which are 6.11 g/cm^3 for V and 1.55 g/cm^3 for Ca.

(*b*) MgO will have a higher melting point. The first consideration is that the smaller cation and anion in MgO allows for closer approach. Further, both the cation and the anion carry twice as much charge as K^+ and Cl^-. This becomes clear when we consider that the electrostatic force is proportional to the product of the charges and inversely proportional to the square of the distance between them. The actual melting points are 2800°C for MgO and 776°C for KCl.

FORCES IN LIQUIDS

10.10. In each case, indicate which liquid will have the higher boiling point and explain your choice.
(*a*) CO_2 or SO_2 (*b*) $(CH_3)_2CHCH(CH_3)_2$ or $CH_3CH_2CH_2CH_2CH_2CH_3$
(*c*) Cl_2 or Br_2 (*d*) C_2H_5SH or C_2H_5OH

(*a*) SO_2. The molecule is angular and has a permanent dipole moment; CO_2 is linear and not polar. Note that CO_2 is never liquid at 1 atm pressure; further, the solid *sublimes* (goes directly to the gaseous state without passing through the liquid state).

(*b*) $CH_3CH_2CH_2CH_2CH_2CH_3$. Assuming the straight-chain isomer, there is a greater area of contact between neighbors.

(*c*) Br_2. The higher the atomic number, the greater the London force attraction between molecules.

(*d*) C_2H_5OH. Hydrogen bonding is present due to the oxygen; the attractions in the sulfur compound are weak enough to not be a consideration.

Supplementary Problems

CRYSTAL DIMENSIONS

10.11. The crystalline structure of lead (207.2 g/mol) is face-centered cubic; lead's density is 11.34 g/cm^3. Calculate the length of a unit cell.

Ans. 4.95 Å

10.12. One of the crystalline forms of plutonium (Pu, 244 g/mol) is assumed to be body-centered cubic. The density of this form is 16.51 g/cm^3; calculate

(*a*) the mass of a unit cell;

(*b*) the length of one side of the unit cell in Å; and

(*c*) the radius of one plutonium atom in Å.

Ans. (*a*) 8.10×10^{-22} g; (*b*) 3.66 Å; (*c*) 1.58 Å

10.13. Potassium crystallizes in a body-centered cubic lattice (unit cell length $a = 520\,\text{pm}$).

(*a*) What is the distance between nearest-neighbors?

(*b*) What is the distance between next-nearest-neighbors?

(*c*) How many nearest-neighbors does each potassium atom have?

(*d*) How many next-nearest-neighbors does each potassium atom have?

(*e*) What is the calculated density of crystalline potassium?

Ans. (*a*) 450 pm; (*b*) 520 pm; (*c*) 8; (*d*) 6; (*e*) 0.924 g/cm^3

10.14. The hexagonal close-packed lattice can be represented by Fig. 10-2 if $c = a\sqrt{\frac{8}{3}} = 1.633a$. There is an atom at each corner of the unit cell and another atom which can be located by moving one-third the distance along the diagonal of the rhombus base, starting at the lower left-hand corner and moving perpendicularly upward by $c/2$. Magnesium crystallizes in this lattice and has the density of 1.74 g/cm^3.

(*a*) What is the volume of the unit cell?

(*b*) What is a?

(*c*) What is the distance between nearest-neighbors?

(*d*) How many nearest-neighbors does each atom have?

Ans. (*a*) $46.4 \times 10^6\,\text{pm}^3$; (*b*) 320 pm; (*c*) 320 pm; (*d*) 12

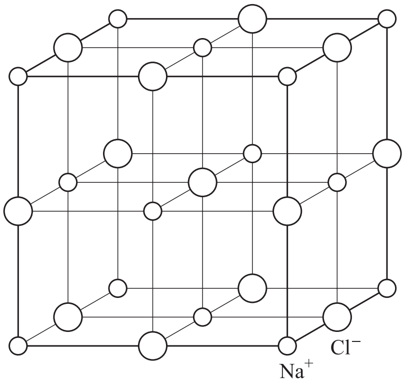


Fig. 10-7 NaCl unit cell.

10.15. The NaCl lattice has the cubic unit cell shown in Fig. 10-7. KBr also crystallizes this lattice.

(*a*) How many K$^+$ ions and how many Br$^-$ ions are in each unit cell?

(*b*) Assuming that ionic radii are additive, what is a?

(*c*) Calculate the density of a perfect KBr crystal.

(*d*) What minimum value of r_+/r_- is needed to prevent anion-anion contact in this structure?

Ans. (*a*) 4 each; (*b*) 656 pm; (*c*) 2.80 g/cm^3; (*d*) 0.414

10.16. MgS and CaS both crystallize in the NaCl-type lattice (Fig. 10-7). From the ionic radii listed in Table 10.1, what conclusion can you draw about anion-cation contact in these crystals?

Ans. Ca^{2+} and S^{2-} can be in contact, but Mg^{2+} and S^{2-} cannot. In MgS, if Mg^{2+} and S^{2-} were in contact, there would not be enough room for the sulfide ions along the diagonal of a square constituting one-quarter of a unit cell face. In other words, for MgS, r_+/r_- is less than 0.414 [see Problem 10.15(*d*)].

10.17. Each rubidium *halide* (Group VIIA element) crystallizing in the NaCl-type lattice has a unit cell length 30 pm greater than that for the corresponding potassium salt of the same halogen. What is the ionic radius of Rb^+ computed from these data?

Ans. 148 pm

10.18. Iron crystallizes in several modifications. At about 910°C, the body-centered cubic α-form undergoes a transition to the face-centered cubic γ-form. Assuming that the distance between nearest-neighbors is the same in the two forms at the transition temperature, calculate the ratio of density of γ-iron to that of α-iron at the transition temperature.

Ans. 1.09

10.19. The ZnS zinc blende structure is cubic. The unit cell may be described as a face-centered sulfide ion sublattice with zinc ions in the centers of alternating minicubes made by partitioning the main cube into eight equal parts.

(*a*) How many nearest-neighbors does each Zn^{2+} have?

(*b*) How many nearest-neighbors does each S^{2-} have?

(*c*) What angle is made by the lines connecting any Zn^{2+} to any two of its nearest-neighbors?

(*d*) What minimum r_+/r_- ratio is needed to avoid anion-anion contact, if closest cation-anion pairs are assumed to touch?

Ans. (*a*) 4; (*b*) 4; (*c*) $109°28'$; (*d*) 0.225

10.20. Why does ZnS not crystallize in the NaCl structure? (*Hint*: Refer to Problem 10.15.)

Ans. The r_+/r_- ratio is 0.402, too low to avoid anion-anion contact in the NaCl structure.

10.21. Calculate the packing factor of spheres occupying (*a*) a body-centered cubic and (*b*) a simple cubic structure, where closest neighbors in both cases are in contact.

Ans. (*a*) 0.680; (*b*) 0.524

10.22. Many oxide minerals can be visualized as a face-centered oxide ion lattice with cations distributed within the tetrahedral and octahedral holes. Calculate the lattice constant, *a*, for a face-centered O^{2-} lattice. If cations occupy all the octahedral holes in MgO and CaO, calculate *a* for these minerals. Use data in Table 10-1.

Ans. For an oxide lattice, $a = 396$ pm. With magnesium and calcium ions in the octahedral holes, anion-anion contact is broken and *a* expands to 410 pm and 478 pm, respectively.

10.23. Lithium iodide crystallizes in the NaCl lattice in spite of the fact that r_+/r_- is less than 0.414. Its density is 3.49 g/cm^3. Calculate from these data the ionic radius of the iodide ion.

Ans. The calculated ionic radius is 224 pm. Note that the value in Table 10-1 is 216 pm.

10.24. Thallium(I) bromide crystallizes in the CsCl lattice. Its density is 7557 kg/m^3 and its unit cell edge-length, *a*, is 397 pm. From these data, estimate Avogadro's number.

Ans. 6.01×10^{23} molecules/mol

CRYSTAL FORCES

10.25. Aluminum can be used in wiring and often is for high-tension lines because it is a reasonably good conductor and is light-weight. The atomic radius for Al is 1.431 Å; a crystal of Al is face-centered cubic. (*a*) Calculate the cube edge length of a crystal. (*b*) What is the number of nearest-neighbors for each atom in the crystal?

Ans. (*a*) 21.02 Å; (*b*) 12

10.26. Calculate the theoretical density of aluminum and compare it to the published density, 2.702 g/cm^3. Refer to the previous problem.

Ans. 2.7023, calculated. The theoretical density is the same as the published density, when considered at the same number of significant digits.

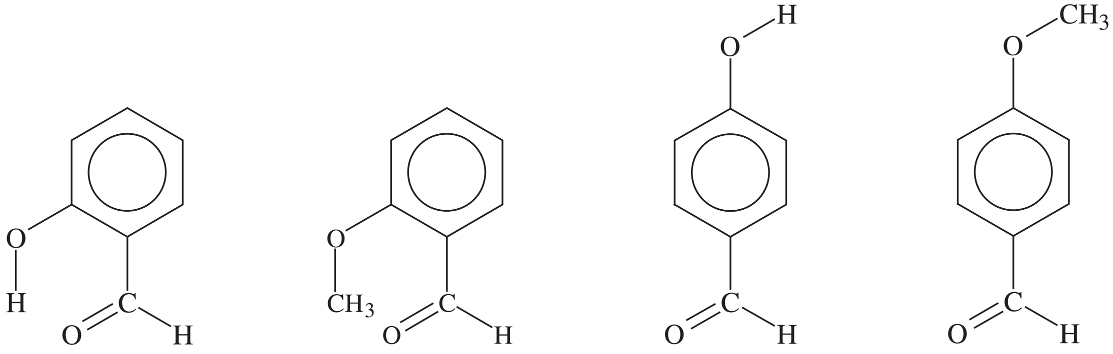
10.27. In solid ammonia, each NH_3 molecule has six other NH_3 molecules as nearest-neighbors. The ΔH of sublimation of NH_3 at the melting point is 30.8 kJ/mol, and the estimated ΔH of sublimation in the absence of hydrogen bonding is 14.4 kJ/mol. What is the strength of a hydrogen bond in solid ammonia?

Ans. 5.5 kJ/mol

10.28. Which of the two crystals in each of the following cases has the higher melting point. Why? (*a*) Cs or Ba; (*b*) Si or P_4; (*c*) Xe or Kr; (*d*) MgF_2 or $CaCl_2$.

Ans. (*a*) Ba—denser electron sea; (*b*) Si—covalently bonded network versus molecular crystal; (*c*) Xe—higher atomic number means stronger London forces; (*d*) MgF_2—cations and anions both smaller.

10.29. Account for the differences in melting point between (*a*) and (*b*), between (*c*) and (*d*), and between these two differences as shown in Fig. 10-8.



o-Hydroxybenzaldehyde
Melting point 266°C
(*a*)

o-Methoxybenzaldehyde
Melting point 309°C
(*b*)

p-Hydroxybenzaldehyde
Melting point 388°C
(*c*)

p-Methoxybenzaldehyde
Melting point 273°C
(*d*)

Fig. 10-8

Ans. The crystal forces in (*b*) and (*d*) are largely van der Waals. Compounds (*a*) and (*c*), containing the polar hydroxide group, are capable of hydrogen bonding. In the case of (*c*), the hydrogen bonding is from the hydroxide of one molecule to the doubly bonded oxygen of the neighboring molecule; and the resulting *inter*molecular (between molecules) attraction leads to a very large increase in the melting point as compared with (*d*), the non-hydrogen-bonded control. In the case of (*a*), the molecular structure allows *intra*molecular (within a molecule) hydrogen bonding from the hydroxide group of each molecule to the doubly bonded oxygen of the same molecule; in the absence of strong *inter*molecular hydrogen bonding the difference in melting point as compared with the reference substance (*b*) should be small, related perhaps to differences in crystal structure or to the van der Waals forces, which should be slightly larger for (*b*) than for (*a*) because of the extra CH_3 group.

FORCES IN LIQUIDS

10.30. Which one of each of the following pairs of liquids has the higher boiling point? Why?
(*a*) $CH_3CH_2CH_2OH$ or $HOCH_2CH_2OH$; (*b*) $CH_3CH_2CH_3$ or CH_3CH_2F; (*c*) Xe or Kr; (*d*) H_2O or H_2S; (*e*) $CH_3CH_2CH_2CH_2CH_2CH_3$ or $CH_3CH_2CH_2CH_3$.

Ans. (*a*) $HOCH_2CH_2OH$, twice as many H-bonds per molecule; (*b*) CH_3CH_2F, strong dipole moment; (*c*) Xe, higher atomic number, greater London forces; (*d*) H_2O, strong H-bonds; (*e*) $CH_3CH_2CH_2CH_2CH_2CH_3$, longer molecule, greater area of intermolecular contact

10.31. Which of the following pairs of liquids is/are *miscible* (can be mixed)? Why, or why not? (*a*) butane (C_4H_{10}) and pentane (C_5H_{12}); (*b*) butane and water; (*c*) 1-butanol (C_4H_9OH) and water.

Ans. (*a*) Miscible; forces of attraction between like and unlike molecules are about the same. (*b*) Not miscible; mixing would disrupt the strong H-bonds in water; there is no especially strong attraction between unlike molecules to compensate. (*c*) Miscible; both components have hydrogen bonding. Breaking of H-bonds in water is compensated for by the formation of H-bonds between unlike molecules.

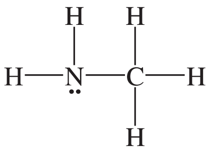
10.32. Explain why UF_6 (molecular mass 352) is more volatile than $SbCl_5$ (molecular mass 299).

Ans. The intermolecular forces are greater for $SbCl_5$ because the *outer* atoms have higher Z values providing for greater London forces than in UF_6.

10.33. Explain why water dissolves in acetone (CH_3COCH_3), but not in hexane (C_6H_{14}).

Ans. When water dissolves, quite a lot of energy is required to break its hydrogen bonds. This is compensated for in acetone by hydrogen bonding between water and the oxygen atom of CH_3COCH_3, but there is no compensating strong interaction with hexane.

10.34. Consider the structure of the methylamine, $H_2N—CH_3$, and predict if it is water-soluble.



$$H-\underset{\cdot\cdot}{\overset{\displaystyle H \atop |}{N}}-\underset{\displaystyle | \atop H}{\overset{\displaystyle H \atop |}{C}}-H$$

Ans. The electron pair associated with the nitrogen can attract the hydrogen from water (hydrogen bonding), providing a strong attraction. The conclusion is that this compound is soluble.

CHAPTER 11

Oxidation-Reduction

OXIDATION-REDUCTION REACTIONS

Up to this point, there has been no special interest in equations having participants that change in charge. There are many such equations that occur and it is important to understand their workings. Keeping in mind that balancing equations is an exercise in the *law of conservation of matter*, a complete accounting of the matter involved in equations is performed during the balancing process. This means that we have to account for *all* matter, even to the point of accounting for electrons.

Reactions in which there is a change in the charges of some or all of the reactants are called *oxidation-reduction* (*redox*) reactions. Because there are changes in charge, equations can be considered with the inclusion of electrons showing the movement of electrons from one participant in the reaction to another. The reaction of metallic copper and sulfur is an example of an oxidation-reduction reaction.

$$\mathrm{Cu + S \rightarrow CuS}$$

During the reaction, copper starts as a neutral atom (0) and becomes charged (+2). At the same time, sulfur, also a neutral atom (0) on the left, becomes charged (−2). Notice that one of the reactants increases in charge ($0 \rightarrow +2$) while the other reactant decreases in charge ($0 \rightarrow -2$).

In recognition of the changes in charge of copper and sulfur in this reaction, we can write reactions that indicate these changes. Further, we can write reactions that show the changes separately as

$$\mathrm{Cu \rightarrow Cu^{2+} + 2e^-} \qquad \text{and} \qquad \mathrm{S + 2e^- \rightarrow S^{2-}}$$

These two reactions are referred to as *half-reactions*. Half-reactions account for all of the matter involved in the reaction, even showing the movement of the electrons. Notice that the electrons released from one of the atoms are picked up by the other, as is required by the *law of conservation of matter*.

The copper half-reaction is an *oxidation reaction*, while the sulfur reaction is a *reduction reaction*. The formal definitions are (*i*) *oxidation* is the result of a loss of electrons and (*ii*) *reduction* is the result of a gain of electrons. A trick for keeping the terminology straight is to consider that a *reduction* reaction includes the *drop in charge* (***reduction*** in charge, $\mathrm{S^0 \rightarrow S^{2-}}$). Since the half-reactions must be paired, the other reaction, the oxidation reaction, occurs when the charge increases ($\mathrm{Cu \rightarrow Cu^{2+}}$). The point is that, if there is a reduction reaction, there ***must*** be an oxidation reaction. And, of course, the reverse is true.

OXIDATION NUMBER

It is not always obvious from the charges alone whether a substance is undergoing oxidation, reduction, or neither process. For example, MnO_2 reacts with hydrochloric acid to produce, among other things, the Mn^{2+} ion and chlorine gas, Cl_2. The neutral chlorine, Cl_2, is produced from the chloride ion, Cl^-, which is an oxidation ($2Cl^- \rightarrow Cl_2$). However, since manganese has a charge in both cases, MnO_2 and Mn^{2+}, it would be easy to miss that there had been a change in charge ($Mn^{4+} \rightarrow Mn^{2+}$, a reduction). The way in which the conclusions were made in this case required that the charges (equivalent terms: *oxidation numbers*, *oxidation state*, *valence state*, and *valence*) be determined for each of the substances individually (individual atoms and/or ions from single atoms) and compared on the left and right of the reaction, as was done in the parentheses earlier in this paragraph. In other words, there is no shortcut; the comparisons must be made and the determination of oxidation and reduction has to be accurate.

Another example is the reaction of arsenous acid (or *arsenious* acid), H_3AsO_3 and I_2, during which the arsenate ion, $HAsO_4^{2-}$, is produced, along with the iodide ion, I^-. ($H_3AsO_3 + I_2 \rightarrow HAsO_4^{2-} + I^-$, incomplete and not balanced) Since the iodine is reduced (neutral iodine to the anion), the arsenic in the acid must be oxidized. The action of the arsenic becomes clear when we look at its oxidation number as determined by the other elements involved in the acid and the ion. Note that hydrogen is a + 1 and oxygen is a − 2, which is nearly always the case for these two elements.

H_3AsO_3	net charge of 0 is determined by	$\begin{matrix} H_3 & As & O_3 & \\ +3 & \underline{+3} & -6 & = 0 \text{ (net charge)} \end{matrix}$
$HAsO_4^{2-}$	net charge of −2 is determined by	$\begin{matrix} H & As & O_4^{\;2-} & \\ +1 & \underline{+5} & -8 & = -2 \text{ (net charge)} \end{matrix}$

Please note that the oxidation number is not the same as the formal charge (Chapter 9). Formal charge is based on an attempted mapping out of the real charge distribution in a molecule or ion considering the detailed structure and electronic binding. Oxidation number is a simpler assignment that does not require information about electronic variables, such as single or multiple bonding and octet versus non-octet structures. Oxidation numbers are computed directly from the formula. The two basic rules for oxidation number assignment are:

1. In **ionic** binary compounds, the oxidation number is the charge per atom.

EXAMPLE 1 $CdCl_2$ is an ionic compound and may be designated as $Cd^{2+}(Cl^-)_2$ to show its ionic character. The cadmium and chloride ions possess oxidation numbers +2 and −1, as this is an ionic compound; there is no sharing of electrons and, therefore, no partial charges. In Hg_2Cl_2, each mercury in Hg_2^{2+} is considered to be +1. The chloride ion is −1, as in $CdCl_2$.

2. In **covalent** (nonionic) compounds, the electrons involved in bond formation are not completely transferred from one element to the other, but are shared more or less equally by the bonding atoms. For the purposes of setting oxidation numbers, the practice is to assign each bonding electron (artificially) to a specific atom. If the atoms are of the same kind (Cl_2, N_2, C in $H_3C{-}CH_3$), half of the bonding electrons are assigned to each of the two atoms. If the atoms are different, all electrons in the bond are assigned to the atom with the greater electronegativity (Chapter 9). *Note*: There are corollaries as follows:

   (*a*) The oxidation number of a **free** element (uncombined) is zero (0).

EXAMPLE 2 In the case of diatomic molecules and other same-atom molecules (as S_8), one electron in a bond is assigned to an atom, the other electron in the bond is assigned to the other atom. As an example: In the case of $H_2(H{-}H)$, one electron goes to each of the hydrogens.

   (*b*) The oxidation number of hydrogen in compounds is usually +1, except in the case of the metallic hydrides (H^-).

EXAMPLE 3 In NH_3, the nitrogen atom is bonded directly to each of the hydrogen atoms. Since nitrogen is more electronegative than hydrogen, all the bonding electrons are assigned to the nitrogen. Each hydrogen, minus its electron, then plays the role of a positive ion (H^+) in order to have a charge of zero on the compound ($N^{-3} + 3H^+$), as is required.

Interestingly, this charge assignment is purely fictional as the ammonia molecule does not ionize in water and does not release H^+ ions (NH_3, not H_3N!).

In CaH_2, each hydrogen, being more electronegative than calcium, is assigned the two electrons in each bond, making the hydrogen ion the hydride anion, H^-.

(*c*) The oxidation number of oxygen in compounds is -2, except in peroxides (-1 each in O_2^{2-}) or in fluoride compounds where it may be positive.

(*d*) Adding the oxidation numbers of all atoms in a compound equals zero (0).

(*e*) Adding the oxidation numbers of all atoms in an ion equals its charge.

EXAMPLE 4 In $HClO_4$, the oxidation state of chlorine is $+7$, conforming with corollary (*d*).

$$\begin{array}{lll} \mathrm{H} & \mathrm{Cl} & \mathrm{O_4} \\ +1 & +7 & +4(-2) = 0 \end{array}$$

In CO_3^{2-}, the oxidation state of C is $+4$, conforming with corollary (*e*).

$$\begin{array}{ll} \mathrm{C} & \mathrm{O_3}^{2-} \\ +4 & +3(-2) = -2 \end{array}$$

OXIDIZING AND REDUCING AGENTS

Every chemical reaction has a driving force—a reason why it proceeds as it does. We can say that the reason why oxidation-reduction reactions proceed is because one atom is giving up electrons and another is accepting them. We can also make the statement a bit more forcefully by saying that an element is grabbing electrons from another. There is some terminology, discussed below, that is based on these ideas. Consider this equation

$$\mathrm{Cu + S \rightarrow CuS}$$

We know from previous discussion in this chapter that the sulfur is being reduced and the copper is being oxidized during this reaction. Taking the more active role, we could say that the sulfur is *causing* the copper to be oxidized—we can refer to the sulfur as an *oxidizing agent*, assuming it is the cause of the oxidation. Conversely, the copper may be causing the sulfur to be reduced, making the copper the *reducing agent*.

EXAMPLE 5 Identify the reducing and oxidizing agents in the reaction

$$\mathrm{H_2SO_4 + HI = H_2SO_3 + I_2} \qquad \text{(Reaction is incomplete and not balanced)}$$

Since the hydrogen is a $+1$ and the oxygens are -2 (neither change oxidation number), we can determine that the sulfur goes from a $+6$ to $+4$, and the iodine goes from a -1 to 0. As the sulfur is being reduced, the iodine is the reducing agent. As the iodine is being oxidized, the sulfur is the oxidizing agent. (Note that both oxygen and hydrogen do not change charge.)

IONIC NOTATION FOR EQUATIONS

Oxidation-reduction reactions can be written leaving out the *spectator ions* (ions that do not change oxidation number during a reaction). An alternate method for writing oxidation-reduction reactions is to include all ions and compounds involved and not pay any attention to eliminating spectators and those items that do not change in oxidation number. This technique identifies ionic compounds within the reaction and uses a series of conventions.

1. Ionic substances are written in the ionic form only if the ions are separated from each other in the reaction medium (most often water). NaCl would be the conventional notation for reactions involving solid salt, because the ions in the solid are bound together in the crystal. Salt reactions in solution, however, would

be indicated by the Na^+ and Cl^- ions, or by either of these ions alone, if only the sodium *or* the chlorine undergoes a change in oxidation number. Fairly insoluble salts, like CuS and $CaCO_3$, are written in the neutral form (compounds, not ions).

2. Partially ionized substances are written in the ionic form only if the extent of ionization is appreciable (about 20 percent or more). Water, which is ionized to the extent of less than one part in a hundred million, is written as H_2O (or, if more convenient, HOH). Strong acids, like HCl and HNO_3, may be written in the ionized form, but weak acids, like nitrous, acetic, and sulfurous acids, are written in the molecular form (HNO_2, $HC_2H_3O_2$ and H_2SO_3). Ammonia, a weak base, is written NH_3. Sodium hydroxide, a strong base, is written in the ionized form when in aqueous solution.
3. Some complex ions are so stable that one or more of the groups from which they are formed do not exist in appreciable amounts outside the complex. In such a case, the formula for the entire complex is written. The ferricyanide ion is written as $[Fe(CN)_5]^{3-}$, not as the separate iron(III) and cyanide ions. Similarly, $[Cu(NH_3)_4]^{2+}$ is the notation for the common blue complex ion formed by copper(II) salts in ammonia solutions.
4. A mixed convention will be used in this chapter as an aid to indicate whether a given compound may be written in the ionized form. We will use Na^+Cl^-, $Ba^{2+}(NO_3^-)_2$, and similar notation, to indicate that compounds are ionic. Naturally, the compounds could be expressed by the molecular formulas, NaCl and $Ba(NO_3)_2$, which works well for those who are intimately familiar with the solubility rules. We are not presenting the solubility rules since we prefer to concentrate on balancing the equations without having the distraction of investigating the solubility rules at the same time.

BALANCING OXIDATION-REDUCTION EQUATIONS

Previously, we have used a technique of balancing chemical reactions by means of trying numbers and, if they do not work, changing the numbers until the proper ratio is achieved. This technique, often called the *trial and error* method, may not work well with oxidation-reduction reactions. An equation can look as though it is balanced, particle-wise, but the electrons may not be balanced as indicated by having a different net charge on the left from the net charge on the right (creating or destroying e^-!!!).

There are basic rules for the writing of the oxidations and reductions so that the products can be predicted when considering the reactants. Some of those rules are as follows:

(*a*) If a free halogen is reduced, the product must be the halogenide anion (-1 oxidation number).

(*b*) If a metal that has only one positive oxidation number is oxidized, the oxidation number of the product can only be that oxidation number.

(*c*) Reductions of concentrated nitric acid, HNO_3, lead to NO_2. The reduction of dilute nitric acid may lead to NO, N_2, NH_4^+, or other products, depending on the nature of the reducing agent and the extent of dilution.

(*d*) MnO_2 and the permanganate ion, MnO_4^-, are reduced to Mn^{2+} in an acid solution. The reduction product of permanganate in neutral or basic (alkaline) solution may be MnO(OH), MnO_2, or MnO_4^{2-}.

(*e*) If a peroxide is reduced, the product of reduction must contain oxygen in the -2 oxidation state, as in H_2O or OH^-. If a peroxide is oxidized, molecular oxygen is formed (a superoxide is possible).

(*f*) Dichromate, $Cr_2\,O_7^{2-}$, is reduced in acid solution to Cr^{3+}.

Two general styles are used when writing oxidation-reduction reactions. The first is to include all species that are in the reaction—that is to say that there is nothing left out, even if it is a spectator. In this style, acids and bases are written into the equation. The second style leaves out spectators. Because the anion in acids and the cation in bases are often spectators (ions common with one or more of the compounds in the reaction), the acidic or basic nature of the reaction medium can be indicated by putting the words *acid* or *base* over the yields sign or beside the equation.

Half-reaction method

The *half-reaction method* is a way of balancing oxidation-reductions reactions by the recognition of oxidation and reduction with separate reactions. Included in the reactions are the number of electrons that move and the nature of movement (gain or loss). The steps for this technique are:

1. Identify those atoms that are being oxidized and those being reduced.
2. Write the half-reaction for reduction.
   a. Make certain that the atom being reduced is balanced (the same number on both sides).
   b. Add electrons to the left side; those electrons are taken up by the reduced atom.
   c. If necessary for the purposes of balancing the half-reaction,
      i. Use H^+ and H_2O, if in an acid solution, to balance the equation.
      ii. Use OH^- and H_2O, if in a basic solution, to balance the equation.
3. Write the half-reaction for the oxidation.
   a. Make certain that the atom being oxidized is balanced (the same number on both sides).
   b. Add electrons to the right side; those electrons are released by the oxidized atom.
   c. If necessary for the purposes of balancing the half-reaction,
      i. Use H^+ and H_2O, if in an acid solution, to balance the equation.
      ii. Use OH^- and H_2O, if in a basic solution, to balance the equation.

   The result of processes 1–3 will yield balanced separate half-reactions from both the standpoint of atomic particles and the net charges of the sides (left charge = right charge).
4. Half-reactions can be added to produce a *net reaction*, which is the oxidation-reduction reaction. However, this summation cannot be performed unless the electron numbers are the same on both sides of the reaction; by agreement among chemists, electrons are not written into summation reactions. The way in which adjustments are made is to preserve the ratio of coefficients in the individual balanced half-reaction by multiplying all of the participants in an equation by the same number. The goal is to have the same number of electrons on opposite sides of the half-reactions. The electrons will then algebraically cancel when the half-reactions are added. Since the summation equation should not have coefficients divisible by a common factor, it is customary to choose numbers that will yield the least number of electrons for cancellation.
5. Add up the half-reactions and cancel those participants that are the same chemical entity on both sides, as well as the electrons. Notice that there will be no electrons in the summation reaction, nor will there be water, hydrogen ion, or hydroxide ion *on both sides of the summation reaction.*
6. It is a good practice to make certain that all matter balances on the left side of the reaction against the right side. Also, check that the net charge of the left side of the reaction is the same as the right. And the last check before pronouncing the equation correctly balanced and written is to make certain that the coefficients cannot be divided by the same factor. Naturally, if any of the checks indicate a problem, review the steps and correct the problem. Don't guess—either the equation is properly balanced or not!

Master the half-reaction method before studying electrochemistry. The studies of electrochemistry rely on the recognition of oxidation and reduction, understanding the half-reactions, and possessing the ability to balance oxidation-reduction reactions. Because of these factors, the half-reaction method will be stressed in this book.

Oxidation-state method

This method of balancing oxidation-reduction reactions is somewhat similar to the half-reaction method. In this method the half-reactions are not written separately. Note that, although the explanation is much shorter than that above, the process is not.

1. Write the complete equation that includes, as principal formulas, those reactants and products that contain the elements undergoing a change in oxidation number.
2. Determine the *change* in oxidation number which some element in the oxidizing agent undergoes. The number of electrons gained is equal to this change times the number of atoms undergoing the change (balance the atoms).
3. Determine the reducing agent and its *change*. The number of electrons lost times the number of atoms undergoing the change is identified.
4. In the equation, multiply the principal formulas by the numbers required to make the total number of electrons lost and gained equal.
5. By inspection, supply the proper coefficients for the rest of the equation (those that do not change).
6. Check the final equation by counting the number of atoms of each element on both sides. Also, make certain that the net charge on the left and right of the equation are the same.

Solved Problems

FORMULAS AND OXIDATION NUMBER

11.1. Assuming the oxidation numbers of H^+, O^{2-}, and F^-, determine the oxidation numbers of the other elements in (*a*) PH_3; (*b*) H_2S; (*c*) CrF_3; (*d*) H_2SO_4; (*e*) H_2SO_3; (*f*) Al_2O_3.

Recalling that the net charge on any compound is zero (0):

(*a*) PH_3—H_3 represents an oxidation-number sum of +3 (+1 for each H). The oxidation number for P must be −3, since the sum of the oxidation numbers of all atoms in a compound must equal zero.

(*b*) H_2S—Since the total oxidation number for hydrogen is +2, sulfur must be −2.

(*c*) CrF_3—Since the total oxidation number for fluorine is −3, chromium must be +3.

(*d*) H_2SO_4—The oxidation number total for H_2 is +2; the oxidation number total for O_4 is −8; then, the oxidation number for sulfur must be +6 since the total for the hydrogen and oxygen is − 6 (+2 −8 = −6).

(*e*) H_2SO_3—The oxidation number total for H_2 is +42; the oxidation number for O_3 is −6; then, since the total for the hydrogen and oxygen is −4 (+2 −6 = −4), the oxidation number for sulfur must be +4.

(*f*) Al_2O_3—Since the total oxidation number for oxygen is −6, the total for the aluminum must be +6. However, there are two Al atoms per formula unit, so the oxidation number for each Al is +3.

BALANCING OXIDATION-REDUCTION EQUATIONS

11.2. Balance the oxidation-reduction equation: $H^+NO_3^- + H_2S \rightarrow NO + S + H_2O$.

Half-Reaction Method

(*a*) The nitrogen is the element being reduced (+5 → +2). The half-reaction is

$$NO_3^{1-} \rightarrow NO$$

Since there is one nitrogen atom on each side of the equation, we can consider its reduction and include the electrons involved. The idea is to add electrons to explain the change in charge.

$$3e^- + NO_3^{1-} \rightarrow NO$$

The oxygen is out of balance and we are told in the given equation that there can be water added. That water is needed on the right.

$$3e^- + NO_3^{1-} \rightarrow NO + 2H_2O$$

There has to be some hydrogen on the left because there have been hydrogens placed on the right. Because the reaction is performed in acid solution (HNO_3 and H_2S), we use H^+ to balance. (Note that the net charge on the left equals that on the right.)

$$4H^+ + 3e^- + NO_3^{1-} \rightarrow NO + 2H_2O$$

(*b*) The oxidation reaction involves the change in the sulfur (−2 to 0).

$$S^{2-} \rightarrow S$$

The next step is to indicate the movement of electrons (2 on the right).

$$S^{2-} \rightarrow S + 2e^-$$

(*c*) In preparation for adding the two half-reactions, we must set up the half-reactions so that the electrons cancel. If we multiply the reduction reaction (N) by 2 and the oxidation reaction (S) by 3, we will end up with six electrons on each side.

$$2(4H^+ + 3e^- + NO_3^{1-} \rightarrow NO + 2H_2O)$$
$$3(S^{2-} \rightarrow S + 2e^-)$$

Then, we can add the two half-reactions providing us with the summation reaction.

$$3S^{2-} + 8H^+ + 2NO_3^{1-} \rightarrow 2NO + 3S + 4H_2O \qquad \text{or} \qquad 3H_2S + 2HNO_3 \rightarrow 2NO + 3S + 4H_2O$$

Oxidation-State Method

For the reduction: We determine that the oxidation number of N changes from +5 on the left to +2 on the right. One way of indicating the change is to write the charges above the element involved (both sides) and indicate the electron motion between them (above the equation).

$$\begin{array}{ll} \quad\quad\mathbf{+3e^-} & \text{(reduction reaction, electron gain)} \\ +5 \text{———} +2 & \\ H^+NO_3^- + H_2S \rightarrow NO + S + H_2O & \\ \quad\quad -2 \text{———} 0 & \\ \quad\quad\quad \mathbf{-2e^-} & \text{(oxidation reaction, electron loss)} \end{array}$$

For the oxidation: We determine that the sulfur changes in charge from −2 to 0, then indicate the change and electron movement below the equation, as well as the electron motion.

Next, determine the factors that will set up the electrons to cancel. To achieve the cancellation, we multiply the reduction participants, including the electrons moved, by 2. We multiply the oxidation participants by 3, including the electrons moved. The electrons will cancel and then,

$$2H^+NO_3^- + 3H_2S \rightarrow 2NO + 3S + H_2O$$

Inspection of the equation shows that both hydrogen and oxygen are out of balance. We can balance the hydrogen by multiplying the water by 4, bringing the number of hydrogens to 8 on both sides.

$$2H^+NO_3^- + 3H_2S \rightarrow 2NO + 3S + 4H_2O$$

Counting the oxygens on both sides shows that they are in balance. A double-check of the atoms tells us that the equation is in balance.

11.3. Balance the following reaction:

$$K^+MnO_4^- + K^+Cl^- + (H^+)_2SO_4^{2-} \rightarrow Mn^{2+}SO_4^{2-} + (K^+)_2SO_4^{2-} + Cl_2 + H_2O$$

The first step is to write the half-reactions and we chose to do so without spectators. The half-reactions are balanced with reference to the atoms being oxidized and reduced (Mn and Cl).

$$\begin{aligned} MnO_4^- &\rightarrow Mn^{2+} \\ 2Cl^- &\rightarrow Cl_2 \end{aligned}$$

Our next step is to identify the number of electrons in each change and place them appropriately.

$$\begin{array}{rl} 5e^- + MnO_4^- \rightarrow Mn^{2+} & \quad \text{(reduction reaction)} \\ 2Cl^- \rightarrow Cl_2 + 2e^- & \quad \text{(oxidation reaction)} \end{array}$$

We see that the chlorine reaction is balanced (atoms and charges), but that the manganese reaction is not. Adding four water molecules to the right will balance the oxygen. That additionally places hydrogen on the right and there is none on the left. Since the reaction medium includes H_2SO_4, we can use H^+ to balance that half-reaction.

$$\begin{aligned} 8H^+ + 5e^- + MnO_4^- &\rightarrow Mn^{2+} + 4H_2O \\ 2Cl^- &\rightarrow Cl_2 + 2e^- \end{aligned}$$

The last step before the summation of the half-reactions is to multiply appropriately so that the electrons cancel.

$$\begin{array}{rcr} 2(8H^+ + 5e^- + MnO_4^- \rightarrow Mn^{2+} + 4H_2O) & \text{becomes} & 16H^+ + \cancel{10e}^- + 2MnO_4^- \rightarrow 2Mn^{2+} + 8H_2O \\ 5(2Cl^- \rightarrow Cl_2 + 2e^-) & \text{becomes} & 10Cl^- \rightarrow 5Cl_2 + \cancel{10e}^-) \end{array}$$

And these steps put us in a position to add the half-reactions.

$$16H^+ + 2MnO_4^- + 10Cl^- \rightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$

Looking at the original equation at the beginning of this problem, we can add back in the spectators in appropriate numbers to form the compounds. A check of the atoms and net charges assures us that the equation is balanced.

$$2K^+MnO_4^- + 10K^+Cl^- + 8(H^+)_2SO_4^{2-} \rightarrow 2Mn^{2+}SO_4^{2-} + 6(K^+)_2SO_4^{2-} + 5Cl_2 + 8H_2O$$

11.4. Balance the following oxidation-reduction reaction:

$$(K^+)_2Cr_2O_7^{2-} + HCl \rightarrow K^+Cl^- + Cr^{3+}(Cl^-)_3 + Cl_2 + H_2O$$

Previously balanced equations are pretty straightforward; each of the elements involved in the oxidations and reductions only occurred once on a side. This equation is different because chlorine appears in more than one place on the right. Not all of the chlorine is taking part in a change in oxidation number. Notice that Cl^- is in HCl on the left, and Cl^- is also in $CrCl_3$ on the right. Additionally, some Cl^- from HCl is being oxidized to Cl_2 (neutral). This dual role of chlorine causes no problems.

Using the half-reaction method, we separate the oxidation and reduction half-reactions and then balance. We use H_2O (reaction in solution) and H^+ (acid medium due to the presence of HCl).

Reduction half-reaction:	$Cr_2O_7^{2-} \rightarrow Cr^{3+}$	
Balance chromium	$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$	
Place electrons	$6e^- + Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$	
Balance oxygen	$6e^- + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$	
Balance hydrogen	$14H^+ + 6e^- + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$	(acid solution, HCl)
Oxidation half-reaction	$Cl^- \rightarrow Cl_2$	
Balance chlorine	$2Cl^- \rightarrow Cl_2$	
Place electrons	$2Cl^- \rightarrow Cl_2 + 2e^-$	

The next step is to multiply the half-reactions by factors to ensure that the electrons cancel when the half-reactions are added.

× 1 (no change)	$1(14H^+ + 6e^- + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O)$
× 3	$3(2Cl^- \rightarrow Cl_2 + 2e^-)$

The addition of the two half-reactions is the next step.

$$\begin{aligned} 14H^+ + \cancel{6e^-} + Cr_2O_7^{2-} &\rightarrow 2Cr^{3+} + 7H_2O \\ 6Cl^- &\rightarrow 3Cl_2 + \cancel{6e^-} \end{aligned}$$

The summation reaction is: $14H^+ + 6Cl^- + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O$

Before pronouncing this summation reaction balanced, we must check the particles (all OK) and the net charges (+6 on the left and on the right). We can now say that the summation reaction is balanced.

Since we were originally given the cations and anions missing from the summation reaction, we need to complete the equation by putting them back in. There are 14 hydrogens on the left that can only have been bound to the chloride ion, providing us with 14HCl. Six of those chlorides are in the neutral chlorine ($3Cl_2$) on the right, leaving us with 8 more chlorides on the left—the two chromium ions take a total of 6 chlorides, and the remaining 2 chloride ions are taken up by the potassium ion (2KCl).

$$(K^+)_2Cr_2O_7^{2-} + 14H^+Cl^- \rightarrow 2K^+Cl^- + 2Cr^{3+}(Cl^-)_3 + 3Cl_2 + 7H_2O$$

11.5. Balance the following oxidation-reduction equation: $FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2$.

This reaction does not take place in solution; however, the balancing is performed as above. The special features of this reaction are that

(*a*) The charges on iron or sulfur are nontraditional. We are assuming iron's oxidation number to be +1 due to the normal −2 oxidation number associated with sulfur.

(*b*) Both the iron and sulfur in FeS_2 undergo a change in oxidation state.

(*c*) Both iron (+1 to +3) and sulfur (−2 to +4) are oxidized.

(*d*) The reduction product of oxygen gas occurs in combination with both iron and sulfur.

The two oxidation reactions can be joined and handled together. The two reduction reactions can be handled in the same manner. The reactions, along with their multipliers, are

$$4(Fe^{+2} + 2S \rightarrow Fe^{3+} + 2S^{+4} + 11e^-)$$
$$11(O_2 + 4e^- \rightarrow 2O^{2-})$$

Multiplying the reactions to eliminate the electrons, then adding the equations together, yields

$$4Fe^{+2} + 8S^{-} + 11O_2 \rightarrow 4Fe^{3+} + 8S^{+4} + 22O^{2-}$$

Collecting ions for compounds yields $\quad 4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$

In problems like this one, there are unusual oxidation numbers involved (S^-). You might well ask, "What will happen if I choose the wrong oxidation numbers?" The answer is that the same result will be obtained so long as the method is followed consistently. If +4 were chosen for Fe and −2 for S, the total oxidation state increase would still be 11. In other words, the *difference* in oxidation numbers is important, not having the exact oxidation numbers.

11.6. Balance the following oxidation-reduction reaction that occurs in basic solution:

$$Zn + Na^+NO_3^{1-} + Na^+OH^- \rightarrow (Na^+)_2ZnO_2^{2-} + NH_3 + H_2O$$

The element that is reduced is the nitrogen (+5 to −3); its half-reaction is

$$NO_3^{1-} \rightarrow NH_3$$

The number of nitrogens is the same on both sides, allowing us to go to the question of the charge and electrons. Since the nitrogen in nitrate is +5 and −3 in ammonia, there are 8 electrons involved.

$$8e^- + NO_3^{1-} \rightarrow NH_3$$

The oxygen and hydrogen are out of balance, as are the net charges on the left and right. One way to balance the half reaction rests on the use of hydroxide ion, OH^-, to balance the charges, then to look at the atoms. In previous reactions, if the medium was acidic, we used hydrogen ions and water. *We can add the hydroxide and water because the reaction occurs in a basic medium.* The net on the left is –9, and that on the right is zero. Let us add $9OH^-$ to the right to balance the net charges.

$$8e^- + NO_3^{1-} \rightarrow NH_3 + 9OH^-$$

Since there are hydrogens on the right and none on the left, we add $6H_2O$ to the left.

$$6H_2O + 8e^- + NO_3^{1-} \rightarrow NH_3 + 9OH^-$$

A count of the oxygen atoms reveals that there are the same number, nine, on both sides. This reduction half-reaction is balanced.

We take note that the zinc is being oxidized (0 to +2). The oxidation half-reaction is

$$Zn \rightarrow ZnO_2^{2-}$$

Since the zinc is already in balance in this half-reaction, we look to the electron movement. The charge change of the zinc is from 0 to +2, which tells us that there were 2 electrons lost.

$$Zn \rightarrow ZnO_2^{2-} + 2e^-$$

We also notice that the oxygen and the charges are out of balance. Since the net charge on the right is −4 and the medium is basic, let us add −4 to the left in the form of 4 hydroxide ions. Of course, that means we have to add some H_2O to the right to conform with the *law of conservation of matter* relating to hydrogen.

$$4OH^- + Zn \rightarrow ZnO_2^{2-} + 2e^- + 2H_2O$$

The two balanced half-reactions need to be multiplied by factors to make certain the electrons cancel, then they can be added to produce the summation reaction for the oxidation-reduction reaction.

$$1(6H_2O + 8e^- + NO_3^{1-} \rightarrow NH_3 + 9OH^-) \quad \text{becomes} \quad 6H_2O + 8e^- + NO_3^{1-} \rightarrow NH_3 + 9OH^-$$

$$4(4OH^- + Zn \rightarrow ZnO_2^{2-} + 2e^- + 2H_2O) \quad \text{becomes} \quad 16OH^- + 4Zn \rightarrow 4ZnO_2^{2-} + 8e^- + 8H_2O$$

Then, the appropriate cancellations are made (e^-, OH^-, and H_2O) and the two half-reactions are added.

$$7OH^- + 4Zn + NO_3^{1-} \rightarrow 4ZnO_2^{2-} + NH_3 + 2H_2O$$

Adding back in the spectator ions restores all ions to the equation.

$$7Na^+OH^- + 4Zn + Na^+NO_3^{1-} \rightarrow 4(Na^+)_2ZnO_2^{2-} + NH_3 + 2H_2O$$

or

$$7NaOH + 4Zn + NaNO_3 \rightarrow 4Na_2ZnO_2^{2-} + NH_3 + 2H_2O$$

11.7. The following procedure handles the need to add missing ions for the formation of incomplete participants in the reaction and indicates how to determine and balance half-reactions by determining the reducing and oxidizing agents. We have been determining what atoms are oxidized and reduced; this example broadens the choices of how to approach the reactions. The equation to be balanced is

$$HgS + HCl + HNO_3 \rightarrow H_2HgCl_4 + NO + S + H_2O$$

or

$$HgS + H^+Cl^- + H^+NO_3^{1-} \rightarrow (H^+)_2HgCl_4^{2+} + NO + S + H_2O$$

The half-reaction for the oxidizing agent is

$$4H^+ + NO_3^{1-} + 3e^- \rightarrow NO + 2H_2O$$

The half-reaction for the reducing agent is $S^{2-} \rightarrow S + 2e^-$. Notice that the mercury has been omitted and will have to be reintroduced later, which can create headaches. We could consider using the half-reaction including the mercury.

$$HgS \rightarrow S$$

The lack of balance does not involve hydrogen or oxygen, as we have seen in previous examples, but mercury. According to the overall equation, the form in which mercury exists among the products is the ion $HgCl_4^{2+}$. If that ion is added to the right to balance the mercury, then chloride ions must be added to the left to balance the chlorine. In general, it is allowable to add ions necessary for complex formation when such an addition does not require the introduction of a new oxidation state (rule 5).

$$HgS + 4Cl^- \rightarrow S + HgCl_4^{2+} + 2e^- \quad \text{(balanced)}$$

The overall equation is obtained by the summation of the two half-reactions after multiplication by the appropriate factors:

$$2(4H^+ + NO_3^{1-} + 3e^- \rightarrow NO + 2H_2O) \quad \text{becomes} \quad 8H^+ + 2NO_3^{1-} + 6e^- \rightarrow 2NO + 4H_2O$$

$$3(HgS + 4Cl^- \rightarrow S + HgCl_4^{2+} + 2e^-) \quad \text{becomes} \quad 3HgS + 12Cl^- \rightarrow 3S + 3\,HgCl_4^{2+} + 6e^-$$

Then, after cancellations have been performed and any spectators replaced, the summation reaction is

$$3HgS + 2H^+NO_3^{1-} + 12H^+Cl^- \rightarrow 3S + (H^+)_2HgCl_4^{2+} + 2NO + 4H_2O$$

or

$$3HgS + 2HNO_3 + 12HCl \rightarrow 3S + H_2HgCl_4 + 2NO + 4H_2O$$

11.8. Complete and balance the following reaction in an acid solution:

$$H_2O_2 + MnO_4^- \rightarrow$$

The permanganate ion contains Mn, which is likely to change in oxidation number. Generally, oxygen is a -2 and remains -2. Mn is $+7$ in this ion and a likely change would be to $+2$, requiring $5e^-$ per Mn. It is possible for Mn^{7+} or Mn^{2+} to reduce to Mn metal, but rather unlikely.

H_2O_2 must be the reducing agent in this reaction, with the only possible oxidation product being O_2.

Setting up the expected half-reactions and proceeding from there provides us with the balanced reaction. This time, we did not perform any cancellations during this step.

$$\begin{array}{r} 2(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O) \\ 5(H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-) \\ \hline 2MnO_4^- + 16H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O + 10H^+ \end{array}$$

After cancellations,

$$2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

Common choices are $KMnO_4$ and H_2SO_4 for the oxidizing agent and the acid when using the reaction in a lab experiment. See if you can write the complete reaction using this oxidizing agent and the acid.

STOICHIOMETRY IN OXIDATION-REDUCTION

11.9. Using the balanced reaction from Problem 11.3, calculate the amount of Cl_2 produced by the reaction of 100 g $KMnO_4$..

The ratio from the balanced equation is $2KMnO_4 : 5Cl_2$, which can be expressed as

$$2KMnO_4 \rightarrow 5Cl_2$$

Using this partial reaction, we can place the information relating to the ratio above the participants and the given information below. We use w for the unknown mass.

From partial reaction	2 mol × 158 g/mol		5 mol × 70.9 g/mol
	$2KMnO_4$	→	$5Cl_2$
From given information	100 g		w

From this setup, we can write the ratio of the mole-related information to the mass in the problem for both sides of the equation and relate them to each other (*ratio and proportion*). Notice that we have canceled moles against moles when we brought the ratios from above to below.

$$\frac{2 \times 158\text{ g KMnO}_4}{100\,g\text{ KMnO}_4} = \frac{5 \times 70.9\text{ g Cl}_2}{w}$$

By cross multiplication, algebraically isolating w, and canceling units, we determine the answer.

$$w = \frac{(5 \times 70.9\text{ g Cl}_2)(100\text{ g KMnO}_4)}{2 \times 158\text{ g KMnO}_4} = 112\text{ g Cl}_2$$

Alternate Setup

The problem can also be solved directly from the balanced ionic equation showing that 5 Cl_2 molecules are produced from 2 MnO_4^- ions (5 Cl_2/2 $KMnO_4$ in terms of moles).

$$w\text{g Cl}_2 = (100\text{ g KMnO}_4)\left(\frac{1\text{ mol KMnO}_4}{158\text{ g KMnO}_4}\right)\left(\frac{5\text{ mol Cl}_2}{2\text{ mol KMnO}_4}\right)\left(\frac{70.9\text{ g Cl}_2}{1\text{ mol Cl}_2}\right) = 112\text{ g Cl}_2$$

Supplementary Problems

11.10. Determine the oxidation number of the bold italic element in (*a*) $K_4\boldsymbol{P}_2O_7$; (*b*) $Na\boldsymbol{Au}Cl_4$; (*c*) $Rb_4Na[H\boldsymbol{V}_{10}O_{28}]$; (*d*) $\boldsymbol{I}Cl$; (*e*) $Ba_2\boldsymbol{Xe}O_6$; (*f*) $\boldsymbol{O}F_2$; (*g*) $Ca(\boldsymbol{Cl}O_2)_2$.

Ans. (*a*) +5; (*b*) +3; (*c*) +5; (*d*) +1; (*e*) +8; (*f*) +2; (*g*) +3

IDENTIFICATION OF OXIDIZING AND REDUCING AGENTS

Identify the element oxidized (EO) and the element reduced (ER). Identify the solitary element, compound or ion behaving as the oxidizing agent, and that which is behaving as the reducing agent for each reaction.

Reactions may not be complete and may not be balanced.

11.11. $Au^{3+}(aq) + H_2O_2(aq) + NaOH(aq) \rightarrow O_2(g) + Au(s)$

Ans. EO—O, ER—Au, oxidizing agent—Au^{3+}, reducing agent— H_2O_2

11.12. $Co^{2+}(aq) + HNO_2(aq) \rightarrow NO(g) + Co^{3+}(aq)$

Ans. EO—Co, ER—N, oxidizing agent—HNO_2, reducing agent—Co^{2+}

11.13. $Zn(s) + HNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + NO(g)$

Ans. EO—Zn, ER—N, oxidizing agent—HNO_3, reducing agent—Zn

11.14. $Hg(s) + HNO_3(aq) \rightarrow Hg(NO_3)_2(aq) + NO$

Ans. EO—Hg, ER—N, oxidizing agent—HNO_3, reducing agent—Hg

11.15. $Cu(s) + H_2SO_4(l) \rightarrow SO_2(g) + CuO(s)$

Ans. EO—Cu, ER—S, oxidizing agent—H_2SO_4, reducing agent—Cu

BALANCING OXIDATION-REDUCTION REACTIONS

Using the method(s) of your choice, write balanced ionic and molecular equations for the following:

11.16. $Au^{3+}(Cl^-)_3 + H_2O_2 + Na^+OH^- \rightarrow Na^+Cl^- + O_2 + Au + H_2O$

11.17. $Co^{2+}(NO_3^-)_2 + H^+NO_2^- \rightarrow NO + Co^{3+}(NO_3^-)_3 + H_2O$

11.18. $Zn + H^+NO_3^- \rightarrow Zn^{2+}(NO_3^-)_2 + NO + H_2O$

11.19. $Hg + H^+NO_3^- \rightarrow Hg^{2+}(NO_3^-)_2 + NO + H_2O$

11.20. $Cu + (H^+)_2SO_4^{2-} \rightarrow SO_2 + CuO + H_2O$

11.21. $Na^+Br^- + Cl_2 \rightarrow Na^+Cl^- + Br_2$

11.22. $Sn + O_2 + H^+Cl^- \rightarrow Sn^{2+}(Cl^-)_2 + H_2O$

11.23. $CuS + H^+NO_3^- \rightarrow Cu^{2+}(NO_3^-)_2 + S + NO + H_2O$ (Dilute HNO_3)

11.24. $Fe^{2+}(Cl^-)_2 + H_2O_2 + H^+Cl^- \rightarrow Fe^{3+}(Cl^-)_3 + H_2O$

11.25. $As_2S_5 + H^+NO_3^- \rightarrow H_3AsO_4 + H^+HSO_4^- + NO_2 + H_2O$ (Concentrated HNO_3)

11.26. $Cu + H^+NO_3^- \rightarrow Cu^{2+}(NO_3^-)_2 + NO_2 + H_2O$ (Concentrated HNO_3)

11.27. $Cu + H^+NO_3^- \rightarrow Cu^{2+}(NO_3^-)_2 + NO + H_2O$ (Dilute HNO_3)

11.28. $Zn + H^+NO_3^- \rightarrow Zn^{2+}(NO_3^-)_2 + NH_4^+NO_3^- + H_2O$ (Dilute HNO_3)

11.29. $(Na^+)_2C_2O_4^{2-} + K^+MnO_4^- + (H^+)_2SO_4^{2-} \rightarrow (K^+)_2SO_4^{2-} + (Na^+)_2SO_4^{2-} + Mn^{2+}SO_4^{2-} + CO_2 + H_2O$

11.30. $K^+ClO_3^- + H^+Cl^- \rightarrow K^+Cl^- + Cl_2$

11.31. $O_2 + H^+I^- \rightarrow H^+(I_3)^- + H_2O$

11.32. $MnO + PbO_2 + H^+NO_3^- \rightarrow H^+MnO_4^- + Pb^{2+}(NO_3^-)_2 + H_2O$

11.33. $Cr^{3+}(I^-)_3 + K^+OH^- + Cl_2 \rightarrow (K^+)_2CrO_4^{2-} + K^+IO_4^- + K^+Cl^- + H_2O$

(Note that both the chromium and the iodide ions are oxidized in this reaction.)

11.34. $(Na^+)_2HAsO_3^{2-} + K^+BrO_3^- + H^+Cl^- \rightarrow Na^+Cl^- + K^+Br^- + H_3AsO_4$

11.35. $(Na^+)_2TeO_3^{2-} + Na^+I^- + H^+Cl^- \rightarrow Na^+Cl^- + Te + I_2 + H_2O$

11.36. $U^{4+}(SO_4^{2-})_2 + K^+MnO_4^- + H_2O \rightarrow (H^+)_2SO_4^{2-} + (K^+)_2SO_4^{2-} + Mn^{2+}SO_4^{2-} + UO_2^{2+}SO_4^{2-}$

11.37. $I_2 + (Na^+)_2S_2O_3^{2-} \rightarrow (Na^+)_2S_4O_6^{2-} + Na^+I^-$

11.38. $Ca^{2+}(OCl^-)_2 + K^+I^- + H^+Cl^- \rightarrow I_2 + Ca^{2+}(Cl^-)_2 + K^+Cl^- + H_2O$

11.39. $Bi_2O_3 + Na^+OH^- + Na^+OCl^- \rightarrow Na^+BiO_3^- + Na^+Cl^- + H_2O$

11.40. $(K^+)_3Fe(CN)_6^{3-} + Cr_2O_3 + K^+OH^- \rightarrow (K^+)_4Fe(CN)_6^{4-} + (K^+)_2CrO_4^{2-} + H_2O$

11.41. $Mn^{2+}SO_4^{2-} + (NH_4^+)_2S_2O_8^{2-} + H_2O \rightarrow MnO_2 + (H^+)_2SO_4^{2-} + (NH_4^+)_2SO_4^{2-}$

11.42. $Co^{2+}(Cl^-)_2 + (Na^+)_2O_2^{2-} + Na^+OH^- + H_2O \rightarrow Co(OH)_3 + Na^+Cl^-$

11.43. $Cu(NH_3)_4^{2+}(Cl^-)_2 + K^+CN^- + H_2O \rightarrow NH_3 + NH_4^+Cl^- + (K^+)_2Cu(CN)_3^{2-} + K^+CNO^- + K^+Cl^-$

11.44. $Sb_2O_3 + K^+IO_3^- + H^+Cl^- + H_2O \rightarrow HSb(OH)_6 + K^+Cl^- + ICl$

11.45. $Ag + K^+CN^- + O_2 + H_2O \rightarrow K^+Ag(CN)_2^- + K^+OH^-$

11.46. $WO_3 + Sn^{2+}(Cl^-)_2 + H^+Cl^- \rightarrow W_3O_8 + (H^+)_2SnCl_6^{2-} + H_2O$

11.47. $V(OH)_4^+Cl^- + Fe^{2+}(Cl^-)_2 + H^+Cl^- \rightarrow VO^{2+}(Cl^-)_2 + Fe^{3+}(Cl^-)_3 + H_2O$

11.48. $Co^{2+}(Cl^-)_2 + K^+NO_2^- + H^+C_2H_3O_2^- \rightarrow (K^+)_3Co(NO_2)_6^{3-} + NO + K^+C_2H_3O_2^- + K^+Cl^- + H_2O$
(*Note*: The organic chemist writes the formula for acetic acid as CH_3COOH; however, the authors prefer $HC_2H_3O_2$, an inorganic chemistry-style notation.)

11.49. $NH_3 + O_2 \rightarrow NO + H_2O$

11.50. $CuO + NH_3 \rightarrow N_2 + Cu + H_2O$

11.51. $PbO_2 + HI \rightarrow PbI_2 + I_2 + H_2O$

11.52. $Ag_2SO_4 + AsH_3 + H_2O \rightarrow Ag + As_2O_3 + H_2SO_4$

11.53. $NaN_3 \rightarrow Na_3N + N_2$

11.54. $KClO_3 + H_2SO_4 \rightarrow KHSO_4 + O_2 + ClO_2 + H_2O$

11.55. $Sn + HNO_3 \rightarrow SnO_2 + NO_2 + H_2O$

11.56. $I_2 + HNO_3 \rightarrow HIO_3 + NO_2 + H_2O$

11.57. $KI + H_2SO_4 \rightarrow K_2SO_4 + I_2 + H_2S + H_2O$

11.58. $KBr + H_2SO_4 \rightarrow K_2SO_4 + Br_2 + SO_2 + H_2O$

11.59. $Cr_2O_3 + Na_2CO_3 + KNO_3 \rightarrow Na_2CrO_4 + CO_2 + KNO_2$

11.60. $P_2H_4 \rightarrow PH_3 + P_4H_2$

11.61. $Ca_3(PO_4)_2 + SiO_2 + C \rightarrow CaSiO_3 + P_4 + CO$

Complete and balance the following reactions in solution by the half-reaction method:

11.62. $I^- + NO_2^- \xrightarrow{\text{acid}} I_2 + NO$

11.63. $Au + CN^- + O_2 \longrightarrow Au(CN)_4^-$ (neutral solution)

11.64. $MnO_4^- \xrightarrow{\text{base}} MnO_4^{2-} + O_2$

11.65. $P \xrightarrow{\text{base}} PH_3 + H_2PO_2^-$

11.66. $Zn + As_2O_3 \xrightarrow{\text{acid}} AsH_3$

11.67. $Zn + ReO_4^- \xrightarrow{\text{acid}} Re^-$

11.68. $ClO_2 + O_2^{2-} \xrightarrow{\text{base}} ClO_2^-$

11.69. $Cl_2 + IO_3^- \xrightarrow{\text{base}} IO_4^-$

11.70. $V \xrightarrow{\text{base}} HV_6O_{17}^{3-} + H_2$

11.71. In Problem 11.8, what volume of O_2 at S.T.P. is produced for each gram of H_2O_2 consumed?

Ans. 0.66 L

11.72. How much $KMnO_4$ is needed to oxidize 100 g $Na_2C_2O_4$? Refer to the reaction in Problem 11.29.

Ans. 52 g

11.73. Automotive air bags can be inflated by the reaction in Problem 11.53, which proceeds very rapidly once initiated. How many grams $NaN_3(s)$ are required to produce 69.5 L (at S.T.P.) $N_2(g)$?

Ans. 151.3 g

11.74. A fatal dose of $HgCl_2$ is in the range of 3 g. Suppose you were involved in the design of an analytical test for the presence of mercury in tissue. By research, you determined that you can convert mercury present in the tissue to metallic mercury via mercury(II) nitrate, which can easily be further treated for detection. The conversion is by

$$Hg(NO_3)_2 + FeSO_4 \rightarrow Fe(NO_3)_3 + Fe_2(SO_4)_3 + Hg$$

How much iron(II) sulfate is required to liberate 0.0063 g Hg? (*Hint*: First, balance the equation.)

Ans. $3Hg(NO_3)_2 + 6FeSO_4 \rightarrow 2Fe(NO_3)_3 + 2Fe_2(SO_4)_3 + 3Hg$, 0.0095 g $FeSO_4$

11.75. Before a load of chromium-containing ore is purchased, an ore sample must be analyzed. During the analysis, all the chromium in the sample is reacted to produce the dichromate ion. It took 82 mL of an acidified solution containing a total of 27.49 mg Fe^{2+} to titrate the sample. (*a*) What is the balanced equation? (*b*) What is the mass (g) of chromium in the sample?

$$Fe^{2+} + Cr_2O_7^{2-} \xrightarrow{\text{acid}} Fe^{3+} + Cr^{3+}$$

Ans. (*a*) $14H^+ + 6Fe^{2+} + Cr_2O_7^{2-} \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$; (*b*) 8.53 mg Cr

11.76. A process that could be used to refine high-purity gold required for the production of computer chips might include a reaction in which gold is reacted to produce an acid, $HAuCl_4$. One way to keep in touch with the process is to account for the use of Cl_2 if the source is a cylinder by simply weighing the cylinder before and during the process, using a flow meter, or some other direct measurement.

$$Au + Cl_2 + HCl \rightarrow HAuCl_4$$

Provide the balanced equation and calculate the mass of Cl_2 used in the production of 1500 kg $HAuCl_4$.

Ans. $2Au + 3Cl_2 + 2HCl \rightarrow 2HAuCl_4$, 470 kg Cl_2

CHAPTER 12

Concentration of Solutions

COMPOSITION OF SOLUTIONS

Solutions are composed of two parts. The substance that has been dissolved is the *solute*. The substance in which the solute dissolves is the *solvent*. It is not necessary to have a liquid as a solvent, even though the term solution probably brings to mind a solid solute, like sugar, disolved in a liquid solvent, like water. For instance, air is a solution where the solvent is N_2 (nearly 80 percent of the air) in which the O_2 (nearly 20 percent) is dissolved (mixed). Another example is gold used in jewelry; it is an *alloy* (a mixture of metals) of gold (solvent) and one or more metals (solutes), including copper and nickel.

CONCENTRATIONS EXPRESSED IN PHYSICAL UNITS

When physical units are used, the concentrations of solutions are generally expressed in one of the following ways:

1. By number of mass units of solute per volume units of solution (as, 20 g KCl per liter solution).
2. By the percentage composition, or the number of mass units of solute per 100 mass units of solution.

EXAMPLE 1 A 10% aqueous NaCl solution contains 10 g NaCl for each 100 g solution. Ten grams NaCl are mixed with 90 g H_2O to form 100 g solution.

The interesting part of this method of expressing concentration is that there is no consideration of the solvent or the solute identities. Note that 10 grams of anything that dissolves in 90 g of any solvent results in a 10% solution. The point is that the chemistry of a particular 10% solution is very likely to be different from another 10% solution because the number of molecules of solute is not the same in solutions produced and measured in this manner.

3. By the mass of solute per mass of solvent (as, 5.2 g NaCl in 100 g H_2O).
4. In some areas of study, such as air and water pollution, there is an interest in very small concentrations of solute. These are frequently specified as parts per million (ppm), parts per billion (ppb), and lesser concentrations based on mass relationships.

CONCENTRATIONS EXPRESSED IN CHEMICAL UNITS

Molar concentration

Molar concentration (M) is defined as the number of moles solute in one liter of solution.

$$M = \frac{\text{moles solute}}{\text{liters solution}}$$

Molarity is a measure of concentration in which the same number of molecules of solute are found in any solution numerically the same. For instance, 1 L of a 3 molar NaCl solution contains the same number of molecules as does 1 L of a 3 molar solution of H_2SO_4 or 1 L of a 3 M CH_3OH solution.

EXAMPLE 2 A 0.500 M H_2SO_4 solution contains 49.04 g H_2SO_4 per liter solution, since 49.04 is half the molar mass of H_2SO_4 (98.08 g/mol). A 1.00 M solution contains 98.08 g H_2SO_4 per liter solution.

Cautions: (*a*) ***M*** is the symbol for the quantity, the molar concentration, and **M** is the symbol for a unit, mol/L. The term often used for molar concentrations is *molarity*. There is another solution concentration called *molality* (alternate name for *molal concentration*, *m*). Be careful to avoid confusion associated with mispronunciation or use of the wrong symbol (M instead of m or the reverse).

Normality

The *normality* of a solution (N) is the number of *equivalents* of the solution contained in one liter of solution. The *equivalent mass* is that fraction of the molar mass which corresponds to the defined unit of chemical reaction, and an *equivalent* (eq) is this same fraction of a mole. Equivalent masses are determined as follows:

1. The defined unit of reaction for acids and bases is the neutralization reaction

$$H^+ + OH^- \rightarrow H_2O$$

The equivalent mass of an acid is that fraction of the molar mass which contains or can supply one mole of H^+. A simple way of looking at the equivalent mass is that it is the mass of the acid divided by the number of H's per molecule, assuming that complete ionization occurs.

EXAMPLE 3 The equivalent masses of HCl and $HC_2H_3O_2$ are the same as their molar masses because each mole of either acid will provide one mole of H^+. On the other hand, one equivalent mass of H_2SO_4 is one-half the molar mass, making an eq $\frac{1}{2}$ mol H_2SO_4. This works pretty well until we come across an acid that does not ionize (disassociate) well, like H_3PO_4. In the case of phosphoric acid, one eq can be the mass of 1 H_3PO_4, $\frac{1}{2}$ molar mass, or $\frac{1}{3}$ molar mass, depending on the extent to which it dissociates (1, 2, or 3 H^+ per mole acid). One equivalent of H_3BO_3 is always 1 mol because only one hydrogen is replaceable in neutralization reactions. The equivalent mass of SO_3 is one-half the molar mass, since SO_3 can react with water to give $2H^+$.

$$SO_3 + H_2O \rightarrow 2H^+ + SO_4^{2-}$$

There aren't any simple rules for predicting how many hydrogens of an acid will be replaced in a given neutralization.

2. The equivalent mass of a base is that fraction of the molar mass which contains or can supply one mole of OH^-, or can react with one mole of H^+.

EXAMPLE 4 The equivalent masses of NaOH, NH_3 (reacts with H_2O to give $NH^+ + OH^-$), $Mg(OH)_2$, and $Al(OH)_3$ are equal to $\frac{1}{1}$, $\frac{1}{1}$, $\frac{1}{2}$, and $\frac{1}{3}$ of their molar masses, respectively, if ionization is complete.

3. The equivalent mass of an oxidizing or reducing agent for a particular reaction is equal to its molar mass divided by the total number of moles of electrons gained or lost when the reaction of one mole occurs. A given

oxidizing or reducing agent may have more than one equivalent mass, depending on the reaction in which it is used. You must determine the electrons moved during each reaction.

Equivalent masses are so defined because equal numbers of equivalents of two substances react exactly with each other. This is true for neutralization because one H^+ neutralizes one OH^-, and for oxidation-reduction reaction because the number of electrons lost by the reducing agent equals the number gained by the oxidation agent (electrons cannot be eliminated—by the *law of conservation of matter*).

EXAMPLE 5 One mole HCl, $\frac{1}{2}$ mol H_2SO_4, and $\frac{1}{6}$ mol $K_2Cr_2O_7$ (as an oxidizing agent), each in 1 L of solution, give 1 N solutions of these substances. A 1 N solution of HCl is also a molar (1 M) solution. A 1 N solution of H_2SO_4 is also a one-half molar (0.5) solution.

Note that N is the symbol for a quantity, the normality, and N is the symbol for a unit, eq/L.

Molality

The *molality* of a solution is the number of moles of solute per kilogram of solvent in the solution. The molality (m) cannot be computed from the molar concentration (M) unless the density of the solution is known (see Problem 12.88).

EXAMPLE 6 A solution made up of 98.08 g H_2SO_4 and 1000 g H_2O would be a 1.000 molal solution. (As with N and N, this book uses m for the quantity, whereas "m" is the unit, mol solute/kg solvent.)

Mole fraction

The *mole fraction* (X or x, depending on the author) of any component in a solution is defined as the number of moles (n) of that component, divided by the total number of moles of all components in the solution. The sum of the mole fractions of all components of a solution in mole fractions is 1. In a two-component solution, the mole fraction of a component is calculated by

$$X(\text{solute}) = \frac{n(\text{solute})}{n(\text{solute}) + n(\text{solvent})} \qquad X(\text{solvent}) = \frac{n(\text{solvent})}{n(\text{solute}) + n(\text{solvent})}$$

The *mole percent* is the same calculation as X, then multiplied by 100 to convert to percent.

COMPARISON OF THE CONCENTRATION SCALES

Molar concentration and *normality* scales are useful for volumetric experiments, in which the amount of solute in a given portion of solution is related to the measured volume of solution. We will see this in later chapters, where the normality scale is very convenient for comparing the relative volumes required for two solutions to react chemically with each other (avoiding a limiting reactant situation). A limitation of the normality scale is that a given solution may have more than one normality, depending on the reaction for which it is used. As an example, different ions in a compound that is not in a 1:1 ratio, such as Ag_2SO_4, will have a different normality when focusing on silver than when sulfate is the important ion for consideration. On the other hand, the molar concentration of a solution is a fixed number because the molar mass of a substance does not depend on the reaction for which the substance is used.

The *molality* scale is useful for experiments in which physical measurements (freezing point, boiling point, vapor pressure, osmotic pressure, etc.) are made over a wide range of temperatures. The molality of a given solution, which is determined solely by the masses of solution components, is independent of temperature. In contrast, the molar concentration (or the normality) of a solution is defined in terms of volume; it may vary appreciably as the temperature is changed, because of the temperature-dependence of the volume. As a point of interest, in dilute aqueous solutions (less than 0.1 M), the molality is very close numerically to the molarity.

The *mole fraction* scale is useful when one is concerned with physical properties of solutions (Chapter 14), which are expressed most clearly in terms of relative numbers of solvent and solute molecules. Sometimes, the physical properties are affected by the number of particles in solution. Then, the molality of ions becomes important, not just that of the molecules—NaCl (Na^+ and Cl^- in solution) and Na_2SO_4 ($2Na^+$ and SO_4^{2-} in solution) affect some physical measurements differently.

SUMMARY OF CONCENTRATION UNITS

$$\text{Molar concentration of a solution} = M = \frac{\text{moles solute}}{\text{liter solution}} \quad \text{or} \quad \frac{\text{millimoles solute}}{\text{milliliter (cm}^3\text{) solution}}$$

$$\text{Normality of a solution} = N = \frac{\text{equivalents solute}}{\text{liter solution}} \quad \text{or} \quad \frac{\text{milliequivalents solute}}{\text{milliliter (cm}^3\text{) solution}}$$

$$\text{Molality of a solution} = m = \frac{\text{moles solute}}{\text{kilograms solvent}}$$

$$\text{Mole fraction of a component} = X = \frac{\text{moles one component}}{\text{total moles all components}}$$

DILUTION PROBLEMS

Molar concentration and normality are expressed in a specific amount of solute per a fixed volume of solvent. Both of these can be expressed in terms of the amount of solute by algebraic manipulation.

$$\text{Amount of solute} = \text{volume} \times \text{concentration}$$

If a solution is diluted by the addition of solvent, the volume will increase and the concentration decrease. In the process of dilution, the amount of solute does not change. If we have two solutions of different concentration, but containing the same amount of solute (different volumes), they will be related by the following expression:

$$\text{Volume}_1 \times \text{concentration}_1 = \text{volume}_2 \times \text{concentration}_2$$

as

$$V_1M_1 = V_2M_2 \quad \text{or} \quad V_1N_1 = V_2N_2$$

where the subscripts refer to the conditions of 1 (before dilution) and 2 (after dilution). If any three of the variables are known, then we can calculate the fourth.

Solved Problems

CONCENTRATIONS EXPRESSED IN PHYSICAL UNITS

12.1. Explain how you would prepare 60 mL of an aqueous solution of $AgNO_3$ that is 0.030 g $AgNO_3$ per mL.

Since each mL of solution is to contain 0.030 g $AgNO_3$, the calculation is

$$(0.030\text{ g/mL})(60\text{ mL}) = 1.8\text{ g AgNO}_3$$

The solution can be prepared by dissolving 1.8 g $AgNO_3$ in much less than 60 mL H_2O ($\frac{3}{4}$ of the final volume works well). Stir until dissolved, then add water to bring up to 60 mL final volume while stirring. The stirring is to make certain that the solution is *homogeneous* (consistent throughout).

If you had used 60 mL of water, there is no guarantee that the final volume will be 60 mL! The only way to make certain of the final volume of 60 mL is *to dilute to* 60 mL, not add 60 mL H_2O.

12.2. What mass of 5.0% by weight NaCl solution is necessary to yield 3.2 g NaCl?

A 5.0% NaCl solution contains 5.0 g NaCl in 100 g solution. Then,

$$1\text{ g NaCl is contained in } \frac{100}{5.0}\text{ g solution}$$

and

$$3.2\text{ g NaCl are contained in } (3.2)\left(\frac{100}{5.0}\text{ g solution}\right) = 64\text{ g solution}$$

Another setup for the problem takes advantage of the ratio and proportion (w is the mass desired):

$$\frac{5.0\text{ g NaCl}}{100\text{ g solution}} = \frac{3.2\text{ g NaCl}}{w}, \text{ then} \qquad w = 64\text{ g solution}$$

12.3. How much $NaNO_3$ do you need make 50 mL of an aqueous solution containing 70 mg Na^+/mL?

The mass of Na^+ in 50 mL of solution = (50 mL)(70 mg/mL) = 3500 mg = 3.5 g Na^+. The molar mass of $NaNO_3$ is 85, of which sodium is 23. The line of logic involved is

$$23\text{ g Na}^+\text{ are contained in 85 g NaNO}_3$$

$$1\text{ g Na}^+\text{ is contained in } \frac{85}{23}\text{ g NaNO}_3$$

and

$$3.5\text{ g Na}^+\text{ are contained in } (3.5)\left(\frac{85}{23}\right)\text{ g} = 12.9\text{ g NaNO}_3$$

The use of quantitative factors can also be used to produce a setup. We use w for the mass.

$$w\text{ g NaNO}_3 = (50\text{ mL solution})\left(\frac{70\text{ mg Na}^+}{1\text{ mL solution}}\right)\left(\frac{85\text{ g NaNO}_3}{23\text{ g Na}^+}\right)\left(\frac{1\text{ g}}{1000\text{ mg}}\right) = 12.9\text{ g NaNO}_3$$

12.4. A 500-mL sample of the water treated by a water softener required 6 drops of standard soap solution to produce a permanent lather. The soap solution had been calibrated against an artificial hard water solution containing 0.136 g $CaCl_2$ per liter. On the average, it required 28 drops of standard soap solution to lather 500 mL of artificial solution. Calculate the "hardness" of the sample expressed as ppm of $CaCO_3$. *Note:* $CaCO_3$ is very insoluble and does not actually exist in hard water. The measure of hardness is really the amount of $CaCO_3$ that would be formed if all the Ca^{2+} were precipitated as $CaCO_3$.

Noticing the effluent's 6-drop requirement against the standard of 28 drops to lather the same volume of hard water, the hardness of the effluent sample is 6/28 of that of the $CaCl_2$ solution. The conversion to standard units per liter, assuming that each mole of $CaCl_2$ is equivalent to 1 mol $CaCO_3$, is

$$\frac{1\text{ mol CaCO}_3}{1\text{ mol CaCl}_2} \times \frac{0.136\text{ g CaCl}_2}{111\text{ g CaCl}_2\text{/mol CaCl}_2} \times 100\text{ g CaCO}_3\text{/mol CaCO}_3 = 0.123\text{ g CaCO}_3$$

One liter of this nearly pure water weighs 1000 g; the conversion to ppm is

$$\frac{0.123\text{ g CaCO}_3}{1000\text{ g H}_2\text{O}} \times \frac{1000}{1000} = \frac{123}{1{,}000{,}000} = 123\text{ ppm}$$

The hardiness of the effluent is calculated as (123)(6/28) = 26 ppm. This value is lower than most natural waters, but pretty poor for treated water; the cartridge needs to be replaced or recharged.

12.5. Describe how to prepare 50 g of a 12.0% solution, starting with $BaCl_2 \cdot 2H_2O$ and distilled or deionized water.

A 12.0% $BaCl_2$ solution contains 12.0 g $BaCl_2$ per 100 g solution, which is 6.00 g $BaCl_2$ in 50.0 g solution. However, you are to start with the hydrate and must account for the water in the molecule when you weigh the substance. The molar mass of $BaCl_2$ is 108, but that of $BaCl_2 \cdot 2H_2O$ is 224. Therefore,

$$208\text{ g BaCl}_2\text{ are contained in }244\text{ g BaCl}_2 \cdot 2\text{H}_2\text{O}$$

$$1\text{ g BaCl}_2\text{ is contained in }\frac{244}{208}\text{ g BaCl}_2 \cdot 2\text{H}_2\text{O}$$

and $$6.00\text{ g BaCl}_2\text{ are contained in }(6.00\text{ g BaCl}_2)\left(\frac{244\text{ g BaCl}_2 \cdot 2\text{H}_2\text{O}}{208\text{ g BaCl}_2}\right) = 7.04\text{ g BaCl}_2 \cdot 2\text{H}_2\text{O}$$

then, $$50\text{ g solution} - 7.04\text{ g of salt } = 43\text{ g water required}$$

The solution is prepared by dissolving 7.0 g $BaCl_2 \cdot 2H_2O$ in 43 g (43 mL) H_2O while stirring. *Note:* A small part of the solvent water came with the hydrated salt.

12.6. Calculate the mass of anhydrous HCl in 5.00 mL of concentrated hydrochloric acid (density 1.19 g/mL) containing 37.23% HCl by weight.

The mass of 5.00 mL of solution is (5.00 mL)(1.19 g/mL) = 5.95 g. Since the solution contains 37.23% HCl by weight, the calculation of the mass of HCl required is (0.3723)(5.95 g) = 2.22 g HCl.

12.7. Calculate the volume of concentrated sulfuric acid (density 1.84 g/mL) containing 98% H_2SO_4 by weight that would be produced from 40.0 g pure H_2SO_4.

One mL solution has a mass of 1.84 g and contains (0.98)(1.84 g) = 1.80 g pure H_2SO_4. Then, 40 g H_2SO_4 are contained in

$$\left(\frac{40.0}{1.80}\right)(1\text{ mL solution}) = 22.2\text{ mL solution}$$

A setup can be produced by the use of conversion factors.

$$(40.0\text{ g H}_2\text{SO}_4)\left(\frac{100\text{ g solution}}{98\text{ g H}_2\text{SO}_4}\right)\left(\frac{1\text{ mL solution}}{1.84\text{ g solution}}\right) = 22.2\text{ mL solution}$$

12.8. Exactly 4.00 g of a sulfuric acid solution were diluted with water, then an excess of $BaCl_2$ was added. The dried $BaSO_4$ weighed 4.08 g. Find the percent H_2SO_4 in the original acid solution.

First, we determine the mass of H_2SO_4 required to precipitate 4.08 g $BaSO_4$ referring to the reaction below and placing the equation information and problem information.

Equation information	1 mol × 98.08 g/mol			1 mol × 233.4 g/mol
	$H_2SO_4 +$	$BaCl_2 \rightarrow$	$2HCl +$	$BaSO_4$
Problem information	w			4.08 g

The next step is to set up the ratio and proportion, then solve for the mass of H_2SO_4.

$$\frac{98.08\text{ g H}_2\text{SO}_4}{w} = \frac{233.4\text{ g BaSO}_4}{4.08\text{ g BaSO}_4},\text{ which resolves to}\qquad w = 1.72\text{ g H}_2\text{SO}_4$$

and $$\text{Fraction of H}_2\text{SO}_4\text{by weight} = \frac{\text{mass H}_2\text{SO}_4}{\text{mass solution}} = \frac{1.72\text{ g H}_2\text{SO}_4}{4.00\text{ g solution}} = 0.430,\text{ which is }43.0\%$$

CONCENTRATIONS EXPRESSED IN CHEMICAL UNITS

12.9. (*a*) How many grams solute are required to prepare 1 L of 1 M $Pb(NO_3)_2$? (*b*) What is the molar concentration of the solution with respect to each of the ions?

(*a*) A one molar solution contains 1 mol of solute in 1 liter of solution. The molar mass of $Pb(NO_3)_2$ is 331.2, meaning that 331.2 g $Pb(NO_3)_2$ are required for 1 L of 1 M $Pb(NO_3)_2$ solution.

(*b*) A 1 M solution of $Pb(NO_3)_2$ is 1 M Pb^{2+} and 2M NO_3^-.

12.10. What is the molar concentration of a solution containing 16.0 g CH_3OH in 200 mL solution?

The molar mass of CH_3OH is 32.0, and the calculation to determine molarity is

$$M = \frac{\text{mole solute}}{\text{L solution}} = \frac{16.0\text{ g/(32 g/mol)}}{0.200\text{ L}} = 2.50\text{ mol/L} = 2.50\text{ M}$$

12.11. Determine the molar concentration of these two solutions: (*a*) 18.0 g $AgNO_3$ per liter solution and (*b*) 12.00 g $AlCl_3 \cdot 6H_2O$ per liter of solution.

$$(a)\ \frac{18.0\text{ g/L}}{169.9\text{ g/mol}} = 0.106\text{ mol/L} = 0.106\text{ M}; \qquad (b)\ \frac{12.00\text{ g/L}}{241.4\text{ g/mol}} = 0.0497\text{ mol/L} = 0.0497\text{ M}$$

12.12. How much $(NH_4)_2SO_4$ is required to prepare 400 mL of M/4 (M/4 $= \frac{1}{4}$M) solution?

The molar mass of ammonium sulfate is 132.1. One liter of M/4 solution contains

$$\tfrac{1}{4}(132.1\text{ g}) = 33.02\text{ g }(NH_4)_2SO_4$$

Then, the 400-mL volume of M/4 solution requires

$$(0.400\text{ L})(33.02\text{ g/L}) = 13.21\text{ g }(NH_4)2SO_4$$

12.13. What is the molality of a solution containing 20.0 g of cane sugar, $C_{12}H_{22}O_{11}$, in 125 g H_2O?

$$m = \frac{\text{moles solute}}{\text{kg solvent}} = \frac{20.0\text{ g/(342 g/mol)}}{0.125\text{ kg}} = 0.468\text{ mol sugar/kg water}$$

12.14. The molality of a solution of ethyl alcohol, C_2H_5OH, in water is 1.54 mol/kg. How many grams of alcohol are dissolved in 2.5 kg H_2O?

The molar mass of ethyl alcohol is 46.1. Since the molality is 1.54, 1 kg of water dissolves 1.54 mol C_2H_5OH. The amount of C_2H_5OH that 2.5 kg water dissolves is

$$(2.5)(1.54) = 3.85\text{ mol } C_2H_5OH,\ \text{which weighs} \qquad (3.85)(46.1\text{ g/mol}) = 177\text{ g } C_2H_5OH$$

12.15. Calculate the (*a*) molar concentration and (*b*) molality of a sulfuric acid solution of density 1.198 g/mL containing 27.0% H_2SO_4 by weight.

It is recommended, when quantities of substances are not stated, to select an arbitrary quantity as the *basis* of calculation. In this case, let the *basis* be 1.000 L solution.

(*a*) One liter has a mass of 1198 g and contains (0.270)(1198) = 323 g H_2SO_4 of molar mass 98.1,

$$M = \frac{\text{mol } H_2SO_4}{\text{L solution}} = \frac{323\text{ g } H_2SO_4/(98.1\text{ g/mol})}{1.000\text{ L}} = 3.29\text{ mol/L} = 3.29\text{ M } H_2SO_4$$

(*b*) From (*a*), there is 323 g (3.29 mol) solute per liter solution. The amount of water in 1 L of solution is 1198 g solution – 323 g solute = 875 g H_2O. The molality is

$$m = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{3.29\text{ mol } H_2SO_4}{0.875\text{ kg } H_2O} = 3.76\text{ mol/kg}$$

12.16. Determine the mole fractions of both substances in a solution containing 36.0 g H_2O and 46 g $C_3H_5(OH)_3$, glycerin (molar masses: 18.0 for water and 92 for glycerin).

The mole fraction requires the expression of the components in moles.

$$\frac{36.0\text{ g } H_2O}{18.0\text{ g/mol}} = 2.00\text{ mol } H_2O \qquad \frac{46.0\text{ g glycerin}}{92\text{ g/mol}} = 0.50\text{ mol glycerin}$$

$$\text{Total number of moles} = 2.00 + 0.50 = 2.50$$

$$X(\text{water}) = \frac{\text{moles water}}{\text{total moles}} = \frac{2.00}{2.50} = 0.80 \qquad X(\text{glycerin}) = \frac{\text{moles glycerin}}{\text{total moles}} = \frac{0.50}{2.50} = 0.20$$

Check: The sum of the mole fractions should be 1, as it is in this problem (0.80 + 0.20 = 1).

12.17. How many equivalents of solute are contained in (*a*) 1 L of 2 N solution; (*b*) 1 L of 0.5 N solution; (*c*) 0.5 L of 0.2 N solution? (*Hint*: Using "of" usually indicates multiplication.)

(*a*) 1 L × 2 eq/L = 2 eq; (*b*) 1 L × 0.5 eq/L = 0.5 eq; (*c*) 0.5 L × 0.2 eq/L = 0.1 eq

12.18. How many (*a*) equivalents and (*b*) milliequivalents (meq) of solute are in 60 mL of a 4.0 N solution? (Refer to the hint in Problem 12.17.)

$$(a)\ (0.060\,\text{L})\left(\frac{4.0\,\text{eq}}{\text{L}}\right) = 0.24\,\text{eq};\quad (b)\ (0.24\,\text{eq})\left(\frac{1000\,\text{meq}}{\text{eq}}\right) = 240\,\text{meq}$$

Alternate setup for (*b*): meq = (number mL)(normality) = (60 mL)(4.0 meq/mL) = 240 meq

12.19. What mass solute is required to prepare 1 L of 1 N solution of (*a*) LiOH; (*b*) Br_2(as an oxidizing agent); (*c*) H_3PO_4 (all three H's are replaceable)?

(*a*) One liter of 1 N LiOH requires (23.95/1) g = 23.95 g LiOH.

(*b*) Note from the partial equation $Br_2 + 2e^- \rightarrow 2Br^-$ that two electrons react per Br_2. The equivalent mass of Br_2 is *half* its molar mass. One liter of 1 N Br_2 requires (159.8/2) g = 79.9 g Br_2.

(*c*) One liter of 1 N H_3PO_4 requires (98.00/3) g = 32.67 g H_3PO_4, assuming total ionization.

12.20. Calculate the normality of each of the following solutions: (*a*) 7.88 g of HNO_3 per liter solution and (*b*) 26.5 g of Na_2CO_3 per liter solution when neutralized to form CO_2.

(*a*) Equivalent mass of HNO_3 for the H^+, not an oxidizing agent (for the N), is the molar mass, 63.02.

$$N = \frac{7.88\text{ g/(63.02 g/eq)}}{1\text{ L}} = 0.125\text{ eq/L} = 0.125\,\text{N HNO}_3$$

(*b*) The reaction is: $CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$, and the equivalent mass of Na_2CO_3 is $(\frac{1}{2})$(molar mass = $(\frac{1}{2})(106.0) = 53.0$ Na_2CO_3.

$$N = \frac{26.5\text{ g/(53.0 g/eq)}}{1\text{ L}} = 0.500\,\text{eq/L} = 0.500\,\text{N HNO}_3$$

12.21. How many milliliters of 2.00 M $Pb(NO_3)_2$ contain 600 mg Pb^{2+}?

One liter of 1 M $Pb(NO_3)_2$ contains 1 mol Pb^{2+}, or 207 g. Then, a 2 M solution contains 2 mol Pb^{2+} or 414 g Pb^{2+} per liter. As 1 mL is 1/1000th of a liter, there would be 1/1000th of the mass of Pb^{2+} in that liter solution, which is 414 mg/mL. Then, 600 mg Pb^+ are contained in

$$\frac{600\,\text{mg}}{414\,\text{mg/mL}} = 1.45\,\text{mL of } 2.00\,\text{M Pb(NO}_3)_2$$

An alternate method recognizes that a 2 M solution contains 2 mmol/mL and,

$$\text{Mass} = M \times \text{volume} \times \text{molar mass} \qquad \text{or, when rearranged} \qquad \text{Volume} = \text{mass}/(M \times \text{molar mass})$$

$$\text{Volume} = \frac{600\,\text{mg}}{(2\text{ mmol/mL})(207\text{ mg/mmol})} = 1.45\,\text{mL}$$

12.22. Given the unbalanced equation

$$K^+MnO_4^- + K^+I^- + (H^+)_2SO_4^{2-} \rightarrow (K^+)_2SO_4^{2-} + Mn^{2+}SO_4^{2-} + I_2 + H_2O$$

(*a*) How many grams of $KMnO_4$ are needed to make 500 mL of a 0.250 N solution?

(*b*) How many grams of KI are needed to make 25 mL of a 0.36 N solution?

(*a*) The Mn in $KMnO_4$ changes in oxidation number from +7 to +2, requiring 5 electrons.

$$\text{Equivalent mass of } KMnO_4 = \frac{\text{molar mass}}{\text{oxidation number change}} = \frac{158}{5} = 31.6\text{ g } KMnO_4\text{/eq}$$

The 0.500-L solution of 0.250 N $KMnO_4$ requires

$$(0.500\text{ L})(0.250\text{ eq/L})(31.6\text{ g/eq}) = 3.95\text{ g } KMnO_4$$

As a different scenario, if the $KMnO_4$ made above were to be used in the reaction:

$$2MnO_4^- + 3H_2O_2 + 2H^+ \rightarrow 2MnO_2 + 3O_2 + 4H_2O$$

the label 0.250 N would no longer be appropriate because the oxidation number change in this case is 3, not 5 ($Mn^{+7} \rightarrow Mn^{+4}$). The appropriate normality would be

$$\left(\frac{0.250\text{ N}}{5}\right)(3) = 0.150\text{ N}$$

(*b*) The oxidation state changes from –1 in I^- to 0 in I_2.

$$\text{Equivalent mass of KI} = \frac{\text{molar mass}}{\text{oxidation number change}} = \frac{166}{1} = 166\text{ g KI g/eq}$$

Then, 0.025 L (25 mL) of 0.36 N solution requires

$$(0.025\text{ L})(0.36\text{ eq/L})(166\text{ g/eq}) = 1.49\text{ g KI}$$

12.23. Calculate the molar concentration of a 2.28 m NaBr solution (density of 1.167 g/cm^3).

The molar mass of NaBr is 102.9. For each kilogram of water there are (2.28)(102.9) = 235 g NaBr, or a total mass of 1000 + 235 = 1235 g. This mass of solution occupies a volume of 1235 g/(1.167 g/cm^3), which is 1058 cm^3. Since 1 cm^3 is 1 mL, the volume is 1.058 L. The molar concentration is

$$\frac{2.28\text{ mol}}{1.058\text{ L}} = 2.16\text{ mol/L or } 2.16\text{ M}$$

12.24. A solution of an organic halide in benzene, C_6H_6, has a mole fraction of halide of 0.0821. Express its concentration in terms of molality.

Benzene's molar mass is 78.1. A total of 0.0821 mol halide is mixed with 1 − 0.0821 = 0.9179 mol benzene, which has a mass of (0.9179 mol)(78.1 g/mol) = 71.7 g = 0.0717 kg. The molality halide is

$$\text{Molality} = \frac{\text{mol component}}{\text{kg solvent}} = \frac{0.0821\text{ mol halide}}{0.0717\text{ kg benzene}} = 1.145\text{ m solution}$$

DILUTION PROBLEMS

12.25. To what extent must a solution containing 40 mg $AgNO_3$ per mL be diluted to yield one that contains 16 mg $AgNO_3$ per mL?

Let V be the volume to which 1 mL of the original solution must be diluted to yield a solution that is 16 mg $AgNO_3$ per mL. (*Note:* The solute amount does not change with dilution; the volume changes.)

$$\text{Volume}_1 \times \text{concentration}_1 = \text{volume}_2 \times \text{concentration}_2$$
$$1\text{ mL} \times 40\text{ mg/mL} = V_2 \times 16\text{ mg/mL} \qquad \text{and, solving} \qquad V_2 = 2.5\text{ mL}$$

Note that 2.5 mL is **not** the volume of water to be added; it is the final volume *after water has been added* to 1 mL of the original solution. Also, notice that there is no provision made for other than the final volume being the result of adding volumes. This works well with dilute solutions (less than 0.1 M), but may not work so well with concentrated solutions. If more concentrated solutions are used, the final volume will probably have to be determined by experimentation.

12.26. How can a 0.50 M $BaCl_2$ solution be diluted to yield one that contains 20.0 mg Ba^{2+}/mL?

One liter of the original solution contains 0.50 mol $BaCl_2$ (or of Ba^{2+}). The mass of Ba^{2+} in 0.50 mol is

$$(0.50\,\text{mol})(137.3\,\text{g/mol}) = 68.7\,\text{g Ba}^{2+}/\text{L} \qquad \text{or} \qquad 68.7\,\text{mg Ba}^{2+}\text{per mL}$$

The problem now is to find the extent to which a solution of 68.7 mg Ba^{2+}/mL must be diluted to yield one containing 20.0 mg Ba^{2+}/mL. At this point, the problem is the same as the previous one.

$$\text{Volume}_1 \times \text{concentration}_1 = \text{volume}_2 \times \text{concentration}_2$$

$$1\,\text{mL} \times 68.7\,\text{mg/mL} = V_2 \times 20.0\,\text{mg/mL} \qquad \text{and, solving} \qquad V_2 = 3.43\,\text{mL}$$

This means that each milliliter of 0.50 M $BaCl_2$ must be diluted with water to 3.43 mL.

12.27. A procedure calls for 100 mL of 20% H_2SO_4, density 1.14 g/mL. How much of the concentrated acid, density 1.84 g/mL, and containing 98% H_2SO_4 by weight, must be diluted with water to prepare 100 mL of the required acid?

The concentrations must first be changed from a mass basis to a volumetric basis, so that the dilution equation will apply. Concentrations include mass, but are not a direct statement of the mass.

$$\text{Mass of H}_2\text{SO}_4 \text{ per mL of 20\% acid} = (0.20)(1.14\,\text{g/mL}) = 0.228\,\text{g/mL}$$

and

$$\text{Mass of H}_2\text{SO}_4 \text{ per mL of 98\% acid} = (0.98)(1.84\,\text{g/mL}) = 1.80\,\text{g/mL}$$

We can now let V_2 be the volume of 98% acid required for 100 mL of 20% H_2SO_4.

$$\text{Volume}_1 \times \text{concentration}_1 = \text{volume}_2 \times \text{concentration}_2$$

$$100\,\text{mL} \times 0.228\,\text{mg/mL} = V_2 \times 1.80\,\text{mg/mL} \qquad \text{and, solving} \qquad V_2 = 12.7\,\text{mL conc. H}_2\text{SO}_4$$

12.28. What volumes of N/2 and of N/10 HCl must be mixed to give 2 L of N/5 HCl?

Let v = volume N/2 required and let 2 L – v be the volume of N/10 required.

$$\text{Number of eq of N/5} = (\text{number of eq of N/2}) + (\text{number of eq of N/10})$$

$$(2\,\text{L})(\tfrac{1}{5}\text{N}) = v(\tfrac{1}{2}\text{N}) + (2\,\text{L} - v)(\tfrac{1}{10}\text{N}) \text{ and,} \qquad \text{solving} \qquad v = 0.5\,\text{L}$$

and, substituting 0.5 for v, the requirements are 0.5 L of N/2 and 1.5 L of N/10 solutions.

12.29. How many mL of concentrated H_2SO_4, density 1.84 g/mL, containing 98% H_2SO_4 by weight do we need to make (*a*) 1 L of 1 N solution; (*b*) 1 L of 3.00 N solution; (*c*) 200 mL of 0.500 N solution?

$$\text{Equivalent mass H}_2\text{SO}_4 = \tfrac{1}{2}(\text{molar mass}) = \tfrac{1}{2}(98.1) = 49.0\,\text{g/eq H}_2\text{SO}_4$$

The H_2SO_4 content of 1 L concentrated acid is (0.98)(1000 mL)(1.84 g/mL) = 1800 g H_2SO_4. The normality of the concentrated acid is calculated by

$$\frac{1800\,\text{g H}_2\text{SO}_4/\text{L}}{49.0\,\text{g H}_2\text{SO}_4/\text{eq}} = 36.7\,\text{eq/L} = 36.7\,\text{N H}_2\text{SO}_4 \text{ (conc)}$$

allowing us to use the dilution formula: $V_{\text{conc}} \times N_{\text{conc}} = V_{\text{dilute}} \times N_{\text{dilute}}$. Solving for V_{conc} in each case,

$$(a) \qquad V_{\text{conc}} = \frac{V_{\text{dilute}} \times N_{\text{dilute}}}{N_{\text{conc}}} = \frac{(1\,\text{L})(1.00\,\text{N})}{36.7\,\text{N}} = 0.0272\,\text{L} = 27.2\,\text{mL concentrated H}_2\text{SO}_4$$

$$(b) \qquad V_{\text{conc}} = \frac{V_{\text{dilute}} \times N_{\text{dilute}}}{N_{\text{conc}}} = \frac{(1\,\text{L})(3.00\,\text{N})}{36.7\,\text{N}} = 0.0817\,\text{L} = 81.7\,\text{mL concentrated H}_2\text{SO}_4$$

$$(c) \qquad V_{\text{conc}} = \frac{V_{\text{dilute}} \times N_{\text{dilute}}}{N_{\text{conc}}} = \frac{(0.200\,\text{L})(0.500\,\text{N})}{36.7\,\text{N}} = 0.00272\,\text{L} = 2.72\,\text{mL concentrated H}_2\text{SO}_4$$

Supplementary Problems

CONCENTRATIONS EXPRESSED IN PHYSICAL UNITS

12.30. How much NH_4Cl is required to prepare 100 mL of a solution containing 70 mg NH_4Cl per mL?

Ans. 7.0 g

12.31. What mass of crystalline Na_2SO_4 do you need in order to mix 1.5 L of a solution containing 0.375 moles of salt per liter of solution?

Ans. 79.899 g Na_2SO_4 required (3-place accuracy matches most chemistry lab balances)

12.32. Among the uses for cartridge brass (30% zinc and 70% copper by weight) are ammunition and radiators for cars. What is the number of moles of each component in an 18-g sample?

Ans. 0.083 mol Zn and 0.198 mol Cu

12.33. Concrete drills can be produced from a steel that includes 0.50 wt% carbon, 1.35 wt% chromium, 0.28 wt% nickel, and 0.22 wt% vanadium. A 1-kg sample of the steel received from a potential supplier is being analyzed by the Quality Control Department. Express each of the components of this sample in terms of moles.

Ans. 0.416 mol C, 0.147 mol Cr, 0.048 mol Ni, and 0.043 mol V

12.34. What mass (g) of concentrated solution containing 37.9% HCl by weight will give 5.0 g HCl?

Ans. 13.2 g

12.35. An experiment requires 100 g of a 19.7% solution of NaOH. How many grams each of NaOH and H_2O do we need to mix the solution?

Ans. 19.7 g NaOH and 80.3 g H_2O

12.36. How much $CrCl_3 \cdot 6H_2O$ is needed to prepare 1 L solution containing 20 mg Cr^{3+}/mL?

Ans. 102 g

12.37. Determine the volume of dilute HNO_3, density 1.11 g/cm^3 and 19% HNO_3, by weight, that contains 10 g HNO_3.

Ans. 47 cm^3 or 47 mL

12.38. What is the percent composition Na_2SO_4 (density 1.03) if it contains 0.001 g salt per mL of solution?

Ans. 0.097% Na_2SO_4

12.39. How many cubic centimeters of a solution containing 40 g $CaCl_2$/L are needed to react with 0.642 g of pure Na_2CO_3? $CaCO_3$ is formed in the metathesis reaction.

Ans. 16.8 cm^3 or 16.8 mL

12.40. What volume of a NaCl solution that is 0.5 g/mL is required to just react with 25 g of a $AgNO_3$ (AgCl is a precipitate produced by this reaction).

Ans. 17.1 mL

12.41. Ammonia gas is passed into water, yielding a solution of density 0.93 g/mL and containing 18.6% NH_3 by weight. What is the mass of NH_3 (mg) per milliliter of solution?

Ans. 173 mg/mL

12.42. Given 100 mL of pure water at 4°C, what volume of a hydrochloric acid solution, density 1.175 g/mL and containing 34.4% HCl by weight, could be prepared?

Ans. 130 mL

12.43. A liter of milk weighs 1.032 kg. The butterfat, which is 4% by volume, has a density of 0.865 g/mL. What is the density of the fat-free milk?

Ans. 1.039 g/mL

12.44. A benzene-soluble cement is produced by melting 49 g of rosin in an iron pan and adding 28 g each of shellac and beeswax. How much of each component should be taken to make 75 kg of cement?

Ans. 35 kg rosin, 20 kg shellac, 20 kg beeswax

12.45. How much $CaCl_2 \cdot 6H_2O$ and water must be weighed out to make 100 g of a solution that is 5.0% $CaCl_2$?

Ans. 9.9 g $CaCl_2 \cdot 6H_2O$ and 90.1 g water

12.46. What mass of $BaCl_2$ would be needed to make 250 mL of a solution having the same concentration of Cl^- as one containing 3.78 g of NaCl per 100 mL?

Ans. 16.8 g $BaCl_2$

12.47. Although not usually calculated, the molality and molarity of an alloy (a metal in a metal solution) can be calculated. Nickel steel contains nickel in small amounts mixed with iron. (*a*) Express the molality of the 2.5 g Ni (atomic mass = 58.69) dissolved in 1000 mL Fe (atomic mass = 55.85, density = 7.66 g/cm^3 under the lab conditions). (*b*) Express the molarity of the metal solution (no volume change).

Ans. (*a*) 0.0056 m; (*b*) 0.0426 M

12.48. Using data from the preceding problem, calculate the mole fraction Ni and the mole fraction Fe.

Ans. 0.000311 for Ni and 0.9997 for Fe

12.49. The sulfate content of 6.00 liters of drinking water is determined by first evaporating off some water, which forms a more concentrated solution of less volume. This volume was then treated with $BaCl_2$ solution, which resulted in the precipitation of 0.0965 g $BaSO_4$. Express the sulfate ion concentration in ppm.

Ans. 6.62 ppm

12.50. Silver nitrate, $AgNO_3$, can be added to drinking water as a test reagent for the concentration of chlorine that has been used to kill bacteria and other disease-causing organisms. Insoluble AgCl is produced as a heavy, white precipitate. A 10-mL water sample required 1.35 mL of $AgNO_3$ containing 0.00366 g Ag^+ per mL to use up all the chlorine. What is the concentration of Cl^- in the sample stated in ppm (sample density = 1.000 g/mL)?

Ans. 162 ppm

12.51. An air sample from a chemical plant was analyzed by a mass spectrometer. The analysis revealed the presence of 1.2×10^{-8} moles benzene per mole of air. Express the concentration of benzene, C_6H_6, in ppb by weight. Assume the average molar mass of air is 29.

Ans. 32 ppb

CONCENTRATIONS EXPRESSED IN CHEMICAL UNITS

12.52. (*a*) Chromium plating of surfaces for protection from corrosion can be done using a solution of $Cr(NO_3)_3$. What is the mass of Cr^{3+} in 25 L of a 1.75 M solution? (*b*) Gold plating can be performed using a 3.50 M $Au(NO_3)_3$ solution. What is the mass of Au^{3+} in 12.75 L of this solution?

Ans. (*a*) 2275 g Cr^{3+}; (*b*) 8790 g Au^{3+}

12.53. (*a*) What mass of silver is weighed to produce 10 L of 6 M $AgNO_3$? (*b*) What mass of gold is required for 10 L of 6 M $Au(NO_3)_3$?

Ans. (*a*) 6.5 kg Ag; (*b*) 11.8 kg Au

12.54. What is the molarity of a solution containing 37.5 g $Ba(MnO_4)_2$ per liter, and what is the molar concentration with respect to each type of ion?

Ans. 0.100 M $Ba(MnO_4)_2$; 0.100 M Ba^{2+}; 0.200 M MnO_4^-

12.55. A solution is labeled "0.100 M $Ba(MnO_4)_2$." With what normality should it be labeled if used as (*a*) an oxidizing agent in strong acid (Mn^{2+} produced), (*b*) an oxidizing agent in slightly acid solution (MnO_2 produced), or (*c*) a precipitant for $BaSO_4$?

Ans. (*a*) 0.500 N; (*b*) 0.300 N; (*c*) 0.100 N

12.56. How many grams of solute are required to prepare 1 L of 1 M $CaCl_2 \cdot 6H_2O$?

Ans. 219.1 g

12.57. The presence of waters of hydration changes the amounts of materials needed to mix up solutions. (*a*) Copper(II) ion in solution is occasionally used to kill bacteria in water. What is the mass of $CuSO_4$ that is required to mix 1 L of 5 M $CuSO_4$? (*b*) What is the mass of $CuSO_4 \cdot 5H_2O$ needed to produce the same solution? Assume no change in volume on mixing.

Ans. (*a*) 800 g $CuSO_4$; (*b*) 1250 g $CuSO_4 \cdot 5H_2O$.

12.58. We can estimate an amount of substance needed to produce a solution as a check on our calculations. (*a*) Using mass numbers 7 for lithium, 12 for carbon and 16 for oxygen, estimate the amount of lithium carbonate needed to produce 1 L of a 3 M Li_2CO_3 solution. (*b*) Now, perform the calculation using the atomic masses as a comparison.

Ans. (*a*) 222 g; (*b*) 221.674 g (0.674 g difference—less than 0.4% error)

12.59. What mass (g) of anhydrous $CaCl_2$ is required to prepare (*a*) 1 L of 1 M $CaCl_2$; (*b*) 2.50 L of 0.200 M $CaCl_2 \cdot 2H_2O$; (*c*) 650 mL of 0.600 M $CaCl_2$?

Ans. (*a*) 111 g; (*b*) 55.5 g; (*c*) 43.3 g

12.60. A single drop of dimethyl mercury, CH_3—Hg—CH_3, can be absorbed through the skin resulting in death. What is the minimum molarity of dimethyl mercury that will deliver 5.0×10^{-5} g Hg^{2+} in one drop, assuming that there are 20 drops/mL?

Ans. 5×10^{-3} M

12.61. A 6.00-g sample of a polymer was dissolved in 280 mL of a solvent. Osmotic pressure measurements show that its concentration was 2.12×10^{-4} M. Calculate the molar mass of the polymer.

Ans. $\mathsf{M} = 1.01 \times 10^5$ g/mol

12.62. Exactly 100 g NaCl are dissolved in sufficient water to give 1500 mL of solution. What is the molar concentration of the solution prepared in this manner?

Ans. 1.14 M

12.63. Suppose you were responsible for producing 2.25 L of a solution that was to be 0.082 M copper(II) sulfate. What is the mass of $CuSO_4$ you must weigh? (Density = 1.00 g/mL and no volume change.)

Ans. 29.5 g $CuSO_4$

12.64. Calculate the molality of (*a*) 0.65 mol glucose, $C_6H_{12}O_6$, in 250 g H_2O; (*b*) 45 g glucose in 1 kg water; (*c*) 18 g glucose in 200 g water.

Ans. (*a*) 2.6 m; (*b*) 0.25 m; (*c*) 0.50 m

12.65. How many grams of $CaCl_2$ should be added to 300 mL of water to make up 2.46 m $CaCl_2$?

Ans. 82 g

12.66. Three compounds can be produced by starting with two $C_4H_8O_4$ molecules and dehydrating (removing a H_2O) to produce $C_8H_{14}O_7$, then dehydrating again between the 8-carbon and 4-carbon molecules, ending up with $C_{12}H_{20}O_{10}$. Three solutions were produced: 50 g of $C_4H_8O_4$ in 2 L water, 50 g of $C_8H_{14}O_7$ in 2 L water, and 50 g of $C_{12}H_{20}O_{10}$ in 2 L solution. What are the molalities of these solutions?

Ans. 0.208 m; 0.113 m; 0.077 m

12.67. A solution contains 57.5 mL ethanol, C_2H_5OH, and 600 mL benzene, C_6H_6. How many grams of alcohol are there per 1000 g benzene? What is the molality of the solution? Densities are 0.80 g/cm^3 for ethanol and 0.90 g/cm^3 for benzene.

Ans. 85 g, 1.85 mol/kg or 1.85 molal

12.68. Benzoic acid, C_6H_5COOH, is soluble in benzene, C_6H_6. What is the molality of a solution in which 3.55 g benzoic acid are dissolved in 75 mL of benzene? (Density benzene is 0.866 g/mL at the temperature of the experiment.)

Ans. 0.45 m

12.69. A solution contains 10.0 g $HC_2H_3O_2$ (alternate formula format—CH_3COOH), acetic acid, in 125 g H_2O. Express as (*a*) mole fractions $HC_2H_3O_2$ and H_2O, (*b*) molality of the acid.

Ans. (*a*) $X(\text{acid}) = 0.024$ and $X(\text{water}) = 0.976$; (*b*) 1.33 molal

12.70. A solution contains 116 g acetone (CH_3COCH_3), 138 g ethanol (C_2H_5OH), and 126 g H_2O. Determine the mole fraction of each.

Ans. $\text{X(acetone)} = 0.167$; $X(\text{alcohol}) = 0.250$; $X(\text{water}) = 0.583$

12.71. What is the mole fraction of the solute in a 1.00 molal aqueous solution?

Ans. 0.0177

12.72. An aqueous solution labeled as 35.0% $HClO_4$ had a density of 1.251 g/mL. Calculate molarity and molality of the solution.

Ans. 4.36 M, 5.36 m

12.73. A sucrose solution was prepared by dissolving 13.5 g $C_{12}H_{22}O_{11}$ in sufficient water to make exactly 100 mL, which was then found to have a density of 1.050 g/mL. Compute the molar concentration and the molality of the solution.

Ans. 0.395 M, 0.431 m

12.74. For a solute of molar mass, M, show that the molar concentration, M, and molality, m, of the solution are related by

$$M\left(\frac{\mathsf{M}}{1000} + \frac{1}{m}\right) = d$$

where d is the solution density in g/cm^3 (g/mL). (*Hint*: show that each cubic centimeter of solution contains $M\mathsf{M}/1000$ g of solution and M/m g of solvent.) Use this relationship to check the answers to Problems 12.70 and 12.71.

12.75. What volume of 0.232 N solution contains (*a*) 3.17 meq solute, (*b*) 6.5 eq solute?

Ans. (*a*) 13.7 mL; (*b*) 28.0 L

12.76. Determine the molarity of each of the following solutions: (*a*) 166 g KI/L solution; (*b*) 33.0 $(NH_4)_2SO_4$ in 200 mL solution; (*c*) 12.5 g $CuSO_4 \cdot 5H_2O$ in 100 cm^3 solution; (*d*) 10.0 mg Al^{3+} per cubic centimeter solution.

Ans. (*a*) 1.00 M; (*b*) 1.25 M; (*c*) 0.500 M; (*d*) 0.370 M

12.77. What volume of 0.200 M $Ni(NO_3)_2 \cdot 6H_2O$ contains 500 mg Ni^{2+}?

Ans. 42.6 mL

12.78. What is the volume of concentrated H_2SO_4 (density 1.835 g/cm^3, 93.2% H_2SO_4 by weight) required to make up 500 mL of 3.00 N acid solution.

Ans. 43.0 mL

12.79. Calculate the volume of concentrated HCl (density 1.19 g/cm^3, 38% HCl by weight) to obtain when making up 18 L of N/50 acid.

Ans. 29 cm^3 or 29 mL

12.80. Determine the mass of $KMnO_4$ required to make 80 mL of N/8 $KMnO_4$ when the final solution is used to act as an oxidizing agent in an acid solution and Mn^{2+} is a product of the reaction.

Ans. 0.316 g

12.81. We are given this unbalanced equation: $Cr_2O_7^{2-} + Fe^{2+} + H^+ \rightarrow Cr^{3+} + Fe^{3+} + H_2O$.

(*a*) What is the normality of a $K_2Cr_2O_7$ solution 35.0 mL of which contains 3.87 g $K_2Cr_2O_7$?

(*b*) What is the normality of an $FeSO_4$ solution 750 mL of which contains 96.3 g $FeSO_4$?

Ans. (*a*) 2.25 N (*b*) 0.845 N

12.82. What mass of $Na_2S_2O_3 \cdot 5H_2O$ is needed to make up 500 mL of 0.200 N solution, assuming

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Ans. 24.8 g

12.83. A 4.51-g sample of a compound was dissolved in 98.0 g of solvent. By close observation of its freezing point, the solution was found to be 0.388 m. What is the molar mass of the unknown compound?

Ans. 119 g/mol or 119 M

12.84. An analyst planned to use $BaCl_2$ to make up 60.0 mL of 0.500 M Ba^{2+} solution, but his only source of $BaCl_2$ in stock was 2.66 g of $BaCl_2 \cdot 2H_2O$. Knowing that nitrate ion would not interfere with his procedure, he decided to make up the difference using $Ba(NO_3)_2$. How much $Ba(NO_3)_2$ is needed?

Ans. 4.99 g $Ba(NO_3)_2$

DILUTION PROBLEMS

12.85. A solution contains 75 mg NaCl per milliliter. To what extent must it be diluted to give a solution that is 15 mg NaCl per mL?

Ans. Each milliliter of original solution is diluted with water to a volume of 5 mL.

12.86. How many cubic centimeters of solution that is 100 mg Co^{2+} per cubic centimeter are needed to prepare 1.5 L of solution that is 20 mg Co^{2+} per cubic centimeter?

Ans. 300 cm^3

12.87. Calculate the approximate volume of water that must be added to 250 mL of 1.25 N solution to make it 0.500 N (neglecting volume changes).

Ans. 375 mL

12.88. What is the volume of 6 M HNO_3 that you must measure to produce 175 mL of 4.5 M HNO_3?

Ans. 131 mL

12.89. What is the resultant molar concentration of HCl when 15 mL of 6 M HCl and 15 mL of 3 M NaOH are mixed?

Ans. 1.5 M HCl

12.90. Determine the volume of dilute nitric acid (density 1.11 g/mL, 19.0% HNO_3 by weight) that can be prepared by diluting with water 50 mL of concentrated acid (density 1.42 g/mL, 69.8% HNO_3 by weight). Calculate the molar concentrations and molalities of the concentrated and dilute acids.

Ans. 234 mL; molar concentrations 15.7 and 3.35; molal concentrations 36.7 and 3.72

12.91. What volume of 95% alcohol by weight (density 0.809 g/cm^3) must be used to prepare 150 cm^3 of 30.0% alcohol by weight (density 0.957 g/cm^3)?

Ans. 56.0 cm^3

12.92. What volumes of 12 N and 3 N HCl must be mixed to produce 1 L of 6 N HCl?

Ans. $\frac{1}{3}$ liter of 12 N, $\frac{2}{3}$ liter of 3 N

12.93. What is the molar concentration of a solution made by mixing 300 mL of 0.0200 M H_2SO_4 with 200 mL of 0.0300 M H_2SO_4?

Ans. 0.024 M

12.94. A chemist boiled down 500 mL of 0.0865 M NaCl until only 127 mL remained. Calculate the molar concentration of the remaining solution.

Ans. 0.341 M NaCl

CHAPTER 13

Reactions Involving Standard Solutions

ADVANTAGES OF VOLUMETRIC STANDARD SOLUTIONS

A *standard solution* is one that is produced so that the concentration is known. A standard solution is especially useful for the determination of the concentration of another solution with which it reacts. The procedure used is *titration*, in which the standard solution is added to a definite volume of the unknown solution until the chemical reaction is complete. The completion of the reaction can be detected by a product, such as a precipitate that forms, or by an *indicator*. Indicators are substances that are sensitive to a change in the solution and may signal completion of the reaction by changing color.

Two cautions about titrations are called for at this point. The first is that the volume of the unknown and the volume of the standard solution must be carefully measured so that the calculations will reflect what is actually present. The second caution deals with running a titration—make certain to perform titrations slowly so that the end-point of the titration is not exceeded. Going past the end-point may occur because the reaction is slower than the addition of drops or the end-point was simply missed because the drops are released faster than the color change can be perceived.

The goal of the titration procedure is to use up all of the unknown while keeping track of the amount of standard solution required for the titration. Once completed, the amount of the standard solution can be used in calculations to determine the concentration of the unknown solution. Determining the unknown by titration is based on the knowledge of the standard solution's composition by

$$\text{Number of moles} = (\text{number of liters}) \times (\text{molar concentration})$$

or

$$\text{Number of millimoles} = (\text{number of milliliters}) \times (\text{molar concentration})$$

SOLUTION STOICHIOMETRY

Sometimes, the calculation involves a monoprotic acid and a dihydroxy base or another set of conditions in which the relationship is not 1:1. We have to keep track of the various concentrations so that the molarities do not get mixed up. However, stoichiometric calculations involving solutions of specified normalities are even simpler. By the definition of equivalent mass in Chapter 12, two solutions will react exactly with each other if they contain the same number of equivalents. The calculation involved is

$$\text{Volume}_1 \times \text{normality}_1 = \text{volume}_2 \times \text{normality}_2 \quad \text{or} \quad V_1N_1 = V_2N_2$$

Suppose we have a standard solution and we need to determine information about a substance that will not dissolve in water. Solutions of given normalities are useful even when only one of the reactants is dissolved. In this case, the number of equivalents (or meq) of the reactant that is not in solution (not dissolved) is determined in the usual way, which is by dividing the mass of the sample in grams (or mg) by the equivalent mass. The reason that this works is that the number of equivalents (or meq) of one reactant must still equal the number of eq (or meq) of the other by the application of $V_1N_1 = V_2N_2$.

Solved Problems

13.1. What volume of 1.40 M H_2SO_4 solution is needed to react exactly with 100 g Al?

As with any problem that includes the word *react*, the chance of needing a balanced chemical equation is pretty much a foregone conclusion. The single replacement reaction, written and balanced, is

$$2\text{Al} + 3\text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2$$

Mole Method

$$\text{Number of moles Al in 100 g Al} = \frac{100\ \text{g}}{27.0\ \text{g/mol}} = 3.70\ \text{mol Al}$$

$$\text{Number of moles H}_2\text{SO}_4 \text{ required for 3.70 mol Al} = \frac{3}{2}(3.70) = 5.55\ \text{mol H}_2\text{SO}_4$$

$$\text{Volume of 1.40 M H}_2\text{SO}_4 \text{ containing 5.55 mol H}_2\text{SO}_4 = \frac{5.55\ \text{mol}}{1.40\ \text{mol/L}} = 3.96\ \text{L}$$

Factor-Label Method

$$\left(\frac{100\ \text{g Al}}{27.0\ \text{g Al/mol Al}}\right)\left(\frac{3\ \text{mol H}_2\text{SO}_4}{2\ \text{mol Al}}\right)\left(\frac{1\ \text{L H}_2\text{SO}_4\ \text{solution}}{1.40\ \text{mol H}_2\text{SO}_4}\right) = 3.96\ \text{L}$$

13.2. In standardizing a solution of $AgNO_3$ it was found that 40.0 mL were required to precipitate all the chloride ions contained in 36.0 mL of 0.520 M NaCl. How many grams of silver could be obtained from 100 mL of $AgNO_3$ solution?

$$\text{AgNO}_3(aq) + \text{NaCl}(aq) \rightarrow \text{AgCl}(s) + \text{NaCl}(aq)$$

The balanced equation tells us that equal numbers of moles $AgNO_3$ and NaCl must be used. (As in previous chapters, n is the number of moles.)

$$n(\text{AgNO}_3) = n(\text{NaCl}) = (0.0360\ \text{L})(0.520\ \text{mol NaCl/L solution}) = 0.01872\ \text{mol solute}$$

Then, 40.0 mL of $AgNO_3$ solution contains 0.01872 mol $AgNO_3$, which provides 0.01872 mol Ag. Using these data, 100 mL of solution contains

$$\left(\frac{100\ \text{mL}}{40.0\ \text{mL}}\right)(0.01872\ \text{mol Ag})(107.9\ \text{g Ag/mol Ag}) = 5.05\ \text{g Ag}$$

13.3. Exactly 40.0 mL of 0.225 M $AgNO_3$ were required to react with 25.0 mL of a solution of NaCN. Calculate the molarity of NaCN, if the reaction is by the following equation:

$$\text{Ag}^+ + 2\text{CN}^- \rightarrow \text{Ag(CN)}_2^-$$

Since $n(\text{AgNO}_3) = (0.0400\,\text{L})(0.225\,\text{mol/L}) = 0.00900\,\text{mol AgNO}_3$

and $n(\text{NaCN}) = 2 \times n(\text{AgNO}_3) = 0.0180\,\text{mol NaCN}$

Then, 25.0 mL of the NaCN solution contains 0.0180 mol NaCN, so that

$$M = \frac{0.0180\,\text{mol}}{0.025\,\text{L}} = 0.72\,\text{M NaCN}$$

13.4. What volume in mL of 6.0 N NaOH is required to neutralize 30 mL of 4.0 N HCl?

Since $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$, and we have access to the formula, $V_1N_1 = V_2N_2$, we can simply substitute and solve for the desired normality.

$$V_{\text{base}}N_{\text{base}} = V_{\text{acid}}N_{\text{acid}}, \quad \text{which becomes,} \quad V_{\text{base}} \times 6.0\,\text{N} = 30\,\text{mL} \times 4.0\,\text{N}$$

then, $$\text{volume NaOH} = \frac{(30\,\text{mL})(4.0\,\text{N})}{6.0\,\text{N}} = 20\,\text{mL NaOH solution}$$

13.5. What is the normality of a H_3PO_4 solution if 40 mL neutralizes 120 mL of 0.531 N NaOH?

Since we are working with normalities, the solutes will react exactly with each other. Therefore,

$$(\text{volume H}_3\text{PO}_4) \times (\text{normality H}_3\text{PO}_4) = (\text{volume NaOH}) \times (\text{normality NaOH})$$

$$(40\,\text{mL})(\text{normality H}_3\text{PO}_4) = (120\,\text{mL})(0.531\,\text{N})$$

$$N\ \text{H}_3\text{PO}_4 = \frac{(120\,\text{mL})(0.531\,\text{N})}{40\,\text{mL}} = 1.59\,\text{N H}_3\text{PO}_4$$

Note: This problem's solution works because we do not have to know whether one, two, or three hydrogens from H_3PO_4 are replaceable (or even the formula of the acid). The normality was determined by reaction of the acid with a base of known concentration. Under the concept of normality, the acid will have the same concentration (N) as the base, 1.59 N, in reactions with any strong base under similar conditions. In order to know the molar concentration of the acid, however, it would be necessary to know the number of replaceable hydrogens in the reaction, which we don't.

In a case like this problem, where a substance can have several equivalent masses, the normality determined by one type of reaction is not necessarily the normality in other reactions. For instance, if a weak base like NH_3 were to be used instead of a strong base for neutralizing the acid, or if the method of detecting the point of neutralization were changed (a different indicator), the equivalent mass of phosphoric acid (and the normality) might well be different.

13.6. (*a*) What volume of 5.00 N H_2SO_4 will neutralize a solution containing 2.50 g NaOH? (*b*)What mass in grams of pure H_2SO_4 is required for the reaction?

(*a*) One equivalent of H_2SO_4 reacts completely with one equivalent of NaOH. The equivalent mass of NaOH is the molar mass, 40.0. Then,

$$\text{Number of equivalents in 2.50 g NaOH} = \frac{2.50\,\text{g}}{40.0\,\text{g/eq}} = 0.0625\,\text{eq NaOH}$$

$$\text{Number of liters} \times N = \text{number of eq}$$

$$\text{Number of liters} = \frac{\text{Number of eq}}{N} = \frac{0.0625}{5.00} = 0.0125\,\text{L or } 12.5\,\text{mL}$$

(*b*) The mass of acid is then calculated from the result of first calculation above.

$$\text{Equivalent mass of H}_2\text{SO}_4 = \frac{1}{2} \times \text{molar mass} = \frac{1}{2}(98.08) = 49.04\,\text{g}$$

$$\text{Mass of H}_2\text{SO}_4\ \text{required} = (0.0625\,\text{eq})(49.04\,\text{g/eq}) = 3.07\,\text{g pure H}_2\text{SO}_4$$

13.7. A 0.250-g sample of solid acid was dissolved in water and neutralized by 40.0 mL of 0.125 N base. What is the equivalent mass of the acid?

$$\text{Number of meq of base} = (40.0\,\text{mL})(0.125\,\text{meq/mL}) = 5.00\,\text{meq}$$

$$\text{Number of meq of acid} = \text{number of meq of base} = 5.00\,\text{meq}$$

$$\text{Equivalent mass of acid} = \frac{250\,\text{mg}}{5.00\,\text{meq}} = 50\,\text{mg/meq} = 50\,\text{g/eq}$$

13.8. Exactly 48.4 mL of HCl solution are required to neutralize completely 1.240 g pure $CaCO_3$. Calculate the normality of the acid.

Each carbonate ion requires two hydrogen ions for neutralization by the reaction

$$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$$

Because of the relationship above, the equivalent mass of $CaCO_3$ is 50.05, one-half the molar mass.

$$\text{Number of equivalents in } 1.240\,\text{g } CaCO_3 = \frac{1.240\,\text{g}}{50.05\,\text{g}} = 0.0248\,\text{eq } CaCO_3$$

So, 48.4 mL of acid solution contains 0.0248 eq HCl

$$N = \frac{\text{number of eq}}{\text{number of liters}} = \frac{0.0248\ \text{eq}}{0.0484\ \text{L}} = 0.512\ \text{N}$$

13.9. When 50 mL of a certain Na_2CO_3 solution was titrated with 0.102 M HCl, 56.3 mL were required for complete neutralization by the same reaction in Problem 13.8 in which two hydrogen ions are required per carbonate ion. Calculate the mass in grams of $CaCO_3$ that would be precipitated if an excess of $CaCl_2$ were added to a separate 50.0-mL portion of the Na_2CO_3 solution.

Factor-Label Method

$$\text{Mass } CaCO_3 = \left(\frac{56.3\ \text{mL}}{1000\ \text{mL/L}}\right)\left(\frac{0.102\ \text{mol HCl}}{1\ \text{L}}\right)\left(\frac{1\ \text{mol } Na_2CO_3}{2\ \text{mol HCl}}\right)\left(\frac{1\ \text{mol } CaCO_3}{1\ \text{mol } Na_2CO_3}\right)\left(\frac{100.1\ \text{g } CaCO_3}{1\ \text{mol } CaCO_3}\right)$$

$$\text{Mass } CaCO_3 = 0.287\,\text{g } CaCO_3$$

13.10. A 10.0-g sample of "gas liquor" is boiled with an excess of NaOH and the resulting ammonia is passed into 60 mL of 0.90 N H_2SO_4. Exactly 10.0 mL of 0.40 N NaOH are required to neutralize the excess sulfuric acid (not neutralized by the NH_3). What is the percent NH_3 in the "gas liquor" examined?

$$\begin{aligned}\text{Number of meq } NH_3 \text{ in 10.0 g of gas liquor} &= (\text{meq } H_2SO_4) - (\text{meq NaOH})\\ &= (60\ \text{mL})(0.90\ \text{meq/mL}) - (10.0\ \text{mL})(0.40\,\text{meq/mL})\\ &= 50\ \text{meq } NH_3\end{aligned}$$

In neutralization experiments, the equivalent mass of NH_3 is the same as the molar mass, 17.0, conforming with the reaction $NH_3 + H^+ \rightarrow NH_4^+$. Then, the mass of ammonia in the sample is (50 meq)(17.0 mg/meq) = 850 mg, which is 0.85 g ammonia. The fraction can be calculated by

$$\text{Fraction } NH_3 \text{ in the sample} = \frac{0.85\,\text{g}}{10.0\,\text{g}} = 0.085, \qquad \text{which is} \qquad 0.085 \times 100 = 8.5\%$$

13.11. A 40.8-mL sample of an acid is equivalent to 50.0 mL of a Na_2CO_3 solution, 25.0 mL of which is equivalent to 23.8 mL of 0.102 N HCl. What is the normality of the first acid?

The volume of HCl that would have been required for 50.0 mL of Na_2CO_3 solution is

$$\left(\frac{50.0}{25.0}\right)(23.8\,\text{mL}) = 47.6\,\text{mL}$$

$$V_1N_1 = V_2N_2 \qquad \text{becomes} \qquad (40.8\,\text{mL})(N_1) = (47.6\,\text{mL})(0.102\,\text{N})$$

$$N_1 = 0.119\,\text{N acid}$$

13.12. Calculate the mass (g) of $FeSO_4$ that will be oxidized by 24.0 mL of 0.250 N $KMnO_4$ in a solution acidified with sulfuric acid. The unbalanced equation for the reaction is below. The statement of normality of $KMnO_4$ is with respect to this reaction (Mn changes from +7 to +2 during this reaction).

$$MnO_4^- + Fe^{2+} + H^+ \rightarrow Fe^{3+} + Mn^{2+} + H_2O$$

It is not necessary to balance the equation. All we need to know is that the oxidation number on the iron changes from +2 to +3, as indicated by the charges on the iron ions. The equivalent mass $FeSO_4$ is

$$\text{Equivalent mass FeSO}_4 = \frac{\text{molar mass}}{\text{oxidation number change}} = \frac{152}{1} = 152\text{ g FeSO}_4/\text{eq}$$

Note: The same result would have been achieved if the balanced half-reaction had been used. That reaction is $Fe^{2+} \rightarrow Fe^{3+} + 1e^-$.

Let w = required mass of $FeSO_4$.

$$\text{Number of eq KMnO}_4 = \text{number of eq FeSO}_4$$

$$(\text{Volume KMnO}_4) \times (\text{normality KMnO}_4) = \frac{\text{mass FeSO}_4}{\text{equivalent mass FeSO}_4}$$

$$(0.0240\,\text{L})(0.250\,\text{eq/L}) = \frac{w}{152\,\text{g/eq}} \qquad \text{becomes} \qquad w = (0.0240\,\text{L})(0.250\,\text{eq/L})(152\,\text{g/eq})$$

$$w = 0.912\,\text{g FeSO}_4$$

13.13. What volume of 0.1000 N $FeSO_4$ is required to reduce 4.000 g $KMnO_4$ in a solution acidified with sulfuric acid?

The normality of the $FeSO_4$ is with respect to the oxidation-reduction reaction in Problem 13.12. In this reaction, the Mn changes in oxidation number from +7 to +2. The net change is 5. Or, from the balanced half-reaction,

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

it can be seen that the electron transfer is 5 for each permanganate ion. The equivalent mass of $KMnO_4$ in this reaction is

$$\frac{1}{5} \times (\text{molar mass}) = \frac{1}{5}(158.0) = 31.6\,\text{g/eq}$$

$$\text{Number of eq FeSO}_4 = \text{number of eq KMnO}_4$$

$$(\text{Volume FeSO}_4) \times (0.1000\,\text{eq/L}) = \frac{4.000\,\text{g}}{31.6\,\text{g/eq}}$$

$$\text{Volume FeSO}_4 = 1.266\,\text{L}$$

13.14. A sample known to contain As_2O_3 was brought into solution by a process which converted the arsenic to H_3AsO_3. This was titrated with a standard I_2 solution according to the equation

$$H_3AsO_3 + I_2 + H_2O \rightarrow H_3AsO_4 + 2I^- + 2H^+$$

Exactly 40.27 mL of standard I_2 solution were required to reach the end-point as indicated by the persistence of a faint I_2 color. The standard solution had been prepared by mixing 0.4192 g of pure KIO_3 with excess KI and acid, then dissolving and diluting to 250.0 mL. The I_2 is formed during the reaction,

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

Calculate the mass of As_2O_3 in the sample.

First, it is necessary to calculate the molar concentration of the I_2 solution. By the *factor-label method*, the calculation is

$$M = \left(\frac{0.4192\,\text{g KIO}_3}{214.0\,\text{g KIO}_3/\text{mol}}\right)\left(\frac{3\text{ mol I}_2}{1\text{ mol KIO}_3}\right)\left(\frac{1000\,\text{mL/L}}{250.0\,\text{mL}}\right) = 0.02351\text{ mol/L} = 0.02351\text{ M I}_2$$

Then, by the same method,

$$(0.04027\,\text{L})(0.02351\text{ mol I}_2/\text{L})\left(\frac{1\text{ mol H}_3\text{AsO}_3}{1\text{ mol I}_2}\right)\left(\frac{1\text{ mol As}_2\text{O}_3}{2\text{ mol H}_3\text{AsO}_3}\right)(197.8\text{ g As}_2\text{O}_3/\text{mol})$$

The above setup provides us with 0.09363 g As_2O_3.

Supplementary Problems

13.15. What is the volume in mL of 0.25 M $AgNO_3$ required to precipitate all the chromate ion from 20 mL of a solution containing 100 g of Na_2CrO_4 per liter? The reaction is

$$2\text{Ag}^+ + \text{CrO}_4^{2-} \rightarrow \text{Ag}_2\text{CrO}_4(s)$$

Ans. 99 mL

13.16. A 25-mL sample of hydrochloric acid that is to be used in treated swimming pools requires 44.2 mL of 6 M NaOH for complete neutralization. (*a*) What is the molarity of the HCl solution? (*b*) Calculate the weight/weight percentage of HCl; the mass of the sample is 25.00 g.

Ans. (*a*) 10.6 M; (*b*) 38.6%

13.17. A 50.0-mL sample of Na_2SO_4 solution is treated with an excess of $BaCl_2$. If the precipitated $BaSO_4$ is 1.756 g, what is the molarity of the Na_2SO_4 solution?

Ans. 0.1505 M

13.18. What was the thorium content of a sample that required 35.0 mL of 0.0200 M $H_2C_2O_4$ to precipitate all the thorium as $Th(C_2O_4)_2$?

Ans. 81 mg

13.19. Ba^{2+} is suspected to be in some effluent water downstream from an industrial installation. A 25-mL sample of the water is titrated with 0.35 M Na_2SO_4 solution until the insoluble $BaSO_4$ is no longer produced, which required 53 mL Na_2SO_4 solution. Provide the concentration of barium in the water in terms of (*a*) molarity and (*b*) g Ba^{2+}/mL

Ans. (*a*) 0.742 M; (*b*) 0.10 g/mL

13.20. What is the molar concentration of a $K_4Fe(CN)_6$ solution if 40.0 mL were required to titrate 150.0 mg Zn (dissolved) by forming $K_2Zn_3[Fe(CN)_6]_2$?

Ans. 0.0382 M

13.21. A 50.0-mL sample of NaOH solution requires 27.8 mL of 0.100 N acid in a titration. (*a*) What is its normality? (*b*) How many mg NaOH are in each cubic centimeter (mL)?

Ans. (*a*) 0.0556 N; (*b*) 2.22 mg/cm^3

13.22. In standardizing HCl, 22.5 mL were required to neutralize 25.0 mL of 0.0500 M Na_2CO_3 solution. What is the molarity and the normality of the HCl solution? How much water must be added to 200 mL of it to make it 0.100 N?

Ans. 0.111 M; 0.111 N; 22 mL

13.23. Exactly 21 mL of 0.80 N acid were required to neutralize completely 1.12 g of an impure sample of calcium oxide. What is the purity of the CaO?

Ans. 42%

13.24. Sulfuric acid is one of the most important acids used in industry and knowledge of its purity is extremely important. Find the (*a*) normality of a 35-mL sample of H_2SO_4 solution that requires 46 mL of 0.5000 M NaOH solution for complete neutralization; also, (*b*) state the concentration in terms of molarity.

Ans. (*a*) 0.66 N; (*b*) 0.33 M

13.25. $Mg(OH)_2$ must have a purity of over 96% to be usable for a certain process. A 5.000 g sample requires 60.60 mL of 0.9000 M HCl for neutralization. The impurity has been found to be $MgCl_2$; calculate the percent composition $Mg(OH)_2$ by mass.

Ans. 31.8% $Mg(OH)_2$

13.26. By the *Kjeldahl method*, the nitrogen contained in a foodstuff is converted into ammonia. If the ammonia from 5.0 g of a foodstuff is just sufficient to neutralize 20 mL of 0.100 M nitric acid, calculate the percentage of nitrogen in the foodstuff.

Ans. 0.56%

13.27. What is the purity of concentrated H_2SO_4 (density 1.800 g/cm^3) if 5.00 cm^3, after diluting in water, is neutralized by 84.6 mL of 2.000 M NaOH?

Ans. 92.2%

13.28. A 10.0-mL portion of $(NH_4)_2SO_4$ solution was treated with an excess of NaOH. The NH_3 gas evolved was absorbed in 50.0 mL of 0.100 M HCl. To neutralize the remaining HCl, 21.5 mL of 0.098 M NaOH were required. (*a*) What is the molar concentration of the $(NH_4)_2SO_4$? (*b*) How many grams of $(NH_4)_2SO_4$ are in a liter of solution?

Ans. (*a*) 0.145 M; (*b*) 19.1 g/L

13.29. Exactly 400 mL of an acid solution, when acted upon by an excess of zinc, evolved 2.430 L of H_2 gas measured over water at 21°C and 747.5 torr. What is the normality of the acid? Vapor pressure of water at 21°C is 18.6 torr.

Ans. 0.483 N

13.30. How many grams of Cu will be replaced from 2.0 L of 0.150 M $CuSO_4$ solution by 2.7 g of Al?

Ans. 9.5 g

13.31. What volume of 1.50 M H_2SO_4 will liberate 185 L of H_2 gas at S.T.P. when treated with an excess of zinc?

Ans. 5.51 L

13.32. How many liters of H_2 at S.T.P. would be replaced from 500 mL of 3.78 M HCl by 125 g Zn?

Ans. 21.2 L

13.33. The mass of 1.243 g of an acid is required to neutralize 31.72 mL of 0.1923 N standard base. What is the equivalent mass of this acid?

Ans. 203.8 g/eq

13.34. The molar mass of an organic acid was determined by the following study of its barium salt. 4.290 g of the salt were to be converted to the free acid by reaction with 21.64 mL of 0.477 M H_2SO_4. The barium salt was known to contain 2 moles water of hydration per mol Ba^{2+}, and the acid was known to be monoprotic. What is the molar mass of the anhydrous acid?

Ans. 122.1 g/mol

13.35. An $FeSO_4$ solution was standardized by titration. A 25.00-mL portion of the solution required 42.08 mL of 0.0800 N ceric sulfate for complete oxidation. What is the normality of the iron(II) sulfate?

Ans. 0.1347 N

13.36. A 15-g sample of tissue is suspected of containing arsenic. It is treated to convert any arsenic present to $As(NO_3)_3$ and diluted to 500 mL. A titration is performed using 0.0050 M H_2S solution to precipitate the arsenic as As_2S_3. The volume of 0.53 mL (a little less than 11 drops at 20/mL) is required. How much arsenic (ppm) was present in the tissue?

Ans. 8.9 ppm arsenic

13.37. How many mL of 0.0257 N KIO_3 would be needed to reach the end-point in the oxidation of 34.2 mL of 0.0416 N hydrazine in hydrochloric acid solution?

Ans. 55.4 mL

13.38. How many grams of $FeCl_2$ will be oxidized by 28 mL of 0.25 N $K_2Cr_2O_7$ in HCl solution? The unbalanced equation is

$$Fe^{2+} + Cr_2O_7^{2-} + H^+ \rightarrow Fe^{3+} + Cr^{3+} + H_2O$$

Ans. 0.89 g

13.39. In a standardization procedure, 13.76 mL of iron(II) sulfate solution were required to reduce 25.00 mL of potassium dichromate solution, which was prepared by dissolving 1.692 g of $K_2Cr_2O_7$ in water and diluting to 500.0 mL. (See reaction in Problem 13.38.) Calculate the molarity and the normality of both the potassium dichromate and the iron(II) sulfate solution.

Ans. $K_2Cr_2O_7$ 0.01150 M; 0.06901 N; $FeSO_4$ 0.1254 M; 0.1254 N

13.40. What mass of MnO_2 is reduced by 35 mL of 0.080 M oxalic acid, $H_2C_2O_4$, in sulfuric acid solution? The unbalanced equation is

$$MnO_2 + H^+ + H_2C_2O_4 \rightarrow CO_2 + H_2O + Mn^{2+}$$

Ans. 0.24 g

13.41. (*a*) What mass of $KMnO_4$ is required to oxidize 2.40 g $FeSO_4$ in a solution acidified with sulfuric acid? (*a*) What is the equivalent mass of $KMnO_4$ in this reaction?

Ans. (*a*) 0.500 g; (*b*) 31.6 g/eq

13.42. Find the equivalent mass of $KMnO_4$ in the reaction

$$Mn^{2+} + MnO_4^- + H_2O \rightarrow MnO_2 + H^+ \text{ (not balanced)}$$

How many grams of $MnSO_4$ are oxidized by 1.25 g $KMnO_4$?

Ans. 52.7 g/eq, 1.79 g

13.43. (*a*) What volume of 0.0667 M $K_2Cr_2O_7$ is required to liberate the chlorine from 1.20 g of NaCl in a solution acidified with H_2SO_4?

$$Cr_2O_7^{2-} + Cl^- + H^+ \rightarrow Cr^{3+} + Cl_2 + H_2O \quad \text{(not balanced)}$$

(*b*) How many grams of $K_2Cr_2O_7$ are required? (*c*) How many grams of chlorine are liberated?

Ans. (*a*) 51 mL; (*b*) 1.01 g; (*c*) 0.73 g

13.44. If 25.0 mL of an iodine solution is equivalent as an oxidizing agent to 0.125 g of $K_2Cr_2O_7$, to what volume should 1000 mL be diluted to make a solution 0.0500 M? The half-reaction for the iodine is

$$I_2 + 2e \rightarrow 2I^-$$

Ans. 1020 mL

13.45. How many grams of $KMnO_4$ should be taken to make up 250 mL of a solution of such concentration that 1 mL is equivalent to 5.00 mg iron in $FeSO_4$?

Ans. 0.707 g

13.46. What mass of iodine is in a solution which requires 40 mL of 0.112 M $Na_2S_2O_3$ to react with it?

$$S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + I^- \quad \text{(not balanced)}$$

Ans. 0.57 g

13.47. All the manganese in a certain solution was converted to MnO_4^- ion by contact with solid sodium bismuthate. A 25.00-mL portion of 0.0200 M $FeSO_4$ was added, which was more than sufficient to completely reduce the permanganate to Mn^{2+} in an acidified medium. The excess Fe^{2+} was then back-titrated in an acid solution, requiring 4.21 mL of 0.0106 M $KMnO_4$. How many milligrams of manganese were in the original solution?

Ans. 3.04 mg

13.48. Reducing sugars are sometimes characterized by a number, R_{Cu}, which is defined as the number of milligrams of copper reduced by 1 gram of the sugar, in which the half-reaction for the copper is

$$Cu^{2+} + OH^- \rightarrow Cu_2O + H_2O \quad \text{(not balanced)}$$

It is sometimes convenient to determine the reducing power of a carbohydrate by an indirect method. In this method, 43.2 mg of the carbohydrate were oxidized by an excess of $K_3Fe(CN)_6$. The $Fe(CN)_6^{4-}$ formed in this reaction required 5.29 mL of 0.0345 N $Ce(SO_4)_2$ for reoxidation to $Fe(CN)_6^{3-}$ (the normality of the ceric sulfate solution is given with respect to the reduction of Ce^{4+} to Ce^{3+}). Determine the R_{Cu}-value for the sample. (*Hint*: The number of meq Cu in a direct oxidation is the same as the number of meq Ce^{4+} in the indirect method.)

Ans. 268

13.49. A volume of 12.53 mL of 0.05093 M selenium dioxide, SeO_2, reacted exactly with 25.52 mL of 0.1000 M $CrSO_4$. In the reaction, Cr^{2+} was oxidized to Cr^{3+}. To what oxidation number was the selenium converted by the reaction?

Ans. 0

13.50. A 150 g sample of ore is treated with nitric acid to remove the copper in the form of $CuCl_2$. The resultant 587 mL of solution were titrated with 0.75 M NaOH to precipitate $Cu(OH)_2$, which requires 41.7 mL. What is the yield from the ore expressed in terms of kg Cu/metric ton ore (1000 kg)?

Ans. 6620 kg Cu/metric ton ore

13.51. An acid solution of $KReO_4$ sample containing 26.83 mg of combined rhenium was reduced by passage through a column of granulated zinc. The effluent solution, including the washings from the column, was then titrated with 0.1000 N $KMnO_4$. A volume of 11.45 mL of the standard permanganate was required for the reoxidation of all the rhenium to the perrhenate ion, ReO_4^-. Assuming that rhenium was the only element reduced, what was the oxidation number to which rhenium was reduced by the zinc column?

Ans. -1

13.52. The iodide content of a solution was determined by titration with ceric sulfate in the presence of HCl, in which I^- was converted to ICl and Ce^{4+} to Ce^{3+}. A 250-mL sample of the solution required 20.0 mL of 0.050 M Ce^{4+} solution. What is the iodide concentration in the original solution (mg/mL)?

Ans. 0.25 mg/mL

13.53. An alloy of silver and copper can be used to make coins. A 75.00-g sample is treated with sufficient HCl to just precipitate all of the silver present as AgCl. The acid required is 16.32 mL of 6.25 M HCl. What is the percentage copper in the alloy?

Ans. 86.4%

13.54. A 0.518-g sample of limestone is dissolved, and then the calcium is precipitated as calcium oxalate, CaC_2O_4. The precipitate is filtered, washed, and dissolved in sulfuric acid solution. It then requires 40.0 mL of 0.0500 M $KMnO_4$ solution to titrate it. What is the percent CaO in the limestone? The unbalanced equation for the titration is

$$MnO_4^- + CaC_2O_4 + (H^+)_2SO_4^{2-} \rightarrow CaSO_4 + Mn^{2+} + CO_2 + H_2O$$

Ans. 54.2%

13.55. Cadaverine is an organic compound that has a strong, disagreeable odor. Treatment of 15.00 mL of a smelly solution with 1.75 mL of 5 M HCl wiped out the odor (your nose was the indicator). (*a*) What was the normality of the smelly solution? (*b*) Why didn't this question ask for molarity, rather than normality?

Ans. (*a*) 0.58N. (*b*) Molarity of the solution depends on the number of H^+ ions that can be accepted by each molecule of cadaverine and there is no hint given to provide that information.

13.56. Assume the reaction between phosphate ions and calcium ions goes to completion to form $Ca_3(PO_4)_2$. If 50.0 mL of 0.400 M $Ca(NO_3)_2$ are mixed with 100.0 mL of 0.300 M Na_3PO_4, what will be the final molarity of Ca^{2+}, NO_3^-, Na^+, and PO_4^{3-} in the resulting solution?

Ans. no Ca^{2+}, 0.267 M NO_3^-, 0.600 M Na^+, 0.111 M PO_4^{3-}

13.57. How many milliliters of 0.0876 M NaOH should be added to 50.0 mL of 0.0916 M HCl to yield a solution in which the H^+ concentration is 0.0010 M?

Ans. 51.1 mL

13.58. One problem with standard NaOH solutions is that they absorb CO_2 from the air, which reacts with OH^- to form CO_3^{2-} obscuring the end-point in titrations of acid. An enterprising young chemist had 975.0 mL of 0.3664 M NaOH, which she suspected had absorbed some CO_2, so she added 10 mL of 0.500 M $Ba(OH)_2$. That addition precipitated all the carbonate ion as $BaCO_3(s)$. After the $BaCO_3$ was filtered off, the solution was restandardized and found to be 0.3689 M OH^-. How many grams of solid $BaCO_3$ had been removed?

Ans. 0.38 g

13.59. Citric acid, like other acids, tastes sour and can cause orange juice to be sour. Assuming that citric acid is the only acid present, a liter-size sample is titrated with 193 mL of 0.75 M NaOH. Also, assuming that citric acid is the only component in the juice reacting, what is the normality of citric acid present?

Ans. 0.15 N

13.60. A solution suspected of containing lead(II) nitrate is titrated with 0.035 M Na_2SO_4. How much Na_2SO_4 solution is required to produce a precipitate of $PbSO_4$ from 1 L of a saturated lead(II) sulfate solution? The solution is saturated at 1.3×10^{-4} M $PbSO_4$?

Ans. Over 3.7 mL added will cause a precipitate to appear.

CHAPTER 14

Properties of Solutions

INTRODUCTION

There is a series of properties solutions display that vary with the concentration of solute particles, often regardless of chemical composition. In other words, these properties tend to change pretty much with the concentration. Such properties are referred to as *collative properties* and include changes in the freezing point, boiling point, vapor pressure, and osmotic pressure.

A good deal of the time, the changes in behavior are over a somewhat narrow range of concentrations, but are predictable over that range. Notably, there are solutions that vary the same way over the entire range of concentrations; these are known as *ideal solutions*. The forces of interaction between solvent and solute molecules of the ideal solution are the same as between the molecules of each component when separated. During the formation of an ideal solution from the separate components, there are no volume changes (additive volumes with no gain or loss) and no enthalpy changes. Pairs of chemically similar substances, such as methanol (CH_3OH) and ethanol (C_2H_5OH), or benzene (C_6H_6) and toluene (C_7H_8), form ideal solutions. Dissimilar substances, such as ethanol and benzene, form nonideal solutions.

VAPOR PRESSURE LOWERING

The vapor pressure of the solvent reduces as the concentration of the solute increases (inverse relationship). Generally, the discussions of vapor pressure are with reference to the concentration of *nonvolatile* solutes and, therefore, we are dealing with the tendency of only the solvent to leave the solution. Experimentation has determined that *dilute* solutions of equal molality, using the same solvent and different nonelectrolytes (no dissociation) as solutes, show *the same amount of vapor pressure lowering* (*depression*) in every case.

Experimentation has revealed an interesting point about vapor pressure changes. Suppose we were to make up two solutions, solution I and solution II, from the same solvent and using solutes that are nonvolatile and nonelectrolytes. Let us take two identical portions of the solvent and place in two different containers. In the case of solution I, mix a solution using one solute to achieve a particular molality. In the case of solution II, mix a solution to the same molality, but use two different solutes to do so. The lowering of the vapor pressure of the solute is the same in both solutions.

Raoult's law states that the *vapor pressure lowering is proportional to the mole fraction of the solute* (or, *the vapor pressure is proportional to the mole fraction of the solvent.*). In equation form:

$$\begin{aligned}&\text{Lowering of solvent vapor pressure}\\ \Delta P &= (\text{vapor pressure of pure solvent}) - (\text{vapor pressure of solution})\\ &= (\text{vapor pressure of pure solvent}) \times (\text{mole fraction of solute})\end{aligned}$$

or

$$\begin{aligned}&\text{Vapor pressure of solvent over solution}\\ &= (\text{vapor pressure of pure solvent}) \times (\text{mole fraction solvent})\end{aligned}$$

In the second form, the vapor pressure of the solution has been identified with the vapor pressure of the solvent over the solution, since the solute is assumed to be nonvolatile.

Further, Raoult's law can be applied when two volatile components are mixed. In systems of liquids that mix in all proportions to form ideal solutions, Raoult's law in the form of the second equation applies to the partial pressure of each volatile component separately.

$$\begin{aligned}&\text{Partial pressure of any component over solution}\\ &= (\text{vapor pressure of that pure component}) \times (\text{mole fraction of the component})\end{aligned}$$

Raoult's law is explained by the hypothesis that solute molecules at the surface of the liquid interfere with the escape of solvent molecules into the vapor phase. Because of the vapor pressure lowering, the *boiling point of the solution is raised* and the *freezing point is lowered*, as compared with the boiling and freezing points of the pure solvent.

FREEZING-POINT LOWERING, ΔT_f

On the cooling of most dilute solutions, the solvent begins to crystallize before the solute crystallizes. The temperature at which the solvent's crystals first begin to appear is the *freezing point* of that solution. The freezing point of a solution is always *lower* than the freezing point of the pure solvent. In dilute solutions, the freezing-point lowering, ΔT_f, is directly proportional to the number of moles solute (number of molecules) present. The change in freezing point is determined by subtracting the true freezing point of the solution from the freezing point of the pure solvent ($\Delta T_{f(\text{solvent})} - \Delta T_{f(\text{solution})}$). The equation for the change in freezing point is

$$\Delta T_f = k_f m$$

where m is the molality of the solution (Chapter 12). If this equation were to be valid up to a concentration of 1 m, the lowering of the freezing point of a 1 m solution of any nonelectrolyte dissolved in the solvent would be k_f, which is called the *molal freezing-point constant* or, more simply, the *freezing-point constant*. The value of k_f is a property characteristic for each solvent.

EXAMPLE 1 The k_f for water is 1.86°C/m (1.86 K/m), which can be expressed as 1.86°C · kg H_2O/mol solute (1.86 K · kg H_2O/mol solute) after some algebraic rearrangement. This means that a solution of 1 mol cane sugar (342 g, over $\frac{3}{4}$ lb) dissolved in 1 kg of water should freeze at $-1.86°$ C.

The freezing-point drop suggested in Example 1 is correct if the relationship holds true for this concentrated solution. As mentioned above (and below), the laws are most accurate for low (dilute) concentrations. Further, some of these calculations would be more accurate if mole fraction were to be used; however, at low concentrations, the error involved in calculations based on molality is very low.

BOILING-POINT ELEVATION, ΔT_b

Compared to the boiling point of the pure solvent, dilute solutions containing that solvent boil *at a higher temperature*. In dilute solutions, the elevation of the boiling point is directly proportional to the number of moles solute (or molecules). The equation for the change in boiling point is

$$\Delta T_b = k_b m$$

The *molal boiling-point constant* of the solvent is k_b. As with k_f, the numerical value is a property of the solvent alone and is independent of the solute, assuming a solute that is nonvolatile and a nonelectrolyte. Also assumed in the tables presenting k_b values is that the pressure is 1 atm (*standard pressure*).

EXAMPLE 2 The molal boiling-point constant for water is 0.512°C/*m*. If 1 mol cane sugar (342 g/mol) is dissolved in 1 kg water, the solution will boil at 100.512°C, assuming standard pressure. By this relationship, a half of a mole of sugar (171 g) would boil at 100.256°C/*m* and 2 mol sugar (684 g) should boil at 101.024°C/*m*. However, these are not necessarily solutions that can be mixed; 684 g of sugar is nearly a pound and a half of sugar, which you are supposed to dissolve in a liter of water!

Note: It would be a good idea to memorize constants relating to water. It is an extremely important compound on this planet, necessary for life, and a very commonly used solvent. Many professors will assume you know them during a test!

OSMOTIC PRESSURE

Imagine a container with a solution that is separated from its pure solvent by a membrane that allows the solvent to pass through, but not the solute. The membrane that allows specific things through, but not others, is a *semipermeable membrane*. Since substances *diffuse* (tend to move from higher concentration to lower concentration), the solvent will diffuse through the semipermeable membrane into the solution (*osmosis*). Let us carry the concept one step further.

Imagine the solvent being separated from the solution by a semipermeable membrane and there is a tube rising from the portion of the container containing the solution, as shown in Fig. 14-1. The solution will increase in volume due to the incoming solvent (and also become diluted by the solvent), forcing some of the solution up the open tube. At some point in time, the weight of the solution exerting a weight downward will become equal to the pressure forcing the solution upward (*osmotic pressure*) and equilibrium will have been reached, after which there will be no further rise in the height of the solution in the tube. The *osmotic pressure* (measurable pressure at this point in the process) can be measured in the usual units of pressure, such as Pa, atm, psi, or torr.

The osmotic pressure, π, of a dilute solution of a nonelectrolyte is given by an equation formally equivalent to the *ideal gas law*:

$$\pi = MRT$$

in which M is molarity and T is in the Kelvin scale. If $R = 0.0821\ \text{L} \cdot \text{atm/mol} \cdot \text{K}$, the value for π will be in atm and it may be expressed in other units of pressure, as can R by conversion from atm to the desired unit.

DEVIATIONS FROM THE LAWS OF DILUTE SOLUTIONS

All the laws discussed so far are valid for dilute solutions of nonelectrolytes. If there is a solute that is an electrolyte, the ions contribute independently to the effective molal (or molar) concentration. The ions interact and, therefore, the effects are not as large as predicted by the mathematical equations.

EXAMPLE 3 A solution containing 0.100 mol of KCl per kilogram of water freezes at −0.345°C. The freezing-point lowering is calculated using the number of independent particles. If KCl were to ionize completely the molality of particles

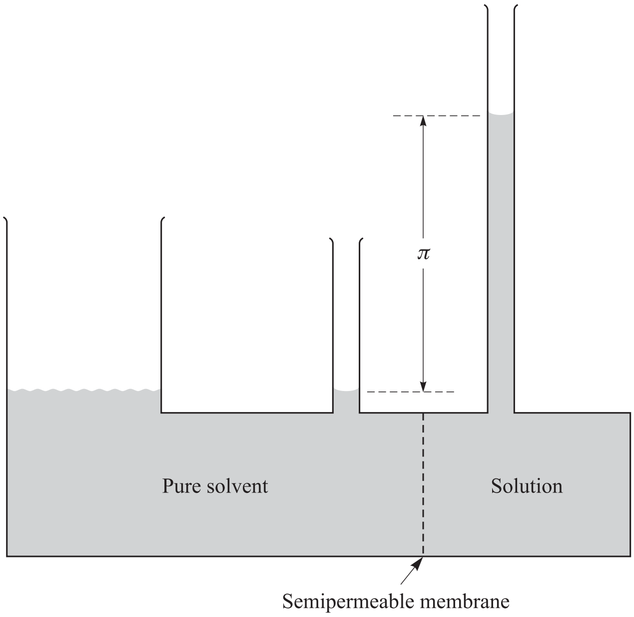


Fig. 14-1

would be 0.200 m, and the calculated freezing point would be lowered from 0°C by

$$\Delta T_f = k_f m = 1.86°\text{C}/m \times 0.200\,m = 0.372°\text{C}$$

providing us with the theoretical freezing point of -0.372°C. This difference in freezing point tells us that the ions do not act completely independently of each other. As a point, it is noted that a $0.100\,m$ $BaCl_2$ solution freezes at -0.470°C, but the predicted (Ba^{2+} and $2Cl^-$, 3 ions) should be ($3 \times 1.86 \times 0.1 = 0.558$°C) a freezing point of -0.558°C.

When discussing ΔT_f and ΔT_b, the theoretical number of ions can be indicated with i as follows:

$$\Delta T_f = ik_f m \qquad \text{and} \qquad \Delta T_b = ik_b m$$

and the value of i, although taken to be a whole number, it is actually not in many cases. The value of i for KCl in Example 3 is actually 1.85, not the 2 we get by assuming independent K^+ and Cl^- ions. In the case of $BaCl_2$, the actual value of i is 2.53, not 3.

For any dilute solution, whether electrolyte or nonelectrolyte, the deviations from any one of the laws of the dilute solution are equal to the deviations from any of the others on a fractional or percentage basis. That is,

$$\frac{\Delta T_f - (\Delta T_f)^\circ}{(\Delta T_f)^\circ} = \frac{\Delta T_b - (\Delta T_b)^\circ}{(\Delta T_b)^\circ} = \frac{\Delta P - (\Delta P)^\circ}{(\Delta P)^\circ} = \frac{\pi - \pi^\circ}{\pi^\circ}$$

in which symbols labeled with ° indicate values predicted by the laws of the dilute solution.

SOLUTIONS OF GASES IN LIQUIDS

Henry's law states that at constant temperature, the concentration of a slightly soluble gas in a liquid is directly proportional to the partial pressure of the gas in the space above the liquid. The concentration can be expressed in either mass or the number of moles of gas dissolved in a specific volume of liquid.

When a mixture of two gases is in contact with a solvent, the amount of each gas that is dissolved is the same as if it were present alone at a pressure equal to its own partial pressure in the gas mixture.

Henry's law applies only to dilute solutions at low pressures. If the gas involved dissolves very well in the solvent, the reason is most likely that the gas is reacting with the solvent. For example, CO_2 appears to dissolve rather well in water, but actually reacts to produce H_2CO_3. Solutions that behave in this manner do not follow Henry's law well at all.

LAW OF DISTRIBUTION

A solute distributes itself between two *immiscible* (substances that do not mix) solvents so that the ratio of its concentrations in dilute solutions in the two solvents is constant, regardless of the actual concentration in either solvent. The solvents will form layers, since they do not mix. In this situation, both concentrations are assumed to be on the same volumetric basis (e.g., mol/L).

EXAMPLE 4 For the distribution of iodine between ether and water at room temperature, the value of the constant is about 200. This means that

$$K = \frac{\text{concentration of iodine in ether}}{\text{concentration of iodine in water}} = 200$$

The value of this ratio of concentrations is called the *distribution ratio* or *distribution coefficient*. It is equal to the ratio of the solubilities (per unit volume) in the two solvents if saturated solutions in these solvents are dilute enough for the law of distribution to apply.

Solved Problems

FREEZING-POINT LOWERING

14.1. The freezing point of pure camphor is 178.4°C and its molal freezing-point constant, k_f, is $40.0°\text{C}/m$. Find the freezing point of a solution containing 1.50 g of a compound that has the molar mass (M) 125 g/mol dissolved in 35.0 g of camphor.

Since the solution for this problem calls for the calculation of ΔT, which is dependent on molal concentration, we must calculate the moles of solute.

$$m = \frac{\text{moles solute}}{\text{kg solvent}} = \frac{\text{g solute/M}}{\text{kg solvent}} = \frac{(1.50/125)\,\text{moles solute}}{(35/1000)\,\text{kg solvent}} = 0.343\,\text{mol/kg}$$

Then, we can calculate the freezing-point lowering by substitution.

$$\Delta T_f = k_f m \qquad \Delta T_f = (40.0°\text{C}/m)(0.343\,m) = 13.7°\text{C}$$

$$\text{Freezing point of solution} = (\text{freezing point of solvent}) - \Delta T_f = 178.4°\text{C} - 13.7°\text{C} = 164.7°\text{C}$$

The solution for the freezing-point lowering could be set up by substituting directly into the T equation after the expansion of m as:

$$\Delta T_f = k_f m = k_f \frac{\text{g solute/M}}{\text{kg solvent}} = \left(40.0\frac{°\text{C}\cdot\text{kg}}{\text{mol}}\right)\left(\frac{\frac{1.50\text{ g solute}}{125\text{g/mol}}}{0.0350\text{ kg solvent}}\right) = 13.7°\text{C}$$

14.2. A solution containing 4.50 g of a nonelectrolyte ($i = 1$) dissolved in 125 g of water freezes at −0.372°C. Calculate the molar mass, M, of the solute.

First compute the molality from the freezing-point equation.

$$T_f = k_f m \qquad 0.372°\text{C} = (1.86°\text{C}/m)m \qquad m = \frac{0.372°\text{C}}{1.86°\text{C}/m} = 0.200\,m$$

Then, from the definition of molality, compute the number of moles solute, n(solute), in the sample.

$$m = \frac{n(\text{solute})}{\text{kg solvent}} \qquad \text{by rearrangement} \qquad n(\text{solute}) = m \times \text{kg solvent}$$

$$n(\text{solute}) = (0.200\,\text{mol solute/kg solvent})(0.125\,\text{kg solvent}) = 0.0250\,\text{mol solute}$$

And since $\quad \text{mol solute} = \dfrac{\text{mass solute}}{\mathsf{M}} \quad \text{by rearrangement} \quad \mathsf{M} = \dfrac{\text{mass solute}}{\text{mol solute}}$

we solve for M: $\quad \mathsf{M} = \dfrac{4.50\,\text{g}}{0.0250\,\text{mol}} = 180\,\text{g/mol}$

BOILING-POINT ELEVATION

14.3. The molar mass of a nonvolatile solute is 58.0. Calculate the boiling point of a solution containing 24.0 g of the solute dissolved in 600 g water. The barometric pressure is such that pure water boils at 99.725°C. *Note*: i is expected to be 1, since there is no mention of disassociation.

$$\text{Molality} = \frac{n(\text{solute})}{\text{kg solvent}} = \frac{(24.0/58.0)\,\text{mol solute}}{0.600\,\text{kg solvent}} = 0.690\,m$$

$$\text{Elevation of boiling point} = \Delta T_b = k_b m = (0.512°\text{C}/m)(0.690\,m) = 0.353°\text{C}$$

$$\text{Boiling point of solution} = (\text{boiling point water}) + \Delta T_b = 99.725°\text{C} + 0.353°\text{C} = 100.079°\text{C}$$

14.4. A solution was produced by dissolving 3.75 g of a nonvolatile solute in 95 g of acetone. The boiling point of pure acetone was observed to be 55.95°C, while the boiling point of the solution was 56.50°C. If the k_b for acetone is 1.71°C/m, what is the approximate molar mass of the solute?

This problem is similar to Problem 14.2 except that the solvent is acetone, not water (disassociation does not occur in organic solvents; $i = 1$). Let us use the same technique as following Problem 14.2.

First compute the molality from the boiling-point equation.

$$T_b = k_b m \qquad (56.50 - 55.95)°\text{C} = (1.71°\text{C}/m)m \qquad m = \frac{0.55°\text{C}}{1.71°\text{C}/m} = 0.322\,m$$

Then, from the definition of molality, compute the number of moles solute, n(solute), in the sample.

$$m = \frac{n(\text{solute})}{\text{kg solvent}} \qquad \text{by rearrangement} \qquad n(\text{solute}) = m \times \text{kg solvent}$$

$$n(\text{solute}) = (0.322\,\text{mol solute/kg solvent})(0.095\,\text{kg solvent}) = 0.0306\,\text{mol solute}$$

And since $\quad \text{mol solute} = \dfrac{\text{mass solute}}{\mathsf{M}} \quad \text{by rearrangement} \quad \mathsf{M} = \dfrac{\text{mass solute}}{\text{mol solute}}$

we solve for M: $\quad \mathsf{M} = \dfrac{3.75\,\text{g}}{0.0306\,\text{mol}} = 123\,\text{g/mol}$

VAPOR PRESSURE

14.5. The vapor pressure of water at 28°C is 28.35 torr. What is the vapor pressure at 28°C of a solution containing 68 g cane sugar, $C_{12}H_{22}O_{11}$, in 1000 g of water?

$$\text{Moles of } C_{12}H_{22}O_{11} = \frac{68\,\text{g}}{342\,\text{g/mol}} = 0.20\,\text{mol cane sugar}$$

$$\text{Moles of } H_2O = \frac{1000\,\text{g}}{18.02\,\text{g/mol}} = 55.49\,\text{mol water}$$

$$\text{Total number of moles} = 0.20 + 55.49 = 55.69\,\text{mol}$$

$$\text{Mole fraction } C_{12}H_{22}O_{11} = \frac{0.20}{55.69} = 0.0036 \qquad \text{Mole fraction } H_2O = \frac{55.49}{55.69} = 0.9964$$

First Method

$$\text{Vapor pressure of solution} = \Delta P = (\text{v.p. solvent}) \times (\text{mole fraction solvent})$$
$$= \Delta P = (28.35\,\text{torr})(0.9964) = 28.25\,\text{torr}$$

Second Method

$$\text{Vapor pressure depression} = \Delta P = (\text{v.p. solvent}) \times (\text{mole fraction solute})$$
$$= \Delta P = (28.35\,\text{torr})(0.0036) = 0.10\,\text{torr}$$
$$\text{Vapor pressure of solution} = \Delta P = (28.35 - 0.10)\,\text{torr} = 28.25\,\text{torr}$$

14.6. At 30°C, benzene ($\mathsf{M} = 78.1$) has a vapor pressure of 121.8 torr. Dissolving 15.0 g of a nonvolatile solute in 250 g of benzene produced a solution with a vapor pressure of 120.2 torr. Determine the approximate molar mass of the solute.

$$\text{Moles of benzene} = \frac{\text{g benzene}}{\mathsf{M}} = \frac{250\,\text{g}}{78.1\,\text{g/mol}} = 3.20\ \text{mol benzene}$$
$$\text{Moles of solute} = \frac{15.0\,\text{g}}{\mathsf{M}}$$

Substituting in the relation v.p. solution = (v.p. pure solvent) × (mole fraction solvent),

$$120.2\,\text{torr} = (121.8\,\text{torr})\left[\frac{3.20\,\text{mol}}{(15.0/\mathsf{M})\,\text{mol} + 3.20\,\text{mol}}\right] \qquad \text{or} \qquad 120.2 = (121.8\,\text{torr})\left(\frac{3.20\,\mathsf{M}}{15.0 + 3.20\,\mathsf{M}}\right)$$

Solving for M, we find the mass to be 350 g/mol. Note that the accuracy of the calculation is limited by the term $121.8 - 120.2$ that appears in the expansion. The answer is significant to only 1 part in 16.

14.7. At 20°C the vapor pressure of methanol (CH_3OH) is 94 torr and the vapor pressure of ethanol (C_2H_5OH) is 44 torr. Being closely related, these two alcohols form a two-component system which behaves pretty much as Raoult's law predicts throughout the entire range of concentrations. A solution produced from 20 g CH_3OH is mixed with 100 g C_2H_5OH. (*a*) Determine the partial pressure of each of the alcohols and the total vapor pressure of the solution. (*b*) Calculate the composition of the vapor above the solution by applying Dalton's law (Chapter 5).

(*a*) In an ideal solution of two liquids, there is no distinction between solute and solvent. Raoult's law holds for each of the components of ideal solutions. When two liquids are mixed to produce an ideal solution, the partial pressure of each liquid is equal to its partial pressure exerted by the pure substance multiplied by its mole fraction in solution. The molar mass of CH_3OH is 32 and that of C_2H_5OH is 46.

$$\text{Partial pressure } CH_3OH = (94\,\text{torr})\left(\frac{\frac{20}{32}\text{mol } CH_3OH}{\frac{20}{32}\text{mol } CH_3OH + \frac{100}{46}\text{mol } C_2H_5OH}\right)$$
$$= (94\,\text{torr})(0.22) = 21\,\text{torr}$$

$$\text{Partial pressure } C_2H_5OH = (44\,\text{torr})\left(\frac{\frac{100}{46}\text{mol } C_2H_5OH}{\frac{20}{32}\text{mol } CH_3OH + \frac{100}{46}\text{ mol } C_2H_5OH}\right)$$
$$= (44\,\text{torr})(0.78) = 34\,\text{torr}$$

The total pressure of the gaseous mixture is the sum of the partial pressures of all the components (Dalton's law). The total pressure is 55 torr (21 + 34).

(*b*) Dalton's law indicates that the mole fraction of any component of a gaseous mixture is equal to its pressure fraction, i.e., its partial pressure divided by the total pressure.

$$\text{Mole fraction of } CH_3OH = \frac{\text{partial pressure } CH_3OH}{\text{total pressure}} = \frac{21\,\text{torr}}{55\,\text{torr}} = 0.38$$

$$\text{Mole fraction } C_2H_5OH = \frac{\text{partial pressure } C_2H_5OH}{\text{total pressure}} = \frac{34\,\text{torr}}{55\,\text{torr}} = 0.62$$

Since the mole fraction of (ideal) gases is the same as the volume fraction, we may also say that the vapor consists of 38% CH_3OH by volume. Note that the vapor is relatively richer in the more volatile component, methyl alcohol (mole fraction 0.38), than is the liquid (mole fraction 0.22).

OSMOTIC PRESSURE

14.8. What would be the osmotic pressure at 17°C of an aqueous solution containing 1.75 g of sucrose ($C_{12}H_{22}O_{11}$, also called cane sugar) per 150 mL of solution?

$$\text{Molar concentration} = \text{M} = \frac{\text{moles solute}}{\text{liter solution}} = \frac{175\,\text{g}/342\,\text{g/mol}}{0.150\,\text{L}} = 0.0341\,\text{mol/L}$$

$$\text{Osmotic pressure} = \pi = MRT = \left(0.0341\,\frac{\text{mol}}{\text{L}}\right)\left(\frac{0.0821\,\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(290\,\text{K}) = 0.812\,\text{atm}$$

14.9. The osmotic pressure of a solution of a synthetic polyisobutylene in benzene was determined at 25°C. A sample containing 0.20 g of solute per 100 mL of solution developed a rise of 2.4 mm at osmotic equilibrium. The density of the solution was 0.88 g/mL. What is the molar mass of the polyisobutylene?

The osmotic pressure is equal to that of a column of the solution 2.4 mm high. By the formula in Chapter 5,

$$\pi = \text{height} \times \text{density} \times g = (2.4 \times 10^{-3}\,\text{m})(0.88 \times 10^{3}\,\text{kg/m}^3)(9.81\,\text{m/s}^2) = 20.7\,\text{Pa}$$

The molar concentration can now be determined from the osmotic pressure equation.

$$M = \frac{\pi}{RT} = \frac{20.7\,\text{N/m}^2}{(8.3145\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298\,\text{K})} = 8.3 \times 10^{-3}\,\text{mol/m}^3 = 8.3 \times 10^{-6}\,\text{mol/L}$$

The solution contained 0.20 g solute per 100 mL solution, or 2.0 g/L, and has been found to contain 8.3×10^{-6} mol/L. Then,

$$\text{Molar mass} = \frac{2.0\,\text{g}}{8.3 \times 10^{-6}\,\text{mol}} = 2.4 \times 10^{5}\,\text{g/mol}$$

14.10. An aqueous solution of urea had a freezing point of −0.52°C. Predict the osmotic pressure of the same solution at 37°C. Assume that the molar concentration and molality are numerically equal.

We can determine the molality by looking at the freezing-point lowering, 0.52°C.

$$m = \frac{\Delta T_f}{k_f} = \frac{0.52°\text{C}}{1.86°\text{C}/m} = 0.280\,m$$

The assumption that the molality and molarity are equal does not introduce serious error into the calculations for dilute aqueous solutions. The relationships discussed in Chapter 12 show that $M \approx m$ when the density is 1 g/mL (1 g/cm^3) and $\mathsf{M} < 1000/m$. Urea has a molar mass of 60.0 g/mol. Then, 0.280 mol/L may be used for the molarity in the osmotic pressure equation.

$$\pi = MRT = \left(0.280\,\frac{\text{mol}}{\text{L}}\right)\left(0.0821\frac{\text{L}\cdot\text{atm}}{\text{mol}}\cdot\text{K}\right)(310\,\text{K}) = 7.1\,\text{atm}$$

SOLUTIONS OF GASES IN LIQUIDS

14.11. At 20°C and a total pressure of 760 torr, 1 L of water dissolves 0.043 g pure oxygen or 0.019 g pure nitrogen. Assuming that dry air is composed of 20% oxygen and 80% nitrogen, both by volume, determine the mass of oxygen and nitrogen dissolved by 1 L of water at 20° C and exposed to air at a total pressure of 760 torr.

The *solubility* of a gas (i.e., the concentration of dissolved gas) may be expressed as

$$\text{Solubility of Y} = k_{\text{H}}(\text{Y}) \times P(\text{Y})$$

This tells us that the solubility of a gas dissolved from a gaseous mixture (air in this problem) is directly proportional to the partial pressure of the gas. The proportionality constant, k_{H}, is called *Henry's law constant*. (*Note*: Some authors define the Henry's law constant as the reciprocal of the k_{H} used here.) To evaluate k_{H} from the data, note that when pure oxygen is in equilibrium with water at a total pressure of 760 torr,

$$P(\text{O}_2) = (760\,\text{torr}) - (\text{vapor pressure of water})$$

Then, allowing v.p. to be the vapor pressure of water, from the data,

$$k_{\text{H}}(\text{O}_2) = \frac{\text{solubility of O}_2}{P(\text{O}_2)} = \frac{0.043\,\text{g/L}}{760\,\text{torr} - \text{v.p.}}$$
$$k_{\text{H}}(\text{N}_2) = \frac{\text{solubility of N}_2}{P(\text{N}_2)} = \frac{0.019\,\text{g/L}}{760\,\text{torr} - \text{v.p.}}$$

When water is exposed to air at a total pressure of 760 torr,

$$P(\text{O}_2) = (0.20)(760 - \text{v.p.}) \qquad \text{and} \qquad P(\text{N}_2) = (0.80)(760\,\text{torr} - \text{v.p.})$$

Therefore,

$$\text{Solubility} = k_{\text{H}}(\text{O}_2) \times \text{P}(\text{O}_2) = \left(\frac{0.043\,\text{g/L}}{760\,\text{torr} - \text{v.p.}}\right)(0.20)(760\,\text{torr} - \text{v.p.}) = 0.0086\,\text{g/L}$$

Using the same technique, the solubility of N_2 from air is (0.80)(0.019 g/L) = 0.015 g/L

14.12. A gaseous mixture of H_2 and O_2 contains 70% H_2 and 30% O_2 by volume. If the gas mixture is at 2.5 atm (excluding the vapor pressure of water) and is allowed to saturate water at 20°C, the water is found to contain 31.5 cm^3 (S.T.P.) of H_2/L. Find the solubility of H_2 (reduced to S.T.P.) at 20°C and 1 atm partial pressure H_2.

Since the volume of a gas at S.T.P. is proportional to its mass, the volume of the dissolved gas (reduced to S.T.P.) is proportional to the partial pressure of that gas.

$$\text{Partial pressure of H}_2 = (0.70)(2.5\,\text{atm}) = 1.75\,\text{atm}$$
$$\text{Solubility of H}_2 \text{ at } 20^\circ\text{C and 1 atm} = \frac{1.00\,\text{atm}}{1.75\,\text{atm}}(31.5\,\text{cm}^3/\text{L}) = 18.0\ \text{cm}^3(\text{S.T.P.})/\text{L}$$

LAW OF DISTRIBUTION: EXTRACTION

14.13. A 25-mL sample of an aqueous solution containing 2 mg iodine is shaken with 5 mL of CCl_4, then is allowed to separate (CCl_4 and water do not mix). The solubility of iodine per unit volume is 85 times greater in CCl_4 than in water at the temperature of the experiment and both saturated solutions may be considered to be "dilute." (*a*) Calculate the quantity of iodine remaining in the water layer. (*b*) If a second extraction is made of the water layer using another 5 mL of CCl_4, calculate the quantity of iodine remaining after this extraction.

(*a*) We can let $w =$ mg of iodine in the water layer at equilibrium
which provides us with $2 - w =$ mg of iodine in the CCl_4 layer at equilibrium

The concentration of iodine in the water will be w mg iodine/25 mL water. The concentration of iodine in the CCl_4 layer will be $(2 - w)/5$ (mg per mL CCl_4). The relationship becomes

$$\frac{\text{conc. } I_2 \text{ in } CCl_4}{\text{conc. } I_2 \text{ in } H_2O} = \frac{85}{1} \quad \text{or} \quad \frac{(2-w)/5}{w/25} = \frac{85}{1} \quad \text{or} \quad \frac{2-w}{w} = 17$$

$$w = 0.11 \text{ mg iodine remaining}$$

Note: Although this problem is given to us and worked in mg/mL, any volumetric concentration units could have been used in this problem, so long as the same units are used throughout because the conversion factors cancel.

(*b*) Let $y =$ mg of iodine in the water layer after second extraction
which provides us with $0.11 - y =$ mg of iodine in the CCl_4 layer after second extraction

The concentration of iodine in the water layer will be $y/25$ and the concentration in the CCl_4 layer will be $(0.11 - y)/5$. This second relationship becomes

$$\frac{\text{conc. } I_2 \text{ in } CCl_4}{\text{conc. } I_2 \text{ in } H_2O} = \frac{85}{1} \quad \text{or} \quad \frac{(0.11-y)/5}{y/25} = \frac{85}{1} \quad \text{or} \quad \frac{0.11-y}{y} = 17$$

$$w = 0.0061 \text{ mg iodine remaining after second extraction}$$

Supplementary Problems

FREEZING-POINT LOWERING AND BOILING-POINT ELEVATION

14.14. A solution containing 6.35 g of a nonelectrolyte dissolved in 500 g of water freezes at −0.465°C. Determine the molar mass of the solute.

Ans. 50.8 g/mol

14.15. A solution containing 3.24 g of a nonvolatile nonelectrolyte and 200 g of water boils at 100.130°C at 1 atm. What is the molar mass of the solute?

Ans. 63.9 g/mol

14.16. Calculate the freezing point and the boiling point at 1 atm of a solution containing 30.0 g cane sugar (molar mass 342) and 150 g water.

Ans. −1.09°C; 100.300°C

14.17. Suppose you were asked to make up a 1.000 *m* solution of cane sugar, $C_{12}H_{22}O_{11}$, using a kilogram of water. (*a*) What is the calculated freezing point of the solution? (*b*) Is this a practical solution to produce?

Ans. (*a*) −1.86°C; (*b*) No, this solution would require 342 g sugar ($\pm\frac{3}{4}$ lb) to be dissolved in ±1 L of water, which is not likely to occur anywhere near the freezing point of water.

14.18. A solution of gold(III) nitrate is to be used in electroplating; it has been produced by dissolving 12.75 g $Au(NO_3)_3$ in 500 mL H_2O (density 1.000). What are the expected freezing point and boiling point?

Ans. Assuming that $i = 4$ (1 gold and 3 nitrate ions), a freezing point of −0.495°C and boiling point of 100.14° C are expected.

14.19. If glycerin, $C_3H_5(OH)_3$, and methanol, CH_3OH, sold at the same price per pound, which would be cheaper for preparing an antifreeze solution for the radiator of an automobile?

Ans. Methanol (methyl alcohol). Since the molecular mass of methanol is much less than that of glycerin, a pound of methanol contains more molecules than a pound of glycerin. The amount of freezing-point depression is dependent on the number of particles (molecules here) in solution. This argument requires that the two substances be soluble in water, the other component in antifreeze.

14.20. How much ethanol, C_2H_5OH, must be added to 1 L of water so that the solution will not freeze above −4°F?

Ans. 495 g ethanol (ethyl alcohol)

14.21. A white powder is suspected of containing thallium(I) nitrate (molecular weight $=$ 266). The freezing point of a solution (0.75 g powder dissolved in 50 g H_2O) was −0.13°C. Assuming complete dissociation, could it be $TlNO_3$?

Ans. No, the freezing point should have been −0.21°C.

14.22. What is the molecular mass of the white powder described in Problem 14.21?

Ans. 215 g/mol

14.23. A chemist must determine the molar mass of an unknown compound using a solvent that had a freezing point of 30.16°C. A solution of 0.617 g paradichlorobenzene, $C_6H_4Cl_2$, in 10.00 g of solvent had a freezing point of 27.81°C, while 0.526 g of the unknown in 10.00 g of solvent lowered its freezing point to 26.47°C. Calculate the molar mass of the unknown.

Ans. 79.8 g/mol

14.24. Ethanol can be used for the short-term preservation of tissue. Calculate the freezing point of a solution mixed if you were to dissolve 0.500 g of a nonvolatile triose, $C_3H_6O_3$, in 25 g ethanol (C_2H_5OH, freezing point pure $= -114.6$°C, $k_f = 1.99$°C/m).

Ans. −115.0°C

14.25. What is the freezing point of a 10% (by weight) solution of CH_3OH in water?

Ans. −6.5°C

14.26. A solution contains 10.6 g of a nonvolatile substance dissolved in 740 g of ether. The boiling point of the solution is 0.284°C over the boiling point of pure ether. Molal boiling-point constant for ether is 2.11°C · kg/mol. What is the molar mass of the substance?

Ans. 106 g/mol

14.27. The freezing point of a sample of naphthalene was found to be 80.6°C. When 0.512 g of a substance were dissolved in 7.03 g naphthalene, the solution's freezing point was 75.2°C. What is the molar mass of the solute? (Molal freezing-point constant for naphthalene is 6.80°C · kg/mol.)

Ans. 92 g/mol

14.28. Pure benzene freezes at 5.45°C. A solution containing 7.24 g $C_2Cl_4H_2$ in 115.3 g benzene was observed to freeze at 3.55°C. From these data, calculate the molal freezing-point constant for benzene.

Ans. 5.08°C · kg/mol

14.29. What is the osmotic pressure at 0°C of an aqueous solution containing 46.0 grams of glycerin ($C_3H_5(OH)_3$, per liter?

Ans. 11.2 atm

14.30. An organic compound is known to be nonvolatile and a nonelectrolyte. A 0.35-g sample is dissolved in water and diluted to 150 mL. The osmotic pressure is measured as 0.04 atm at 25°C. What is the approximate mass number for this compound?

Ans. Approximately 1400 g/mol

14.31. From the data provided in Problem 14.30 and knowing that the density of the solution is 1.00 g/mL, (*a*) calculate the freezing point of the solution, and (*b*) determine if the freezing-point change would be a good way to determine the molecular mass of the compound. (*c*) Would the boiling-point change be a better determining factor than the freezing-point change?

Ans. (*a*) 0.0031°C; (*b*) The slight change in freezing point would be difficult to measure, making the freezing-point change not suitable for this determination. (*c*) The boiling-point change is only 0.00087°C and, therefore, even harder to measure with accuracy.

14.32. Salt is often used to melt ice and snow on roads in the winter and the temperature right now is −4.500°C. How much NaCl (complete dissociation) would be necessary to melt 1000 kg of ice by bringing down the freezing temperature to −4.500°C?

Ans. 70.7 kg

VAPOR PRESSURE AND OSMOTIC PRESSURE

14.33. A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.750 g in 125 mL of an aqueous medium. An osmotic pressure rise of 2.6 mm of the solution was detected at 4° C. The solution had a density of 1.00 g/mL. Determine the molar mass of the protein.

Ans. 5.4×10^5 g/mol (*Note:* Hemocyanin is to crabs as hemoglobin is to humans.)

14.34. The osmotic pressure of blood is 7.65 atm at 37°C. How much glucose, $C_6H_{12}O_6$, should be used per liter for an intravenous injection to have the same osmotic pressure as blood?

Ans. 54.2 g/L

14.35. The vapor pressure of water at 26°C is 25.21 torr. What is the vapor pressure of a solution that contains 20.0 g glucose in 70 g water?

Ans. 24.51 torr

14.36. The vapor pressure of water at 25°C is 23.76 torr. The vapor pressure of a solution containing 5.40 g of a nonvolatile substance in 90 g water is 23.32 torr. What is the molar mass of the solute?

Ans. 57 g/mol

14.37. Ethylene bromide, $C_2H_4Br_2$, and 1,2-dibromopropane, $C_3H_6Br_2$, form ideal solutions over the entire range of composition. At 85°C the vapor pressures of the pure liquids are 173 torr and 127 torr, respectively. (*a*) Calculate the partial pressure of each component and the total pressure of the solution at 85°C if 10.0 g of ethylene bromide are dissolved in 80.0 g of 1,2-dibromopropane. (*b*) Calculate the mole fraction of ethylene bromide in the vapor in equilibrium with the above solution. (*c*) What would be the mole fraction of ethylene bromide in a solution at 85°C of a 50:50 mole mixture in the vapor?

Ans. (*a*) ethylene bromide, 20.5 torr; 1,2-dibromopropane, 112 torr; total, 132 torr; (*b*) 0.155; (*c*) 0.42

14.38. At 25°C, ethanol (C_2H_5OH) has a vapor pressure of 63 mm Hg, while 2-propanol's (C_3H_7OH) vapor pressure is 45 mm Hg. What is the vapor pressure of a solution composed of 12 g ethanol and 27 g 2-propanol?

Ans. 53 mm Hg (53 torr)

14.39. An organic compound was found by combustion analysis to contain 38.7% C, 9.7% H, and the remainder oxygen. In order to determine its molecular formula, a 1.00 g sample was added to 10.00 g of water. The freezing point of the solution was found to be −2.94°C. What is the compound's molecular formula?

Ans. $C_2H_6O_2$

14.40. (*a*) A 0.100 molal solution of $NaClO_3$ freezes at −0.3433°C. What would you predict for the boiling point of this aqueous solution at 1 atm? (*b*) At 0.001 molal concentration of this same salt, the electrical interferences between the ions no longer exist because the ions are, on the average, too far apart from each other for interaction. Predict the freezing point of the more dilute solution.

Ans. (*a*) 100.095°C; (*b*) −0.0037°C

14.41. The molar mass of a newly synthesized organic compound was determined by the *isothermal distillation* method. In this procedure two solutions, each in an open calibrated vial, are placed side by side in a closed chamber. One of the solutions contained 9.3 mg of the new compound, the other 13.2 mg of azobenzene (molar mass 182). Both were dissolved in portions of the same solvent. The experiment was untouched for three days, during which solvent distilled from one vial into the other until the same partial pressure of solvent was reached in both vials. After this, there was no further net distillation of solvent. Neither of the solutes distilled at all. The solution containing the new compound occupied 1.72 mL and the azobenzene solution occupied 1.02 mL. What is the molar mass of the new compound? The mass of solvent in solution may be assumed to be proportional to the volume of the solution.

Ans. 76 g/mol

14.42. Calculate the freezing point of a solution of 3.46 g of a compound, X, in 160 g of benzene, C_6H_6. When another sample of X was vaporized, its density was found to be 3.27 g/L at 116°C and 773 torr. The freezing point of benzene is 5.45°C and k_f is 5.12°C kg/mol.

Ans. 4.37°C

14.43. In a particular chemical process, it is necessary to monitor a stream of benzene, C_6H_6, which may be contaminated with toluene, C_7H_8. How finely calibrated should the thermometer scale be to detect 0.10% by weight of toluene in the benzene by measuring its freezing point? (Refer to Problem 14.42.)

Ans. The freezing point is lowered to 0.056°C. You would need calibrations every 0.1°C at least; 0.01°C would be better. Such thermometers are not uncommon.

14.44. An alternative to the method of Problem 14.43 might be to measure the vapor pressure of the benzene stream at 25°C. Compare the two methods. Benzene and toluene form ideal solutions. The vapor pressure at 25°C is approximately 95 torr for benzene and 30 torr for toluene.

Ans. The lowering of the total vapor pressure of the liquid by the addition of 0.10% toluene is about 0.06 torr (0.06 mm Hg). Such an observation would require a microscope to read! Worse yet, since the vapor pressure of benzene increases about 3 torr/°C, it would be extremely difficult to control the sample temperature adequately to avoid error (better than within 0.01°C).

14.45. A method of producing drinkable water from salt water is reverse osmosis, in which a pressure just in excess of the osmotic pressure is applied to the solution in order to reverse the flow of the solvent (H_2O). In principle, what pressure would be required to produce pure water from sea water at 25°C? Assume that sea water has a density of 1.021 g/mL and can be considered equivalent to 3.00% by weight NaCl, which is 100% ionized. Express your answer in atm, kPa, and psi.

Ans. 25.6 atm; 2.59×10^3 kPa; 376 psi

SOLUTIONS OF CASES IN LIQUIDS

14.46. At 20°C and 1.00 atm partial pressure of hydrogen, 18 cm^3 H_2 (measured at S.T.P.) dissolve in 1 L of water. If water at 20°C is exposed to a gaseous mixture having a total pressure of 1400 torr (dry air) and containing 68.5% H_2 by volume, what volume of H_2 (at S.T.P.) which will dissolve in 1 L water.

Ans. 23 cm^3

14.47. A liter of CO_2 gas at 15°C and 1.00 atm dissolves in a liter of water also at 15°C when the pressure of the CO_2 is 1 atm. Calculate the molar concentration of CO_2 in solution over which the partial pressure of CO_2 is 150 torr, also at 15°C.

Ans. 0.0083 M

14.48. (*a*) The solubility of iodine per unit volume is 200 times greater in ether than in water at a particular temperature. If an aqueous solution of iodine, 30 mL in volume and containing 2.0 mg of iodine, is shaken with 30 mL of ether and the ether is allowed to separate, what quantity of iodine remains in the water layer? (*b*) What quantity of iodine remains in the water layer if only 3 mL of ether are used? (*c*) How much iodine is left in the water layer if the extraction in (*b*) is followed by a second extraction, again using 3 mL of ether? (*d*) Which method is more efficient, a single large washing or repeated small washings?

Ans. (*a*) 0.010 mg; (*b*) 0.095 mg; (*c*) 0.0045 mg; (*d*) repeated small washings

14.49. The ratio of solubility of stearic acid per unit volume of *n*-heptane to that in 97.5% acetic acid is 4.95. How many extractions of a 10-mL solution of stearic acid in 97.5% acetic acid with successive 10-mL portions of *n*-heptane are needed to reduce the residual stearic acid content of the acetic acid layer to less than 0.5% of its original value?

Ans. 3 portions

LAW OF DISTRIBUTION: EXTRACTION

14.50. Penicillin can be purified by extraction. The distribution coefficient for penicillin G between isopropyl ether and an aqueous phosphate medium is 0.34 (lower solubility in ether). The corresponding ratio for penicillin F is 0.68. A preparation of penicillin G has penicillin F as a 10.0% impurity. (*a*) If an aqueous phosphate solution of this mixture is extracted with an equal volume of isopropyl ether, what will be the % recovery of the initial G in the residual aqueous-phase product after one extraction? What will be the % impurity of this product? (*b*) Calculate the same two quantities for the product remaining in the aqueous phase after a second extraction with an equal volume of ether.

Ans. (*a*) 75% recovery and 8.1% impurity; (*b*) 56% recovery and 6.6% impurity

CHAPTER 15

Organic Chemistry and Biochemistry

INTRODUCTION

Most carbon compounds are called *organic* compounds while others are called *inorganic* compounds. The historic reason for the name was the mistaken idea that living matter, organic matter, was chemically different from nonliving matter (inorganic matter). We now know that organic compounds, the vast majority of all compounds, can be synthesized not only by the natural processes of living organisms, but also in the laboratory without the help of living things.

The principles of chemistry presented in this text apply equally to inorganic chemistry (general chemistry), organic chemistry, and biochemistry. This chapter has been included because of the needs of those students who are headed toward the biologically oriented fields of study and the increasing incidences of organic examples included in inorganic texts (those for General Chemistry). Also, many academicians consider organic processes to be different, which they really aren't! We will briefly cover a selection of the more important chemical reactions, special nomenclature (naming and/or identification) of isomerism, attention to the details of isomerism, and some examples from biochemistry.

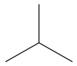
NOMENCLATURE

Carbon atoms are capable of forming strong bonds with each other, which leads to many organic compounds typically having a large number of atoms per molecule with a variety of ways the atoms can connect. The naming system for organic compounds must indicate the number of carbon atoms and the pattern of the atoms' connections. *Hydrocarbons* are the compounds that are composed of only hydrogen and carbon. If there are no multiple bonds, these are called *alkanes*, and if there are no ring structures, they have the empirical formula C_nH_{2n+2} in order to satisfy the rules for bonding as in Chapter 9. The name of an organic compound generally provides the number of carbon atoms. The root of the name indicates the number of carbons—*meth* meaning one, *eth* for two, *prop* for three, *but* for four, *pent* for five, *hex* for six, etc. The number of atoms of other elements is often implied. For instance, in cyclic compounds each ring of carbon atoms reduces the number of hydrogens by 2; each double bond (*alkenes* or *olefins*) also reduces hydrogens by 2; and each triple bond (*alkyne*) reduces hydrogens by 4.

In older, less systematic nomenclature, the root counted all the carbons. As an example, "butane" meant C_4H_{10}, with the suffix (word ending) *ane* indicating an alkane. However, there is more than one structure with

C_4H_{10}, which is really a simple count of atoms. There could be the straight chain of carbon or there could be a chain of three carbons with one branching off the center carbon as shown.

Butane

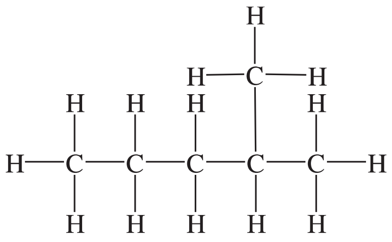


iso-Butane

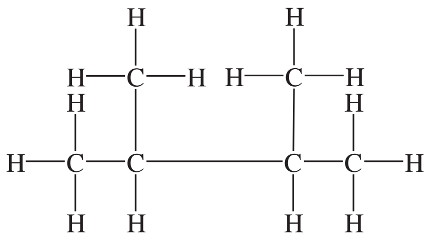
This style of sketching assumes carbon atoms at each end of line and at each intersection of lines. Also, the hydrogens are left out with sufficient hydrogens assumed to complete the four bonds to each carbon. Note that *iso* is added to "butane" to indicate a branched structure. This system will not work if there are more than four carbons because there are too many possible isomers to allow for convenient naming.

The International Union of Pure and Applied Chemistry (IUPAC) adopted a system that is clear. For noncyclic alkanes, the root gives the number of carbons in the longest chain. Each branch is described by a prefix indicating the number of carbons in the branch, and a number indicating the point of connection to the longest chain. (Numbering starts at the end of the chain which produces the smallest numerals.) The IUPAC names for the structures above are "butane" and "2-methyl propane."

EXAMPLE 1 Before the IUPAC rules were developed, "hexane" would have been the name of both compounds. Note the IUPAC names for these structures:



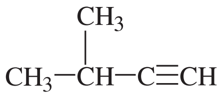
2-Methylpentane



2,3-Dimethylbutane

The naming system is extended to include alkenes by changing the suffix from -ane to -ene, and to alkynes by the suffix -yne. A number before the suffix gives the location of the multiple bond. The terminal carbon is that closest to the multiple bond; it has priority over branching of the carbon skeleton.

EXAMPLE 2 Provide the IUPAC names for these hydrocarbons. (Notice that this is another style of sketching that is a type of shorthand for the locations of the hydrogens.)



$$CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}C{\equiv}CH$$

3-Methyl-1-butyne

$H_2C{=}CH{-}CH{=}CH_2$

Buta-1,3-diene

The prefix cyclo- appears before the root of the name in ring compounds, except for those involving the benzene ring (Problem 9.9). The benzene compounds form a special category of compounds referred to as *aromatic* compounds. The opposite of *aromatic* is *aliphatic*. Further modifications of the system, such as those when elements other than carbon and hydrogen are involved, will be noted when *functional groups* are discussed.

ISOMERISM

In keeping with the principles and definitions in Chapter 9, isomers are compounds with the same number of atoms of each kind per molecule, but they are different substances because of differences in molecular structure. There are three classes of isomers: *structural*, *geometric*, and *optical*.

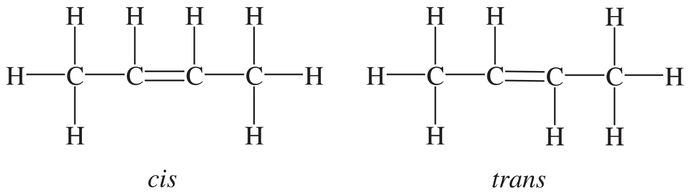
Structural isomerism is when the molecules differ in the sequence of atomic attachments in the skeleton of the molecule. The compounds in Example 1 are structural isomers. The IUPAC names clearly state the difference between compounds with the same molecular formula, but different structures.

Geometric isomerism occurs when the three-dimensional shape of the molecules differs. This occurs when a significant part of the molecule is rigidly fixed because of the presence of a double bond or a ring. In simple cases, geometrical isomers can be distinguished by their names containing *cis-* or *trans-* according to whether two groups are on the same side (close) of the double bond or on opposite sides (far apart).

Optical isomerism is when two molecules are nonsuperimposable mirror images of each other (Think of a pair of gloves. They can only stack palm to palm, not one on top of the other.) Such molecules are termed *asymmetric* or *chiral*. (*Note*: Chiral carbons have 4 different substituents.) Two optical isomers can be distinguished in their names by the prefixes *dextro-* or *levo-* according to whether a solution of the compound rotates a beam of polarized light to the right or the left. The abbreviations D- and L- are commonly used for dextro- and levo-. A new system of naming uses *R*- (rectus) and *S*- (sinister).

EXAMPLE 3 Draw the geometric isomers of 2-butene. (*b*) Draw the optical isomers of 1-bromo-1-chloroethane.

(*a*) Because of the double bond, all atoms except the six end-hydrogens are found only in one plane, which we chose as the plane of the paper.



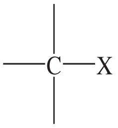
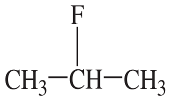
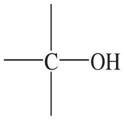
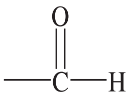
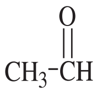
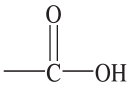
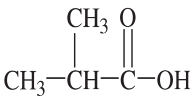
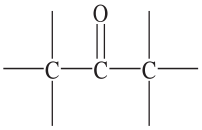
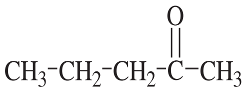
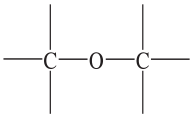
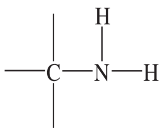
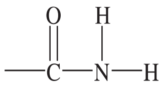
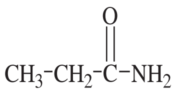
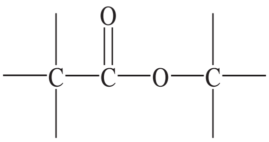
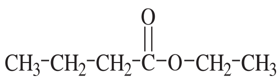
(*b*) If both carbons and the bromine are placed in the plane of the paper, the chorine and hydrogen atoms are on opposite sides of the plane with their bonds to carbon forming approximately 109° angles to the other bonds of that carbon atom. Relative to the plane of the paper, chlorine is shown toward you and the hydrogen away from you.

FUNCTIONAL GROUPS

Alkanes are somewhat nonreactive and their chemistry is not very interesting. But if a multiple bond is formed on the loss of hydrogens or an atom is substituted for a hydrogen, characteristic properties and reactions result. These properties do not depend on the number or arrangement of carbon atoms in the rest of the molecule. A group of atoms that determines these properties of the compound is called a *functional group*. Learning the properties and reactions of the functional groups simplifies the study of organic chemistry. Table 15-1 lists some of the common functional groups. In the case of acids, *acid* is added in addition to the suffix *-oic*. The word *ether* appears separate from the rest of the name, and esters have a two-part name indicating the structures of the two parts of the molecule joined by the ester group.

Aldehydes, acids, and esters have roots for one and two carbons that are usually *form-* and *acet-*, rather than *meth-* and *eth-*, because these prefixes had been used so long they were grandfathered into the naming system (formaldehyde and acetic acid, rather than methanal and ethanoic acid). Departures from IUPAC nomenclature often occur for very common substances and, fortunately, they rarely can be misunderstood (ethyl alcohol instead of ethanol).

Table 15-1

Structure	Group Name	Example	Name of Example
$-C{=}C-$	Alkene, double bond	$CH_3-CH{=}CH-CH_3$	2-Butene
$-C{\equiv}C-$	Alkyne, triple bond	$CH_3-C{\equiv}CH$	1-Propyne
 $-\underset{\mid}{\overset{\mid}{C}}-X$ (X = F, Cl, Br, I)	Halide	 $CH_3-\overset{F}{\overset{\mid}{C}H}-CH_3$	2-Fluoropropane
 $-\underset{\mid}{\overset{\mid}{C}}-OH$	Alcohol (hydroxyl)	CH_3-OH	Methanol (Methyl alcohol)
 $-\overset{O}{\overset{\Vert}{C}}-H$	Aldehyde	 $CH_3-\overset{O}{\overset{\Vert}{C}}H$	Ethanal (Acetaldehyde)
 $-\overset{O}{\overset{\Vert}{C}}-OH$	Carboxylic acid	 $CH_3-\overset{CH_3}{\overset{\mid}{C}H}-\overset{O}{\overset{\Vert}{C}}-OH$	2-Methylpropanoic acid
 $-\underset{\mid}{\overset{\mid}{C}}-\overset{O}{\overset{\Vert}{C}}-\underset{\mid}{\overset{\mid}{C}}-$	Ketone	 $CH_3-CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-CH_3$	2-Pentanone
 $-\underset{\mid}{\overset{\mid}{C}}-O-\underset{\mid}{\overset{\mid}{C}}-$	Ether	$CH_3-O-CH_2-CH_3$	Methyl ethyl ether
 $-\underset{\mid}{\overset{\mid}{C}}-\overset{H}{\overset{\mid}{N}}-H$	Amine	$H_2N-CH_2-CH_3$	Ethylamine
 $-\overset{O}{\overset{\Vert}{C}}-\overset{H}{\overset{\mid}{N}}-H$	Amide	 $CH_3-CH_2-\overset{O}{\overset{\Vert}{C}}-NH_2$	Propanamide
 $-\underset{\mid}{\overset{\mid}{C}}-\overset{O}{\overset{\Vert}{C}}-O-\underset{\mid}{\overset{\mid}{C}}-$	Ester	 $CH_3-CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-O-CH_2-CH_3$	Ethyl butanoate

PROPERTIES AND REACTIONS

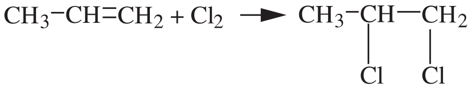
Alkanes

Alkanes are colorless, insoluble in water, have low boiling points, and are commonly used as fuels (butane, propane, octane, etc.). *Combustion* (usually, burning in oxygen) reactions (alkane + O_2) yield CO_2 and H_2O and may produce some CO (C^{2+}) if there isn't sufficient oxygen present to produce the C^{4+} oxidation state. The reaction of alkanes with halogens (F, Cl, Br, and I) can be controlled, resulting in the *substitution* of a halogen for a hydrogen without disruption of the carbon skeleton.

$$CH_3CH_2CH_3 + Cl_2 \rightarrow CH_3CH_2CH_2Cl + HCl$$

Alkenes

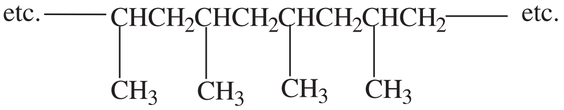
Alkenes are similar to alkanes in structure and also undergo combustion. However, they are much more likely to undergo *addition* reactions with halogens, rather than *substitution*. Addition reactions occur with a wide variety of reagents.



$$CH_3{-}CH{=}CH_2 + Cl_2 \rightarrow CH_3{-}\underset{\substack{|\\ Cl}}{CH}{-}\underset{\substack{|\\ Cl}}{CH_2}$$

$$CH_3{-}CH{=}CH_2 + HCN \rightarrow CH_3{-}\underset{\substack{|\\ CN}}{CH}{-}\underset{\substack{|\\ H}}{CH_2}$$

A very important reaction, especially in the plastics industry, is *additional polymerization*, in which alkene molecules add to themselves to form long chains. As an example, a polymerization of $CH_3CH{=}CH_2$ results in the production of



$$\text{etc.}\text{———}\underset{\substack{|\\ CH_3}}{CH}CH_2\underset{\substack{|\\ CH_3}}{CH}CH_2\underset{\substack{|\\ CH_3}}{CH}CH_2\underset{\substack{|\\ CH_3}}{CH}CH_2\text{———}\ \text{etc.}$$

Halides

The halogens are F, Cl, Br, and I. Halogenated compounds are water-insoluble and have higher boiling points than the corresponding hydrocarbon. They find wide use as solvents, cleaning fluids, insecticides, refrigerants, and (when in polymers) as plastics. They are also important starting materials for the synthesis of other compounds since the halogen can be *replaced* with OH (using NaOH) and other groups.

Alcohols

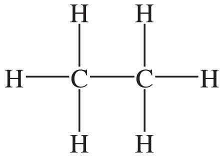
Many alcohols have a definite scent as the small (low mass) alcohols evaporate at room temperature. Water solubility and high boiling point for the relative size of the molecules are due to extensive hydrogen bonding. Two very important *condensation* reactions are (*a*) with another alcohol molecule to form an ether, and (*b*) with an acid to form an *ester* (*esterification* produces an organic salt). A *condensation* reaction in general is one in which two molecules become joined with the elimination of water or some other small molecule. Esterification can be reversed by means of *hydrolysis*, the reaction with water in which the original acid and alcohol are recovered. If an ester happens to be a natural fat, the process of its production is *saponification* since the sodium salt of the acid is a *soap*. The specific reaction that occurs, including condensation and hydrolysis, is quite dependent on the reaction conditions including temperature, pH, and presence of a catalyst.

There are groupings of atoms that act together and are called *functional groups*. For example, *methyl* alcohol (methanol) contains the *methyl* group, $-CH_3$, derived from methane, CH_4. Similarly, other function groups can be derived from other alkanes by the loss of one hydrogen atom; these groups are the *alkyl* groups. An alkyl group can accept various atoms to replace the hydrogen including chlorine, bromine, and iodine. There are other groups that can replace the hydrogen, such as the alcohol group (—OH), carboxyl group (—COOH), and others. Each of these atoms or groups replacing the hydrogen contributes to the nature of the compound.

Aldehydes and ketones

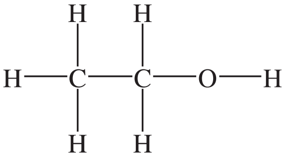
Aldehydes and ketones have much lower boiling points and are less water-soluble than the corresponding alcohols. In all cases, whether alcohols, aldehydes, ketones, or acids, water solubility gradually decreases as the number of carbon atoms increases within each class of compounds.

An alcohol can be viewed as the product of the first step in the oxidation of a hydrocarbon because there is an oxygen atom inserted between a carbon and a hydrogen. The addition of oxygen (or insertion) is one of the definitions of oxidation. If another oxygen atom is inserted on the same carbon and water is eliminated, the result is an aldehyde (if the carbon is at the end of the chain) or a ketone (if the carbon is in the middle of the chain). Inserting one more oxygen on the carbon of an aldehydes results in an acid—this is a *carboxylic* acid with the affected carbon often referred to as a *carboxylic carbon* (—COOH).



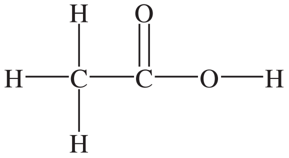
$$\mathrm{H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H}$$

Ethane



$$\mathrm{H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-O-H}$$

Ethyl alcohol

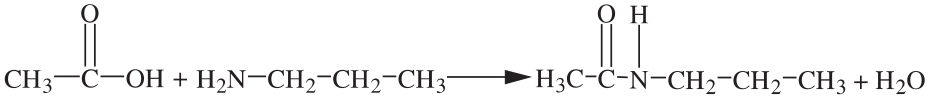


$$\mathrm{H-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-H}$$

Ethanoic acid (acetic acid)

Acids

Short-chain carboxylic acids are quite soluble in water and tend to ionize slightly (typically, a few percent depending on concentration). These acids undergo the typical acid-base reactions. Besides the condensation reaction with alcohols, acids condense with ammonia or amines to form amides.



$$\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-OH + H_2N-CH_2-CH_2-CH_3 \longrightarrow H_3C-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-CH_2-CH_2-CH_3 + H_2O}$$

Acetic acid Propylamine *n*-Propylacetamide Water

Salts of carboxylic acids and inorganic bases (KOH, NaOH, etc.) are fully ionized in the solid state and in aqueous solution. Salts of fatty acids (from hydrolysis of fats) with an inorganic base are *soaps*.

Amines and amides

Amines can be considered derivatives of ammonia, NH_3, in which one or more of the hydrogen atoms is replaced by an organic group, such as an alkyl group. The example in Table 15-1 is a *primary* amine (one H replaced); replacement of two H atoms is a *secondary* amine; replacement of all three results in a *tertiary* amine. Amines are somewhat soluble in water in which, like ammonia, they take up a proton leaving the solution basic. They dissolve readily in strong acid forming salts similar to ammonium salts.

The condensation of a carboxylic acid with ammonia or an amine yields an amide. The amide in Table 15-1 resulted from the condensation of propanoic acid with ammonia. The example in the preceding section involved the condensation of acetic acid with a primary amine. A very important class of biochemical molecules are the amino acids, which join to form protein molecules by the condensation of the amine group of one molecule to the acid group of the next. The amide linkage in this case has the special name *peptide.*

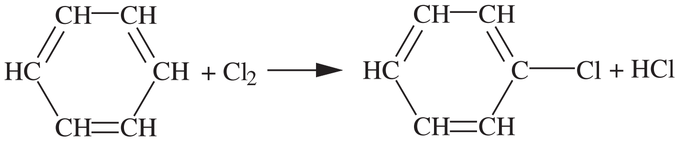
Ethers and esters

When an alcohol is heated under proper conditions with concentrated sulfuric acid, water is eliminated by the condensation of two molecules of alcohol and the combining groups, which may be alkyl groups. The groups are joined through an oxygen atom forming and *ether*. The product formed from ethanol, diethyl ether, is the familiar "ether" known for its use as a general anesthetic dating from the 1800s. Mixed ethers, such as methylethyl ether, may be formed by a condensation reaction of two, different alcohols. Ethers are only very slightly soluble in water, but are very good solvents for many other organic substances.

As discussed under alcohols, esters are the condensation products of alcohols and acids They are generally good organic solvents and are insoluble in water. Many found in nature are flavorful and sweet-smelling—amyl acetate is the fragrant component of banana oil ("amyl" is a traditional name for a five-carbon group). Natural fats and oils are esters of glycerol, a *triol* (3—OH groups), and fatty acids.

Aromatic compounds

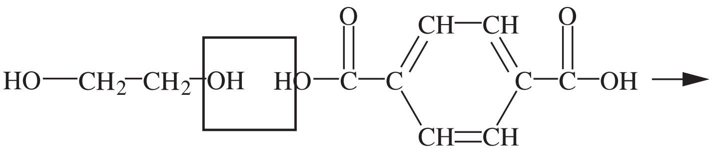
Benzene and compounds containing the benzene ring are the *aromatic* compounds. These compounds have somewhat different chemical properties than their aliphatic counterparts. For instance, the hydroxyl group (alcohol group) attached to a benzene ring is a weak acid (although much weaker than the carboxylic acid). The three alternating double bonds of the benzene ring are not readily *saturated* (containing no multiple bonds—the multiple bonds are broken and hydrogen bonded). If benzene is treated with chlorine (in the dark), substitution will occur, rather than addition.



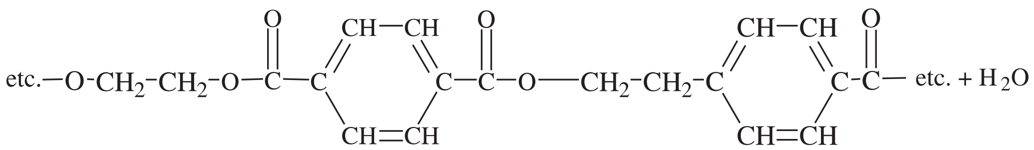
Functional groups on the aliphatic side-chains attached to aromatic rings behave in a manner typical of aliphatic compounds.

Multifunctional molecules

Many molecules contain more than one function group (either the same or different). In such cases, condensation reactions involving two or more groups per molecule can lead to the formation of polymers, as mentioned above in the formation of proteins from amino acids (—NH_2 and —COOH groups). From the standpoint of terminology, the unit or units that are joined together to produce a polymer are *monomers* with multiple units possible (*dimer*, *trimer*, etc.). An example of a man-made polymer involves the synthesis of polyester fiber, such as Dacron® polyester on which the textile industry depends.



1,2-Ethanediol Terephthalic acid



Dacron® polyester

Thousands of molecules of each reagent combine, eliminating a water molecule for each condensation forming the ester linkages. Note that the reaction, if continued, could theoretically form a molecule infinitely long.

BIOCHEMISTRY

Below is a listing of some of the factors that are special when considering *biochemistry*, the chemistry of living things.

1. As discussed directly above, molecules may be very large, but unlike a synthetic polymer, a biopolymer usually has a definite number and sequence of monomer units. Often, there is a fixed three-dimensional shape.
2. Classes of molecules are based primarily on structure, but also on their function in the living cell.
3. Reactions occur at a modest temperature and extremely sensitive catalysts (enzymes) are usually required. The energy to drive one reaction may come from the energy released by another reaction forming a sequence of reactions.
4. Throughout the animal and plant kingdoms, there is little or no difference in the structures of molecules that perform a given biological function.

As there are classes of organic molecules, there are also classes of biochemical molecules.

Proteins are polymers produced from amino acids that are joined by peptide linkages (amine-group carboxylic acid bonds). These compounds form the bulk of living tissue. Enzymes, those very selective and powerful catalysts, are also proteins. Enzymes may contain a group based on a metal atom, as may molecules from other classes of compounds (hemoglobin, chlorophyll, etc.). Some proteins serve special functions, such as hemoglobin, an oxygen carrier.

Carbohydrates that are sugars consist of relatively small molecules typically based on four to six carbons atoms in the skeleton. Sugars have hydroxyl and aldehyde or ketone functional groups. These molecules may function as fuels or as building blocks (monomers) for polymeric materials. Plants contain polymers of sugars called starch and cellulose formed by ether linkages. These polymers store energy (starches) and provide for rigid structure (cellulose).

Fats are esters of glycerol and the fatty acids. In plants, may of the fats are unsaturated (containing double bonds in the carbon skeleton) and liquid (*oils*). Fats also function as fuels, but for long-term energy storage, rather than the short-term storage and quick delivery of energy provided by sugars and starches. Fats are part of a class of compounds called *lipids* based on their insolubility in water and solubility in ether. Among other lipids are cholesterol and some materials important in the construction of cell membranes.

Nucleic acids are large polymers joined by ester linkages between phosphate and sugar monomer units (deoxyribose in DNA, and ribose in RNA). These sugars carry nitrogen-containing side-chains called *purines* or *pyramidines*, both referred to a *nitrogen bases*. The monomers, then, contain a phosphate, a sugar, and one nitrogen base. The monomers are joined with a phosphate of one linking to a point on the sugar of another. This system holds the nitrogen bases in a definite sequence along the molecule that constitutes the genetic code (DNA) of an individual organism and controls the sequencing of amino acids during the synthesis of proteins (DNA and RNA), as well as other functions.

Solved Problems

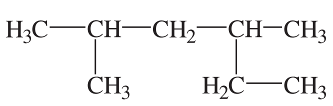
NOMENCLATURE

15.1. Name each of the following compounds according to the IUPAC rules:

(*a*) The difficulty is the manner in which the structure is drawn. Find the *longest* chain, which is six carbon atoms, and start the numbering at the left to minimize the numbers indicating the points of substation: 2,4-dimethylhexane.

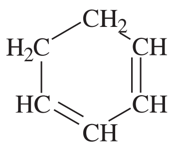
(*b*) The ring carbons are numbered so as to minimize the sum of the numbers: cyclohexa-1,3-diene.

(*c*) Chloro is treated as a prefix, but the carbonyl oxygen as a suffix: 1-chloro-3-pentanone.

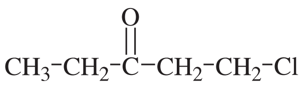


$H_3C-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{H_2C-CH_3}{\underset{|}{CH}}-CH_3$

(*a*)

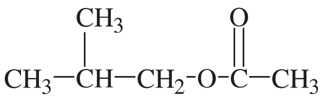


(*b*)



$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-Cl$

(*c*)

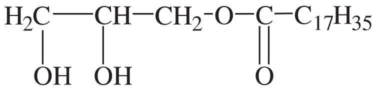


$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3$

(*d*)

$CH_3-NH-CH_2-CH_2-CH_3$

(*e*)



$\underset{OH}{\underset{|}{H_2C}}-\underset{OH}{\underset{|}{CH}}-CH_2-O-\underset{O}{\underset{\|}{C}}-C_{17}H_{35}$

(*f*)

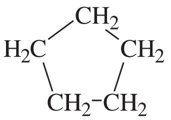
(*d*) The compound is an ester. Contrary to the example in Table 15-1, the alcohol residue is to the left. In either case, the alcohol part is always named first: 2-methylpropyl ethanoate (or acetate).

(*e*) This compound is a secondary amine: methlypropylamine.

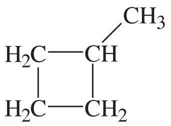
(*f*) The 18-carbon carboxylic acid reacted to form this compound is stearic acid, making the compound 2,3-dihydroxypropyl stearate. The alcohol residue is glycerol. Since only hydroxyl is esterified, this type of ester is called a monoglyceride and the compound may be named monoglyceryl stearate. It is valuable in food processing as an emulsifier.

ISOMERISM

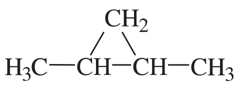
15.2. Identify all the isomers with C_5H_{10} as their formula. Provide the IUPAC names.



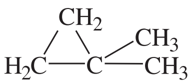
(*a*) Cyclopentane



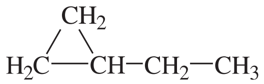
(*b*) Methylcyclobutane



(*c*) 1,2-Dimethylcyclopropane



(*d*) 1,1-Dimethylcyclopropane



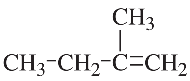
(*e*) Ethylcyclopropane

$CH_3-CH_2-CH_2-CH=CH_2$

(*f*) 1-Pentene

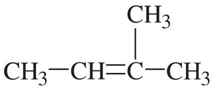
$CH_3-CH_2-CH=CH-CH_3$

(*g*) 2-Pentene



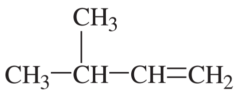
$CH_3-CH_2-C(CH_3)=CH_2$

(*h*) 2-Methyl-1-butene



$CH_3-CH=C(CH_3)-CH_3$

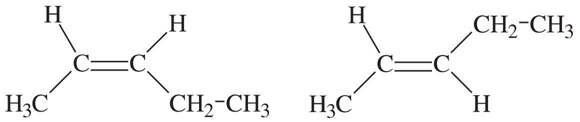
(*i*) 2-Methyl-2-butene



$CH_3-CH(CH_3)-CH=CH_2$

(*j*) 3-Methyl-1-butene

There is the possibility of *cis-trans* isomerism. The only case among the alkenes is (*g*), as below.



Structure (*c*) also shows *cis-trans* isomerism. The three carbons in the ring define a plane, the plane of the paper. Either both hydrogens of the CH groups are on the same side of this plane or one is above and the other below.

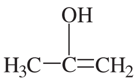
Structure (*c*) is also the only one which has a chiral carbon atom (the carbons of the two CH groups). However, the *cis* isomer has a plane of symmetry and cannot have an optical isomer. Only the *trans* isomer has an optical isomer.

15.3. Draw all of the structural isomers with the formula C_3H_6O. Point out any that have geometrical or optical isomers. (Not all structures satisfying Lewis rules correspond to stable chemical substances.)

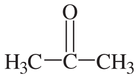
$CH_3-CH=CH-OH$

cis-trans forms

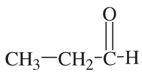
$H_2C=C-CH_2\text{-}OH$



$H_3C-C(OH)=CH_2$

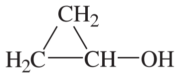


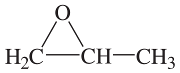
$H_3C-C(=O)-CH_3$



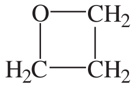
$CH_3-CH_2\text{-}C(=O)\text{-}H$

$H_2C=CH-O\text{-}CH_3$





CH carbon is chiral



FUNCTIONAL GROUPS AND REACTIONS

15.4. Draw the structure of the organic produce results from each of these reactions.

(*a*) 1-Propanol in dehydrating medium.

(*b*) 1-Propanol in mildly oxidizing medium.

(*c*) 2-Propanol in mildly oxidizing medium.

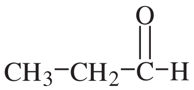
(*d*) 1-Propanol plus butanoic acid in dehydrating medium.

(*e*) 1-Propanol plus metallic sodium.

(*a*) A condensation results in the elimination of water and the formation of an ether.

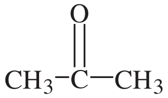
$$CH_3CH_2CH_2-O-CH_2CH_2CH_3$$

(*b*) One stage of oxidation of a hydroxyl group produces a carbonyl carbon (—C=O). When the alcohol is at the end of the chain (primary alcohol), the product is an aldehyde.



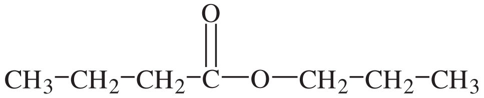
$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

(*c*) When the alcohol is not at the end (secondary alcohol in this case), the product is a ketone.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

(*d*) A condensation results in the elimination of water and the formation of an ester.



$$CH_3-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_2-CH_3$$

(*e*) Considering the alcohol to be a derivative of water, one expects the sodium to displace the hydrogen of the hydroxyl group. One product is H_2; the other is the sodium salt of the alcohol.

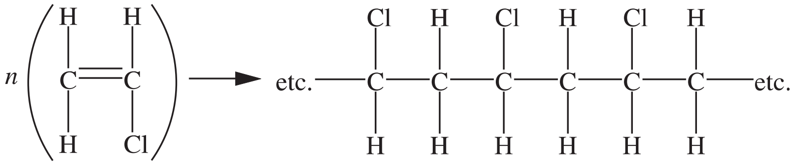
$$CH_3CH_2CH_2O^-Na^+$$

15.5. Using structural formulas, describe these reactions.

(*a*) Vinyl chloride (alternate name: chloroethene) is treated with a polymerization catalyst.

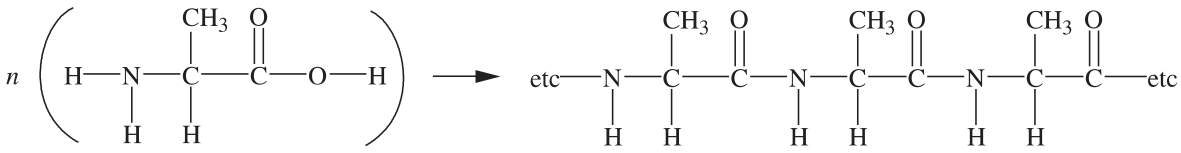
(*b*) The amino acid alanine (2-aminopropanoic acid) is treated with the appropriate polymerase and the energy source to cause it to polymerize.

(*a*) The product is a saturated polymer since the double bonds have been used up in joining the monomers together to form polyvinyl chloride (PVC used to make plastic pipes and other materials).



$$n\begin{pmatrix} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & Cl \end{pmatrix} \longrightarrow \text{etc.}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\text{etc.}$$

(*b*) Water is removed, H from the amino group of one molecule and OH from the acid of the next, and polyalanine is formed. The boxed area encloses the peptide linkage formed between monomers.

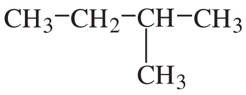


$$n\left(H-\underset{\underset{\displaystyle H}{|}}{N}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-O-H\right) \longrightarrow \text{etc}-\underset{\underset{\displaystyle H}{|}}{N}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-\text{etc}$$

Supplementary Problems

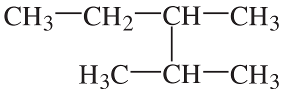
NOMENCLATURE

15.6. List the IUPAC name of each of these compounds:



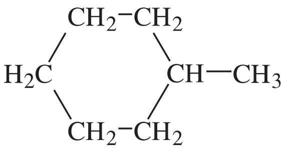
$CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$

(*a*)



$CH_3-CH_2-\underset{\underset{\displaystyle H_3C-CH-CH_3}{|}}{CH}-CH_3$

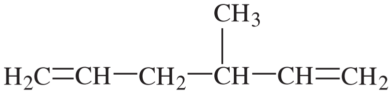
(*b*)



(*c*)

$CH_3-CH_2-CH{=}CH-CH_3$

(*d*)



$H_2C{=}CH-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH{=}CH_2$

(*e*)

$CH_3-C{\equiv}C-CH_3$

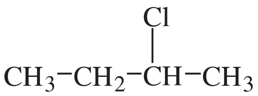
(*f*)

Ans. (*a*) 2-methylbutane; (*b*) 2,3-dimtheylpentane; (*c*) methylcyclohexane; (*d*) 2-pentene; (*e*) 3-methyl-1, 5-hexadiene; (*f*) 2-butyne

15.7. Name each of the following using the IUPAC system.

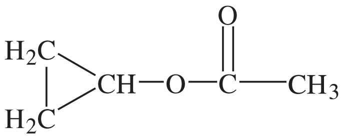
$H_3C-O-CH_2-CH_3$

(*a*)



$CH_3-CH_2-\overset{\overset{\displaystyle Cl}{|}}{CH}-CH_3$

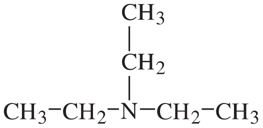
(*b*)



(*c*)

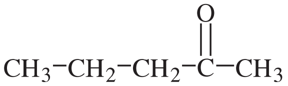
$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_2-OH$

(*d*)



$CH_3-CH_2-\overset{\overset{\overset{\displaystyle CH_3}{|}}{\overset{\displaystyle CH_2}{|}}}{N}-CH_2-CH_3$

(*e*)

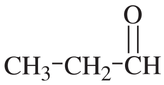


$CH_3-CH_2-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

(*f*)

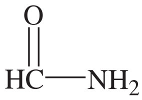
Ans. (*a*) methyl ethyl ether; (*b*) 2-chlorobutane; (*c*) cyclopropyl acetate (or ethanoate); (*d*) 3-methyl-1-pentanol; (*e*) triethylamine; (*f*) 2-pentanone

15.8. Name each of the following using the IUPAC system.



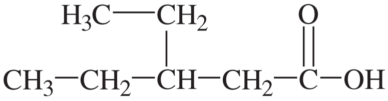
$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}H$

(*a*)



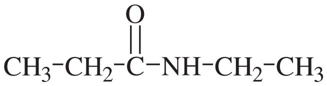
$H\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$

(*b*)



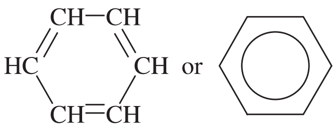
$CH_3-CH_2-\overset{\overset{\displaystyle H_3C-CH_2}{|}}{CH}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$

(*c*)

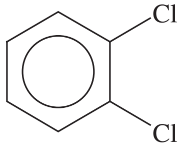


$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_2-CH_3$

(*d*)



(*e*)

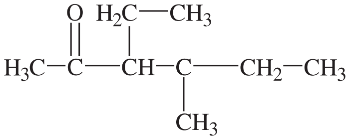


(*f*)

Ans. (*a*) propanal; (*b*) formamide (methanamide); (*c*) 3-ethylpentanoic acid; (*d*) *N*-ethylpropanamide; (*e*) benzene; (*f*) 1,2-dichlorobenzene

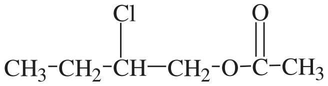
15.9. Draw the structures of the following compounds: (*a*) 3-ethyl-4-methyl-2-hexanone; (*b*) 2-chloro-buytl acetate; (*c*) ethylbenzene; (*d*) 3-ethylcyclohexene; (*e*) 2-methyl-3-pentanol; (*f*) 2-methylpropyl methyl ether.

Ans. (*a*)



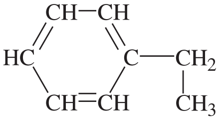
$H_3C-\overset{O}{\overset{\|}{C}}-\overset{H_2C-CH_3}{\overset{|}{CH}}-\underset{CH_3}{\underset{|}{C}}-CH_2-CH_3$

(*b*)

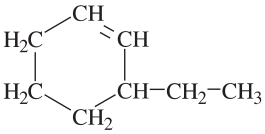


$CH_3\text{-}CH_2\text{-}\overset{Cl}{\overset{|}{CH}}-CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$

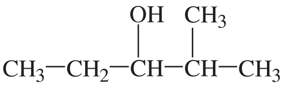
(*c*)



(*d*)

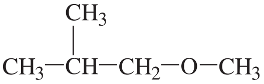


(*e*)



$CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_3$

(*f*)



$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-O-CH_3$

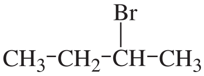
15.10. Explain what is wrong with each of the following names: (*a*) 3-methyl-2-propanol; (*b*) 3,3-dimethyl-2-pentene; (*c*) 1,4-dichlorocyclyobutane; (*d*) 2-propanal; (*e*) 2-methyl-1-butyne; (*f*) pentanoicacid.

Ans. (*a*) The longest chain is four carbons. The correct name is 2-butanol. (*b*) Such a compound is impossible because it would require five bonds on the third carbon. (*c*) Positions 1 and 4 are equivalent to 1 and 2. The correct name is 1,2-dichlorocyclobutane. (*d*) Such a compound is not possible because the aldehyde carbon must be at the end of the chain. (*e*) Such a compound won't work because it would require five bonds on the second carbon. (*f*) The suffix "acid" should be a separate word. The correct name is pentanoic acid.

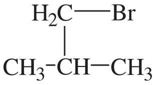
ISOMERISM

15.11. Draw the structures of all the structural isomers having the formulas: (*a*) C_4H_9Br; (*b*) C_4H_8; (*c*) $C_2H_4O_2$ (omit any peroxides, —O—O—); (*d*) C_6H_{14}; (*e*) $C_4H_8Cl_2$.

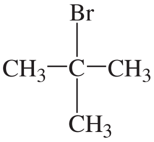
Ans. (*a*) $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Br$



$CH_3\text{-}CH_2\text{-}\overset{Br}{\overset{|}{CH}}\text{-}CH_3$

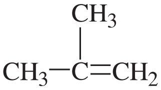


$CH_3\text{-}\overset{H_2C-Br}{\overset{|}{CH}}-CH_3$

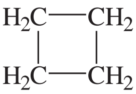


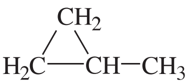
$CH_3-\overset{Br}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$

(*b*) $CH_3\text{-}CH_2\text{-}CH{=}CH_2$ $\quad CH_3-CH=CH-CH_3$

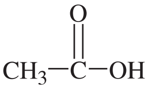


$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2$

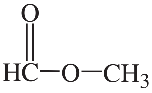




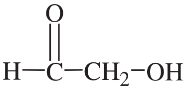
(*c*)



$CH_3-\overset{O}{\overset{\|}{C}}-OH$

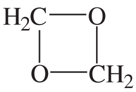


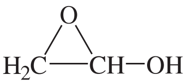
$H\overset{O}{\overset{\|}{C}}-O-CH_3$



$H-\overset{O}{\overset{\|}{C}}-CH_2\text{-}OH$

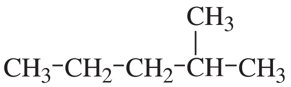
$HO-CH=CH-OH$

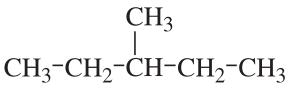


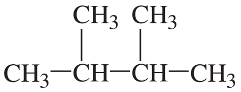


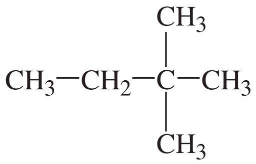
Note: Not all the compounds above may be stable. The structure with two hydroxyl groups on the same carbon does not occur.

(*d*) $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

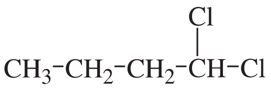

$CH_3-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_3$


$CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_3$

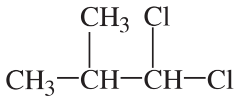

$CH_3-\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{CH_3}{|}}{C}H-CH_3$

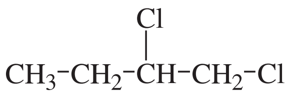

$CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

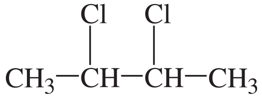
(*e*)

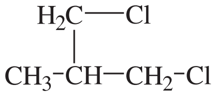

$CH_3-CH_2-CH_2-\overset{\overset{Cl}{|}}{C}H-Cl$

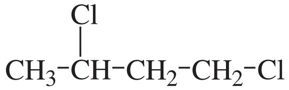
$Cl-CH_2-CH_2-CH_2-CH_2-Cl$

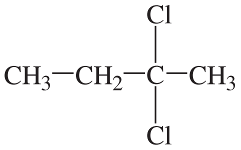

$CH_3-\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{Cl}{|}}{C}H-Cl$

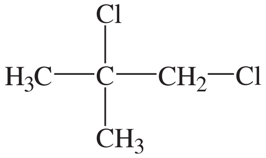

$CH_3-CH_2-\overset{\overset{Cl}{|}}{C}H-CH_2-Cl$


$CH_3-\overset{\overset{Cl}{|}}{C}H-\overset{\overset{Cl}{|}}{C}H-CH_3$


$CH_3-\overset{\overset{H_2C-Cl}{|}}{C}H-CH_2-Cl$


$CH_3-\overset{\overset{Cl}{|}}{C}H-CH_2-CH_2-Cl$


$CH_3-CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_3$

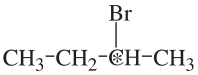

$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2-Cl$

15.12. Examine all the answers to Problem 15.11 and select all that exhibit geometric isomerism, pointing out the two carbon atoms involved in each.

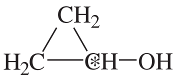
Ans. $CH_3-\circledast H=\circledast H-CH_3$ (*a*) $HO-\circledast H=\circledast H-OH$ (*b*)

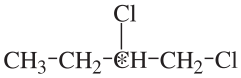
15.13. Examine all the answers to Problem 15.11 and select all that exhibit optical isomerism, pointing out the chiral carbon (or carbons) involved in each.

Ans.

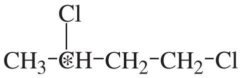

$CH_3-CH_2-\overset{\overset{Br}{|}}{\circledast}H-CH_3$

(*a*)

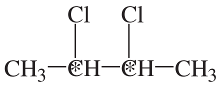

(*c*)


$CH_3-CH_2-\overset{\overset{Cl}{|}}{\circledast}H-CH_2-Cl$

(*e*)


$CH_3-\overset{\overset{Cl}{|}}{\circledast}H-CH_2-CH_2-Cl$

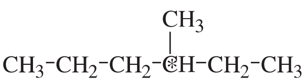
(*e*)

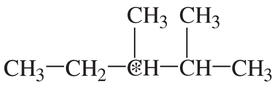

$CH_3-\overset{\overset{Cl}{|}}{\circledast}H-\overset{\overset{Cl}{|}}{\circledast}H-CH_3$

(*e*)

15.14. Draw the structure for the smallest noncyclic alkane that has a chiral carbon and mark that carbon. Name the compound.

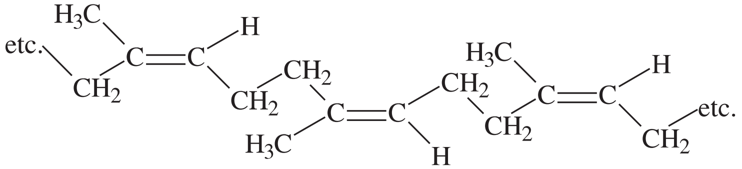
Ans.


$CH_3-CH_2-CH_2-\overset{\overset{CH_3}{|}}{\circledast}H-CH_2-CH_3$


$CH_3-CH_2-\overset{\overset{CH_3}{|}}{\circledast}H-\overset{\overset{CH_3}{|}}{C}H-CH_3$

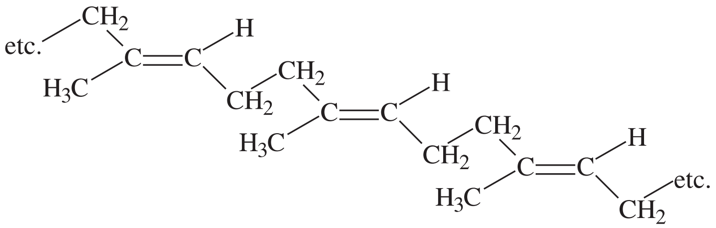
3-Methylhexane also 2,3-Dimethylpentane

15.15. Natural rubber is a polymer of isoprene and has the following structure:



There is another product called gutta-percha, which is a geometric isomer of rubber, but is useless as an elastomer. Draw its structure and identify which is *cis* and which is *trans*.

Ans. Natural rubber is *cis*; gutta-percha is *trans*.



15.16. Which has more isomers, (*a*) dimethylbenzene or (*b*) dimethylcyclohexene? Explain.

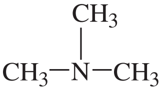
Ans. Because all corners of the benzene ring are equivalent, (*a*) has only three isomers (structural) with the methyl groups in positions 1,2; 1,3; or 1,4. However, (*b*) can have many more structural isomers; for example, 1,2 is different from 1,6 and 1,3 is different from 2,4. There are also many geometric isomers; for example, the 3,4 structural isomer must have *cis* and *trans* forms. Optical isomerism also occurs; for instance, both carbons 3 and 4 of the 3,4 isomer are chiral.

FUNCTIONAL GROUPS

15.17. Name the functional group in each of the following molecules:

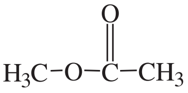
$CH_3\text{-}CH_2\text{-}CH_2\text{-}OH$

(*a*)



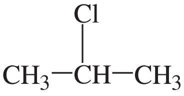
$(CH_3)_3N$

(*b*)



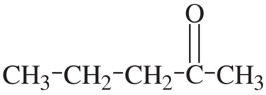
$H_3C\text{-}O\text{-}C(=O)\text{-}CH_3$

(*c*)



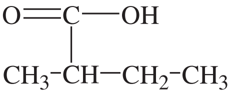
$CH_3\text{-}CH(Cl)\text{-}CH_3$

(*d*)



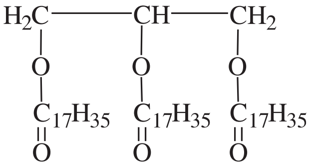
$CH_3\text{-}CH_2\text{-}CH_2\text{-}C(=O)\text{-}CH_3$

(*e*)

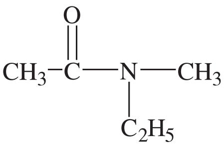


$CH_3\text{-}CH(COOH)\text{-}CH_2\text{-}CH_3$

(*f*)



(*g*)

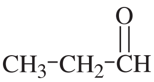


$CH_3\text{-}C(=O)\text{-}N(C_2H_5)\text{-}CH_3$

(*h*)

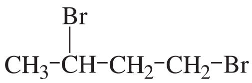
$C_4H_9OC_4H_9$

(*i*)



$CH_3\text{-}CH_2\text{-}CHO$

(*j*)



$CH_3-CH(Br)-CH_2-CH_2-Br$

(*k*)

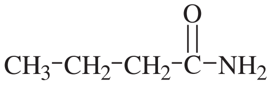
$CH_3-CH_2-C\equiv C-CH_3$

(*l*)

Ans. (*a*) alcohol (hydroxyl); (*b*) amine (tertiary amine); (*c*) ester; (*d*) chloride; (*e*) ketone; (*f*) carboxylic acid; (*g*) ester (triglyceride); (*h*) amide; (*i*) ether; (*j*) aldehyde; (*k*) bromide (dibromide); (*l*) alkyne (triple bond)

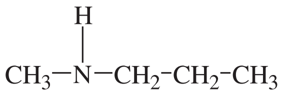
15.18. Draw the structures for the following compounds: (*a*) butanamide; (*b*) methylpropylamine; (*c*) diethyl ether; (*d*) 2,3-dimethyl-1-hexanol; (*e*) ethyl 2-methylpropionate; (*f*) 3-iodo-2-pentanone.

Ans.



$CH_3-CH_2-CH_2-C(=O)-NH_2$

(*a*)

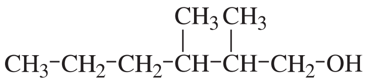


$CH_3-N(H)-CH_2-CH_2-CH_3$

(*b*)

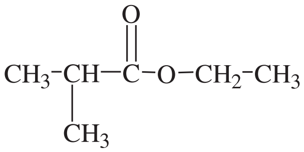
$CH_3-CH_2-O-CH_2-CH_3$

(*c*)



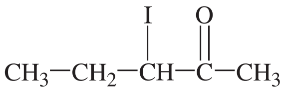
$CH_3-CH_2-CH_2-CH(CH_3)-CH(CH_3)-CH_2-OH$

(*d*)



$CH_3-CH(CH_3)-C(=O)-O-CH_2-CH_3$

(*e*)



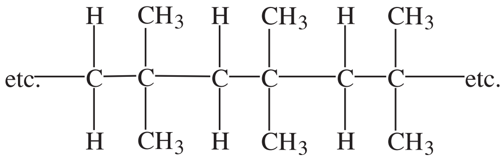
$CH_3-CH_2-CH(I)-C(=O)-CH_3$

(*f*)

REACTIONS

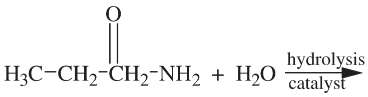
15.19. Draw the structure of the polymer formed by addition polymerization of 2-methyl-1-propene.

Ans.



15.20. What are the main products of the following reactions? Give the structures of the organic products.

(*a*)



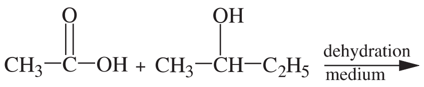
$H_3C-CH_2-CH_2(=O)-NH_2 + H_2O \xrightarrow[\text{catalyst}]{\text{hydrolysis}}$

(*b*) $C_3H_8 + O_2 \xrightarrow[\text{temp}]{\text{high}}$

(*c*) $C_2H_5OH \xrightarrow[\text{medium}]{\text{dehydration}}$

(*d*) $C_2H_5OH \xrightarrow[\text{mild}]{\text{oxidizer}}$

(*e*)

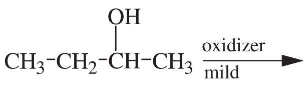


$CH_3-C(=O)-OH + CH_3-CH(OH)-C_2H_5 \xrightarrow[\text{medium}]{\text{dehydration}}$

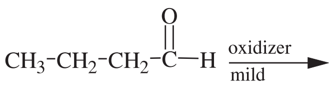
(*f*) $CH_3-CH_2-CH_3 + Cl_2 \rightarrow$ 1st stage

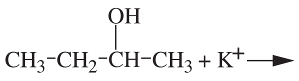
(*g*) $H_2C=CH-CH_3 + Cl_2 \rightarrow$ 1st stage

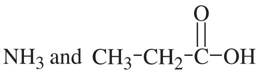
(*h*)



$CH_3-CH_2-CH(OH)-CH_3 \xrightarrow[\text{mild}]{\text{oxidizer}}$

(*i*)

$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{—}H \xrightarrow[\text{mild}]{\text{oxidizer}}$

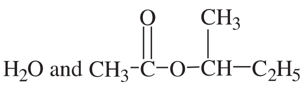
(*j*)

$CH_3\text{-}CH_2\text{-}\overset{OH}{\overset{|}{C}}H\text{-}CH_3 + K^+ \longrightarrow$

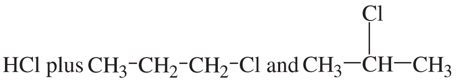
Ans. (*a*)

NH_3 and $CH_3\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH$

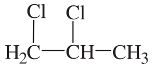
(*b*) CO_2 and H_2O (*c*) H_2O and $CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$

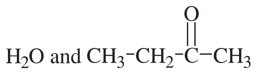
(*d*)

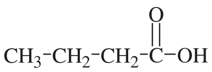
H_2O and $CH_3\text{-}\overset{O}{\overset{\|}{C}}H$

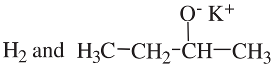
(*e*)

H_2O and $CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\overset{CH_3}{\overset{|}{C}}H\text{—}C_2H_5$

(*f*)

HCl plus $CH_3\text{-}CH_2\text{-}CH_2\text{-}Cl$ and $CH_3\text{—}\overset{Cl}{\overset{|}{C}}H\text{—}CH_3$

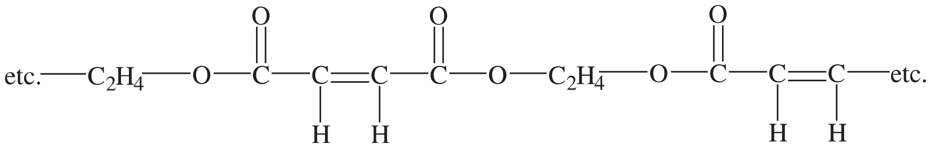
(*g*)

$H_2\overset{Cl}{\overset{|}{C}}\text{—}\overset{Cl}{\overset{|}{C}}H\text{—}CH_3$

(*h*)

H_2O and $CH_3\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$

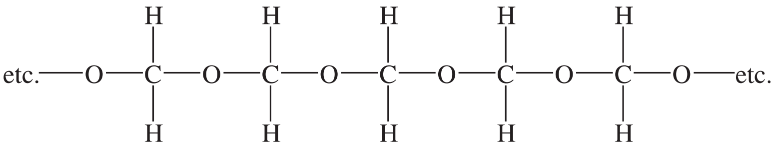
(*i*)

$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH$

(*j*)

H_2 and $H_3C\text{-}CH_2\text{-}\overset{O^- K^+}{\overset{|}{C}}H\text{—}CH_3$

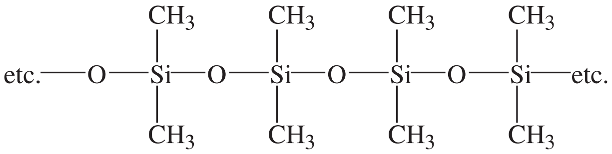
15.21. Draw a portion of the polymer formed by condensation of 1,2-ethanediol and maleic acid (IUPAC name: *cis*-butenedioic acid). This, and similar polymers, are copolymerized with styrene to form the "polyester resins," which are widely used to make structural plastic moldings.

Ans.

$$\text{etc.}\text{—}C_2H_4\text{—}O\text{—}\overset{O}{\overset{\|}{C}}\text{—}\underset{H}{\underset{|}{C}}\text{=}\underset{H}{\underset{|}{C}}\text{—}\overset{O}{\overset{\|}{C}}\text{—}O\text{—}C_2H_4\text{—}O\text{—}\overset{O}{\overset{\|}{C}}\text{—}\underset{H}{\underset{|}{C}}\text{=}\underset{H}{\underset{|}{C}}\text{—etc.}$$

15.22. Formaldehyde (methanal) can form addition polymers. Imagine adding a water molecule to a methanal molecule to form a diol, which then forms an ether linkage with a similar neighboring molecule (splitting out water) and so on. Draw a portion of the resultant product.

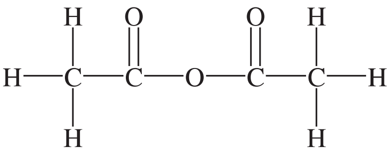
Ans.

$$\text{etc.}\text{—}O\text{—}\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}\text{—}O\text{—}\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}\text{—}O\text{—}\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}\text{—}O\text{—}\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}\text{—}O\text{—}\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}\text{—}O\text{—etc.}$$

15.23. "Silicones" are polymers that find widespread uses from high-temperature hydraulic fluids to medical prostheses. Draw a portion of the polymer formed by condensing out water from dimethylsilanediol, $(CH_3)_2Si(OH)_2$.

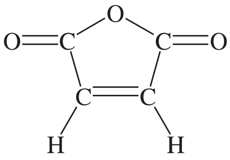
Ans.

$$\text{etc.}\text{—}O\text{—}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{Si}}}}\text{—}O\text{—}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{Si}}}}\text{—}O\text{—}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{Si}}}}\text{—}O\text{—}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{Si}}}}\text{—etc.}$$

15.24. Two carboxylic acid groups can combine by condensing out a water molecule to form an acid anhydride. Draw the structures of (*a*) acetic anhydride, which involves two molecules, and (*b*) maleic anhydride (see Problem 15.21), in which only one molecule is involved.

Ans.

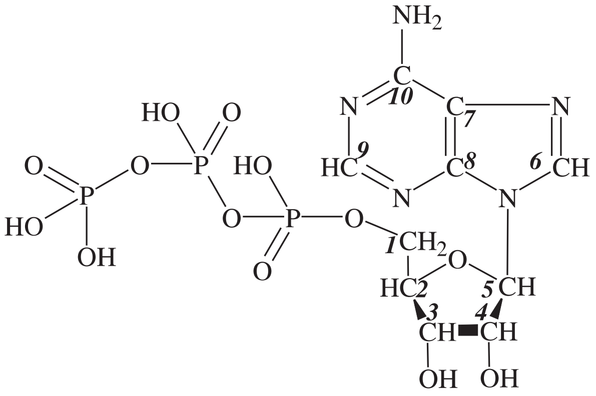


(*a*)



(*b*)

15.25. Adenosine triphosphate, ATP, is an extremely important molecule because it stores energy that is released as needed for energy for living organisms. (*a*) If there is a chiral carbon in ATP, identify that carbon by the number provided in the sketch (*b*) Considering the structure and composition of ATP, identify the elements involved at the points of the strongest negative charges. (*c*) If there are any, identify carbons that are substituted with an alcohol group. (*d*) This compound contains three rings. Identify which of the three rings, if any, are heterocyclic.



Ans. (*a*) The chiral carbons are 2, 3, 4, and 5 (four different substituents). (*b*) Both nitrogen and oxygen are expected to be negative points; however, the oxygens that are doubly bound to the phosphorus in the three phosphates are the most negative points. There are oxygens that are negative poles in the alcohol groups (—OH). It is true that there are nitrogens that service a negative pole, but the oxygens are more electronegative, eliminating the nitrogens from consideration. (*c*) #3 and #4; (*d*) All three rings are heterocyclic because they contain at least one atom other than carbon (N and O in these rings).

CHAPTER 16

Thermodynamics and Chemical Equilibrium

THE FIRST LAW

The first law of thermodynamics (referred to in Chapter 7) can be stated as *energy can neither be created nor destroyed*, which can also be expressed as *the total amount of energy that exists is a constant*. Modern science has confirmed the law by recognizing that one type of energy can be converted into another (electricity running a light bulb, which produces both light and heat) and has found that the total energy of the system has not changed. However, the state of the system can change.

E and H are properties of a system that, along with others, define the state of the system. Those properties are *state functions*. If any of these properties change, the system is said to have undergone a *change in state*. Any change in E must be equal to the amount of heat absorbed by the system plus the amount of work performed on the system. A formal statement of the first law is:

$$\Delta E = q + w \tag{16-1}$$

In equation (*16-1*), q is the heat absorbed from the surroundings and w is the work done on the system. A few examples of work are (*1*) if a chemical reaction occurs within a system, work may be done upon it if gases are consumed and its volume is decreased, or (*2*) the system may perform work if gases are produced, or (*3*) work may be done if the system delivers an electric current to an external circuit.

THE SECOND LAW

Pertinent terminology related to these studies includes *system*, which refers to what specifically is under investigation, while the *surroundings* is the location under investigation. Practically, the surroundings is the portion of the environment that is affected by the system. The encompassing term for these factors is the *universe* (system + surroundings). Although universe usually refers to everything outside the system, practically, the system and immediate surroundings are more often the subject of the considerations. Utilizing these terms, the second law of thermodynamics states that *the entropy* (disorder) *of the universe increases during spontaneous reaction*. For example, a reaction taking place in a test tube (the system) giving off energy to the air around the test tube (the surroundings) tends to heat up that air. We could say that the test tube and reaction, along with the air that is measurably affected by the reaction, are the universe.

The existence of an energy balance is not sufficient to answer all questions about a chemical reaction. Does a given reaction take place at all? If so, to what extent does it proceed? Questions relating to the processes and extent of chemical reactions require the introduction of some new thermodynamic functions which, like E and H, are properties of the state of the system. These new functions are *entropy*, S, and *Gibbs free energy*, G. In order to answer these and other questions, a mathematical statement of the second law of thermodynamics is required:

$$\Delta S \geq \frac{q}{T} \qquad (16\text{-}2)$$

In words: when a system undergoes a change, the increase in entropy of the system is equal to or greater than the heat absorbed in the process divided by the temperature. On the other hand, the equality, which provides a definition of entropy increment, applies to any *reversible process*, whereas the inequality refers to a *spontaneous* (or *irreversible*) *process*, defined as one which proceeds without intervention from the outside. Example 1 illustrates the *reversible* and *irreversible* reactions.

EXAMPLE 1 Consider a mixture of liquid and solid benzene at its normal freezing point, 5.45°C. If the temperature is raised by the slightest amount, for instance 0.01°C, the solid portion will gradually melt. But if, instead, the temperature were lowered by that amount, the liquid would gradually crystallize. The freezing process (as well as the melting process) at 5.45°C is *reversible*.

It is possible to cool liquid benzene carefully to a temperature below its normal freezing point, say to 2.00°C, without crystallization occurring. The liquid is then said to be *supercooled*. If a tiny crystal of solid benzene is added, the entire mass will crystallize *spontaneously* and *irreversibly*. Raising the temperature by 0.01°C (or even 1.00°C) will not stop the crystallization. One would have to raise and maintain the temperature above 5.45°C to restore the liquid state. The crystallization of liquid benzene at 2.00°C is an example of an irreversible process.

The above statement of the second law (*16-2*) implies that there is a difference between those reactions that occur spontaneously (for which $\Delta S > Q/T$) and those that cannot ($\Delta S < Q/T$).

The spontaneity of a reaction can be predicted with a mathematical *model* (an equation/formula fitting known data) to explain the state function, G, the free energy. A usable model is

$$G = H - TS \qquad (16\text{-}3)$$

Equation (*16-2*) leads by complex argument to the following free-energy principle:

$$\Delta G_{T,P} \leq 0 \qquad (16\text{-}4)$$

In other words, equation (*16-4*) states that the change in free energy at constant temperature and pressure can be negative or zero—negative in the case of a spontaneous irreversible process, or zero in the case of a reversible process. This rule is restricted to processes in which the only form of work is the increase in volume pressing against the surroundings (or the reverse). Processes for which $\Delta G_{T,P}$ is positive can occur only with the application of work (or energy) from some external source (such as the process of electrical decomposition by the application of an electrical potential or coupling with another chemical reaction for which $\Delta G_{T,P}$ is negative). Another statement of the free-energy principle is that the maximum amount of work which a system can perform at constant temperature and constant pressure in forms other than expansion or contraction is equal to the decrease in the free energy of the system.

For all practical purposes, we can state that *all spontaneous processes in nature result in an increase in the entropy of the universe*. We can also generalize with the statement that *any system* (even the universe) *will tend to run down over time* (tend in increase in entropy until total chaos—disorder—is reached).

Entropy

Entropy is often defined as an *increase in disorder*. A way of understanding entropy is to think in terms of the increase in entropy as an *increase in the chaotic state* (disorganized, untidy, or hectic state) of the system. Then, the greater the number of arrangements in a system, the greater the entropy.

The value of the entropy, S, is positive above absolute zero with the numerical value becoming higher with an increase in temperature. Using (*16-2*), changes in entropy, ΔS, can be calculated from gross thermal measurements of reversible processes. However, changes in entropy may also be related to the molecular properties of matter. Some general statements and examples relating to entropy are:

1. Liquids have more entropy than their corresponding crystalline forms. Every atom or molecule in a crystal is in a position in the lattice. In a liquid, the positions of the atoms or molecules are not as fixed in space and in those positions. Many liquids are composed of loosely attracted atoms or molecules in a crystalline structure, but that structure is not fixed throughout the mass of the liquids, as it is in solids.
2. Gases have more entropy than their corresponding liquids (or solids in the case of sublimation). Although the molecules in a liquid are free to occupy a variety of positions, they are held in close contact with their nearest neighbors. In a gas, the number of possible positions for the molecule is much greater because there is much more free space available per molecule.
3. Gases at low pressure have higher entropy than at high pressure. The argument for this factor is similar to 2 above—the amount of space per molecule is greater at low pressure than at high pressure.
4. A large molecule has a greater entropy than any of its submolecular fragments existing in the same phase of matter. The internal vibrations and rotations of atoms within molecules give many possibilities for distribution of intramolecular motions when considering the larger molecule as opposed to those available within each of the fragments.
5. The entropy of a substance always increases when its temperature is raised. The temperature is a measure of the average energy per molecule and, therefore, the total energy. The higher the temperature, the greater the total energy. The greater the total energy, the greater the number of ways of apportioning this energy among the fixed number of molecules. So, we can expect a different number of collections of molecular (energy) states if the temperature is higher, rather than lower.
6. If a chemical reaction is accompanied by a change in the number of gas molecules, ΔS is positive in the reaction direction that results in an increase in the number of gas molecules.
7. When one substance dissolves in another, ΔS is positive. The number of possible configurations of randomly arranged, unlike particles (solvent and solute) is greater than the number of configurations of separately packaged, like particles.

THE THIRD LAW

Equation (*16-2*) allows the calculations of *changes* in the entropy of a substance, specifically by measuring the heat capacities at different temperatures and the enthalpies of phase changes. If the absolute value of the entropy were known at any one temperature, the measurements of changes in entropy in going from that temperature to another temperature would allow the determination of the absolute value of the entropy at the other temperature. The third law of thermodynamics provides the basis for establishing absolute entropies. The law states that the entropy of any perfect crystal is zero (0) at the temperature of absolute zero (0 K or $-273.15°\text{C}$). This is understandable in terms of the molecular interpretation of entropy. In a perfect crystal, every atom is fixed in position, and, at absolute zero, every form of internal energy (such as atomic vibrations) has its lowest possible value.

STANDARD STATES AND REFERENCE TABLES

The use of standard entropies and free energies of formation to determine the value of ΔG for a reaction requires a little understanding. Consider the following:

1. Although enthalpies of substances are relatively independent of pressure (for gases) and of concentration (for dissolved species), their entropies (and free energies, too) depend on these variables. The values in tables for

S^o and G^o usually refer to the idealized state of 1 bar or 1 atm pressure for gases, 1 M for concentrations in solution, and to the pure substances for liquids and solids.

2. Table 16-1 compiles some data for S^o, the molar entropy, and ΔG_f^o, the free energy of formation from the elements. All values in Table 16-1 are presented at 25°C and at standard states. Notice that the units of entropy and free energy are stated *per mole*, mol^{-1}. This means that the moles used to balance a chemical reaction are included by the multiplication of the coefficient (mol in balanced equation) and the value from the table so that unit *mol* cancels. This is also the way in which we handled calculations involving ΔH values.
3. The third law allows the determination of the entropy of a substance without reference to its specific elements. However, if elements are important to the procedure, ΔG in the ground state is zero. As an example: the standard state of Br_2 is a liquid at 25°C (the temperature of Table 16-1's entries) and its ΔG is 0; but bromine can exist as a liquid at 25°C, which is not the ground state. The ΔG for $Br_2(l)$ is 3.14 kJ/mol.
4. Unless otherwise stated, standard state values are provided at 1 atm. Although 1 bar can also be used, there is a slight difference in the values. We choose to use atm, rather than bar.

In general, for the reaction

$$aA + bB \rightleftharpoons cC + dD$$

Table 16-1 Standard entropies and free energies of formation (25°C and 1 atm)

Substance	S^o (J/mol)	ΔG_f^o (kJ/mol)
$Ag_2O(s)$	121.3	−11.21
$Br_2(l)$	152.23	0
$Br_2(g)$	245.35	+3.14
$C(s$, graphite)	5.74	0
$CH_3OH(l)$	126.8	−166.36
$CH_3OH(g)$		−162.00
$C_2H_5OH(g)$	282.6	−168.57
$CO(g)$	197.56	−137.15
$CO_2(g)$	213.8	−394.37
$Cl_2(g)$	222.96	0
$Cl_2O(g)$	266.10	+97.9
$H_2(g)$	130.57	0
$H_2O(l)$	69.95	−237.19
$H_2O(g)$	188.72	−228.59
$N_2(g)$	191.50	0
$NO_2(g)$	239.95	+51.30
$N_2O_4(g)$	304.18	+97.82
$O_2(g)$	205.03	0
$PCl_3(l)$	217.1	−272.4
$PCl_3(g)$	311.7	−267.8
$PCl_5(g)$		−305.0
$SO_3(s)$	52.3	−369.0
$SO_3(l)$	95.6	−368.4
$Sn(s$, white)	51.5	0
$Sn(s$, gray)	44.1	+0.12

Note: S is in J, but ΔG_f^o is in kJ.

the concentration dependence of the free-energy change may be expressed as

$$\Delta G = \Delta G^{\circ} + RT \ln \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} \qquad (16\text{-}5)$$

In this equation, the square brackets [substance] are used to state that the substance is expressed in concentration units of mol/L. Further, the mathematical relationship relies on the natural log, abbreviated ln, not the log base 10, log. ΔG is the free-energy change at the given concentrations. ΔG° (*standard* free energy change) is the free-energy change for the hypothetical reaction in which all reactants and products are in their standard states. A point of interest is, if the concentration of every species is 1, the logarithmic term in (*16-5*) becomes 0. This makes $\Delta G = \Delta G^{\circ}$, which is as it should be, because unit concentration implies the standard state.

In (*16-5*), if ΔG is to be expressed in joules, the universal gas constant must be taken as

$$R = 8.3145\ \mathrm{J/K \cdot mol}$$

Because the units included in Table 16-1 are in joules and kilojoules, the value of R must be stated in terms of joules, not calories. However, if there is a necessity for expressions in calories, the conversion from joules to calories is $4.184\ \mathrm{J} = 1\ \mathrm{cal}$. (*Note*: $1\ \mathrm{kcal} = 1\ \mathrm{Cal} = 4.184\ \mathrm{kJ}$.)

On the right side of equation (*16-5*), the term ΔG° lacks the unit mol^{-1}, which must be removed from the second term as well, having been absorbed into the logarithmic term (the fraction) by mathematical manipulation.

The generalization of (*16.5*) to any number of reactants and products is

$$\Delta G^{\circ} = -RT \ln Q \qquad (16\text{-}6)$$

where Q is the *reaction quotient*, which is the term following the "ln" (natural logarithm) in (*16-5*), but, of course, must include all reactants and products in the chemical reaction, except pure solids and liquids.

CHEMICAL EQUILIBRIUM

In theory, any chemical reaction could proceed at the same time in the reverse direction to some extent. In practice, this is not usually the case. Often, the *driving force* of a reaction favors one direction so greatly that the extent of the reverse reaction is so small that it is impossible to measure. The driving force of a chemical reaction is the *change in free energy* accompanying the reaction and it is an exact measure of the tendency of the reaction to go to completion. The possibilities are:

1. When the magnitude of ΔG° is very large and the sign negative, the reaction may go practically to completion in the forward direction. (Note that the positive sign on ΔG° indicates that the reaction will tend to go in the reverse direction from that written.)
2. If ΔG° is only slightly negative, the reaction may proceed to a small extent until it reaches a point where ΔG (calculated from ΔG° values) for any further reaction would be zero. The reaction could be reversed with a slight change in concentrations.

In the last case, the reaction is said to be thermodynamically reversible. Since many organic and metallurgical reactions are of this reversible type, it is necessary to learn how conditions should be altered to obtain economically advantageous yields, speed up desirable reactions, and cut down on undesirable reactions.

A chemical system which has reached the reversible thermodynamic state shows no further *net* reaction, since $\Delta G^{\circ} = 0$. This does not mean that nothing is occurring. Actually, the chemical reactions in both directions continue, but at the same rate. This means that each move to the right has an equal move to the left, which is the definition of a *dynamic equilibrium*. (*Dynamic* means that something is happening, as opposed to a *static* situation, which is unchanging.) Dynamic reactions are characterized by the forward and reverse reactions occurring at the same rate, but in opposite directions. The result is no net change in concentrations, but there is still a lot going on chemically.

THE EQUILIBRIUM CONSTANT

For a reversible reaction at equilibrium,

$$0 = \Delta G^{\text{o}} + RT \ln Q_{eq}$$

or

$$\Delta G^{\text{o}} = -RT \ln Q_{eq} \tag{16-7}$$

Equation (*16-7*) is a remarkable statement. It implies that Q_{eq}, the value of the reaction quotient under equilibrium conditions, *depends only on thermodynamic quantities that are constant in the reaction* (the temperature, and the *standard* free-energy change for the reaction at that temperature), *and is independent of the actual starting concentrations of reactants or products*. For this reason, Q_{eq} is usually denoted the *equilibrium constant*, K, and (*16-7*) is rewritten as

$$\Delta G^{\text{o}} = -RT \ln K \tag{16-8}$$

EXAMPLE 2 Consider the reversible reaction below in which the participants are gases:

$$H_2 + I_2 \rightleftharpoons 2HI$$

A reaction mixture could be made up by starting with H_2 and I_2 alone, HI and I_2, HI alone, or a mixture of all three substances. Regardless of how we start, a net reaction would occur in one direction or the other until the system comes to an eventual state of no further net change (an *equilibrium*). That equilibrium could be described by specifying the concentration of the three substances. Because of the variety of ways of making up the initial mixture (differing relative amounts of substances), there are an infinite number of equilibrium states. Each of these equilibrium states can be described by a set of concentrations of the three substances. However, a ratio describes the relationships of the concentrations K:

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

That is, the particular function of the three concentrations defined by Q (reaction quotient) is always the same at equilibrium. This is true even though any individual concentration may vary by as much as a magnitude of 10. This unifying principle allows the calculation of conditions at equilibrium under virtually any set of conditions.

Experimental measurements show that molecules in highly compressed gases or highly concentrated solutions, especially if electrically charged, abnormally affect each other. In such cases the true *activity* or *effective concentration* may be greater or less than the measured concentration. Therefore, when the molecules involved in equilibrium are relatively close together, the concentration should be multiplied by an *activity coefficient*, which is determined experimentally. At moderate pressure and solutions, the activity coefficient for nonionic compounds is close to unity, indicating little in the way of molecular interactions. In any event, the activity coefficient correction will not be made in the problems in this book.

The equilibrium constant, K, is a pure number (no units) whose magnitude depends not only on the temperature, but also, generally, on the standard-state concentration to which all concentrations are referred. In this chapter, the standard state for dissolved substances will be taken as a 1 M concentration, unless a statement is made to the contrary. The magnitude of K is independent of the choice of standard concentration in the special case where the sum of the concentration exponents in the numerator equals the sum of the exponents in the denominator.

The concentration of a gas is proportional to its partial pressure ($n/V = P/RT$ where [gas] $= n/V$). Consider the following equilibrium in which all the participants are gases:

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$

The equilibrium constant for this reaction can be written as

$$K_p = \frac{P^c(\mathrm{C})P^d(\mathrm{D})}{P^a(\mathrm{A})P^b(\mathrm{B})}$$

K_p can replace K in equation (*16-8*). If ΔG° is obtained from a table based on the standard state of 1 atm, K_p will normally be correct only for P in atmospheres. If the values are for a standard state of 1 bar, then K_p will normally apply only to P in bars. When the equation shows no change in the total number of moles of gas as the reaction proceeds (e.g., $N_2 + O_2 \rightleftharpoons 2NO$), K_p will be the same, regardless of the pressure units used and will be identical with the K expressed in molar concentrations.

The values for pure solids and liquids are usually omitted from the K expression because their concentrations vary only slightly. Additionally, the concentrations of pure solids and liquids are extremely large in comparison to the concentrations of gases and dissolved materials (normally, as measured in mol/L). This includes situations when the solvent is one of the products or reactants, as in the following, the hydrolysis of urea in aqueous solution:

$$\mathrm{CO(NH_2)_2 + H_2O \rightleftharpoons CO_2 + 2NH_3} \qquad \mathrm{K} = \frac{[\mathrm{CO_2}][\mathrm{NH_3}]^2}{[\mathrm{CO(NH_2)_2}]}$$

1. Notice that water has been left out of the K expression; this is because it is the solvent. The concentration of water cannot be much less than that of pure water, 55.6 mol/L. This concentration is much larger than the solute, especially in moderately dilute to very dilute solutions (nearly all the solutions that are used in laboratories).
2. Also, notice that the molar concentration of ammonia, NH_3, is squared. The reason for this is that the K expression is *the* ***product*** *of the products divided by the* ***product*** *of the reactants* and ammonia appears twice (coefficient of 2). Notice that there are *three* products and one usable reactant (no water).

$$\mathrm{CO(NH_2)_2 + H_2O \rightleftharpoons CO_2 + 2NH_3} \qquad \text{rewritten as} \qquad \mathrm{CO(NH_2)_2 + H_2O \rightleftharpoons CO_2 + NH_3 + NH_3}$$

$$K = \frac{[\mathrm{CO_2}] \times [\mathrm{NH_3}] \times [\mathrm{NH_3}]}{[\mathrm{CO(NH_2)_2}]} = \frac{[\mathrm{CO_2}][\mathrm{NH_3}]^2}{[\mathrm{CO(NH_2)_2}]}$$

LE CHATELIER'S PRINCIPLE

The statement of Le Chatelier's principle is generally *if a system at equilibrium is stressed, the reaction will shift to relieve that stress.* Chemical reactions can be exposed to stresses including a change in temperature, a change in pressure, a change in concentration of one or more of the participants, and others.

Effect of changes in temperature

The effect of an increase in temperature of a system at equilibrium is a shift in the direction which absorbs heat.

EXAMPLE 3 In the equation for the synthesis of methanol, where all substances are gases,

$$\mathrm{CO + H_2 \rightleftharpoons CH_3OH} \qquad \Delta H = -22\,\mathrm{kcal}$$

the forward reaction liberates heat ($-\Delta H$, exothermic), while the reverse reaction absorbs heat ($+\Delta H$, endothermic, numerically to the same extent). If the temperature of the system is raised, the reverse reaction (right to left) occurs in an attempt to absorb the heat being supplied. Eventually, a new equilibrium will be established, which would have a higher concentration of reactants (CO and H_2) and less product than at the initial temperature. Of course, if the production of methanol is important commercially, a lower temperature would favor the forward reaction, producing more methanol.

There are calculations that will support the above argument. The equation required is

$$\Delta G = \Delta H - T\Delta S \tag{16-9}$$

or, if all are in standard states,

$$\Delta G^{\mathrm{o}} = \Delta H^{\mathrm{o}} - T\Delta S^{\mathrm{o}} \tag{16-10}$$

Combination of (*16-8*) and (*16.10*) gives

$$\ln K = -\frac{\Delta H^{\mathrm{o}}}{RT} + \frac{\Delta S^{\mathrm{o}}}{R} \tag{16-11}$$

If ΔH^{o} and ΔS^{o} are fairly independent of temperature, as they are for most reactions, (*16-11*) shows that ln K is a decreasing function of T for $\Delta H^{\mathrm{o}} < 0$ (exothermic reaction). Then, K itself is a decreasing function of T. A decrease in K means a shift of the equilibrium to favor the formation of the substances whose concentrations appear in the denominator of the K expression (the reactants).

In the event that $\Delta H^{\mathrm{o}} > 0$ (endothermic), K increases with T, and the equilibrium shifts to favor the formation of the products.

Effect of changes in pressure

When the pressure of a system at equilibrium increases, the reaction occurs in the direction that lowers the pressure by reducing the volume of gas.

EXAMPLE 4 In the synthesis of methanol (all substances gases), the forward reaction is accompanied by a decrease in volume. The total number of moles gas is less on the right than on the left of this reaction:

	$CO + 2H_2$	$\rightleftharpoons$	CH_3OH	
	3 moles gas		1 mole gas	
Then,	3 volumes gas		1 volume gas	ideal gas behavior assumed

A shift to the right will relieve the increase in pressure. It is important to recognize that the value for K does not change with the increase in pressure; only the pressures change.

Another way to increase the yield of methanol is shown in Fig. 16-1. This a way to increase the pressure by reducing the volume of the system. The system will respond to reduce the pressure by shifting to the right, increasing the yield of methanol.

A pressure change will *not* affect the relative amounts of the substances at equilibrium in any gaseous system where the number of molecules reacted equals the number produced. For example, there is no change in concentration in the reaction, $H_2 + CO_2 \rightleftharpoons CO + H_2O$, because there is no advantage offered by a lower number of molecules (moles of gas) on a side. In other words, neither the forward nor the reverse reaction changes the net number of gas molecules.

Any effect of pressure on equilibrium systems involving mixed physical states (gas and solid or gas and liquid) is due to a change in the concentration of the molecules of gas. Generally, pure solids and pure liquids are

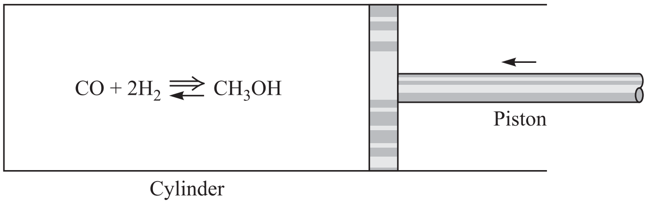


Fig. 16-1

not compressible and, therefore, there should not be a change in concentration of them with a change in pressure. It is possible to have changes in pressure that change the volume of solids or liquids, but the pressures involved are at or above thousands of atmospheres (not commonly encountered).

Effect of changes in amount of solvent

For reactions that take place in solution, increasing the amount of solvent (dilution) will displace the equilibrium in the direction of forming the larger number of dissolved particles. This is pretty much the same concept as discussed above in relation to the behavior of gases.

EXAMPLE 5 Consider the production of a *dimer* (a molecule composed of two building blocks) of acetic acid in benzene solution.

$$2HC_2H_3O_2(\textit{2 particles in solution}) \rightleftharpoons (HC_2H_3O_2)_2(\textit{1 particle in solution}) \qquad K = \frac{[(HC_2H_3O_2)_2]}{[HC_2H_3O_2]}$$

Let us imagine this reaction at equilibrium. If the solution is suddenly diluted to twice its original volume, and if the reaction has not yet occurred, the concentrations are $\frac{1}{2}$ what they were before the dilution. In the equilibrium constant expression, the numerator would be $\frac{1}{2}$ its original value and the denominator would be $\frac{1}{4}$ its former value $\left(\frac{1}{2}\text{ squared}\right)$. The ratio of the numerator to the denominator would become 2 times its original value $\left(\frac{1}{2}\text{ divided by }\frac{1}{4}\right)$. But this ratio must return to its original value of K (K does not change under these conditions). It can do this if the numerator becomes smaller and the denominator larger. In other words, some of the dimer, $(HC_2H_3O_2)_2$, must decompose to form acetic acid, $2HC_2H_3O_2$.

Changes in the amount of solvent will not affect the equilibrium in any system where the number of dissolved particles of reactants is the same as the dissolved particles of products. For example, the esterification of methyl alcohol with formic acid in an inert solvent, as below, does not respond to concentration changes. Note that, if the solvent is not water, then H_2O must be in the K expression.

$$CH_2OH + HCO_2H \rightleftharpoons HCO_2CH_3 + H_2O$$

Effect of varying the concentration

Increasing the concentration of any component of a system at equilibrium will cause a shift resulting in using up some of the added substance. For examples, suppose we were to add some hydrogen to the reaction below in which all participants are gases.

$$H_2 + I_2 \rightleftharpoons 2HI$$

The reaction is no longer at equilibrium (more iodine than originally); the response to this stress is to shift to the right (using up some of the iodine). Naturally, some hydrogen is used up and some HI is produced during the shift. Since the value of K does not change, the final concentrations are calculated from it by substituting into the K expression.

A note of caution: Many of problems where concentrations change cannot be solved by a simple algebraic technique because there are exponents involved. For those solutions that involve a square, the quadratic formula may be necessary [Problem 16.12(*c*)]. Memorization of the formula is a good idea because many professors expect you to know it during a test (assuming you cannot use a formula sheet).

Effect of catalysts

Catalysts accelerate both forward and reverse reaction rates equally. However, catalysts can be used to shorten the amount of time it takes to reach equilibrium when the original concentrations do not match equilibrium concentration.

Solved Problems

THERMODYNAMICS

16.1. Without consulting entropy tables, predict the sign of ΔS for each of the following:

(*a*) $O_2(g) \rightarrow 2O(g)$
(*b*) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
(*c*) $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$
(*d*) $Br_2(l) \rightarrow Br_2(g)$
(*e*) $N_2(g, 10\,\text{atm}) \rightarrow N_2(g, 1\,\text{atm})$
(*f*) Desalination of seawater.
(*g*) Devitrification of glass.
(*h*) Hard-boiling an egg.
(*i*) $C(s, \text{graphite}) \rightarrow C(s, \text{diamond})$

(*a*) Positive. There is an increase in the number of gas molecules.

(*b*) Negative. There is a decrease in the number of gas molecules.

(*c*) Positive. There is an increase in the number of gas molecules.

(*d*) Positive. S is always greater for a gas than for its corresponding liquid.

(*e*) Positive. Entropy increases on expansion.

(*f*) Negative. Desalination is the opposite of solution; a solute must be removed from a solution.

(*g*) Negative. Devitrification is the onset of crystallization in a supercooled liquid.

(*h*) Positive. The process of "boiling" an egg is not boiling, but the denaturation of the egg protein (the egg does not boil). A protein is a large molecule which exists in a particular configuration in the so-called native state. But it may occupy a large number of almost random configurations in the denatured state resulting from rotations around the bonds. The change in configuration during the cooking process requires energy and results from rotations around the bonds.

(*i*) Negative. Diamond, being a harder solid, would be expected to have more restricted atomic motions within the crystal. Therefore, diamond is more dense and has less entropy than graphite.

16.2. Calculate ΔS for the following phase transitions: (*a*) melting of ice at 0°C, and (*b*) the vaporization of water at 100°C. Use data from Chapter 7.

(*a*)
$$\Delta H \text{ of fusion of ice} = 1.44\,\text{kcal/mol} \qquad \text{or} \qquad 6.02\,\text{kJ/mol}$$

Since the melting of ice at 0°C is a reversible process, (*16-2*) may be used with the equals sign. (Recall that $q = \Delta H$ at constant pressure.)

$$\Delta S = \frac{q_{\text{reverse}}}{T} = \frac{6.02 \times 10^3\,\text{J/mol}}{273\,\text{K}} = 22.0\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \qquad \text{or} \qquad 22.0\,\text{J/K}\cdot\text{mol}$$

(*b*)
$$\Delta H_{\text{vaporization of water}} = 9.72\,\text{kcal/mol} \qquad \text{or} \qquad 40.7\,\text{kJ/mol}$$

Since the vaporization at 100°C is reversible, (*16-2*) may be used with the equals sign.

$$\Delta S = \frac{q_{\text{reverse}}}{T} = \frac{4.07 \times 10^4\,\text{J/mol}}{373\,\text{K}} = 109\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \qquad \text{or} \qquad 109\,\text{J/K}\cdot\text{mol}$$

16.3. After comparing data in Table 7-1 and the answer to Problem 16.1(*i*), how do you account for the fact that ΔH and ΔS for the phase transition from diamond to graphite are not related by the same equation that applied in Problem 16.2?

From Table 7-1, the formation of diamond from graphite (the standard state of carbon) is accompanied by a *positive* ΔH of 1.88 kJ/mol at 25°C. From Problem 16.1(*i*), ΔS for the same process is *negative*. Since 25°C is not the transition temperature, the process is not a reversible one. In fact, it is not even a spontaneous irreversible process, and (*16-2*) does not apply with the inequality sign. On the contrary, the opposite process, the conversion of diamond to graphite at 1 atm, is thermodynamically spontaneous. The ΔS for *this* process would obey (*16-2*) with the inequality sign. This means that "diamonds are *NOT* forever!" The term "spontaneous" does not cover the speed of reaction; in this case, the reaction is so slow at normal life temperatures that it is not considered to be happening. So, the diamonds will be around for a long, long time.

16.4. Calculate ΔH_f° for $C_2H_5OH(g)$.

For the special process in which a substance in its standard state is formed from its elements in their standard states, *(16-12)* gives

$$\Delta G_f^{\circ} = \Delta H_f^{\circ} + T\Delta S_f^{\circ} \qquad \textit{(16-12)}$$

ΔH_f° can be calculated from *(16-12)* with the use of data from Table 16-1. Write the balanced equation for 1 mol $C_2H_5OH(g)$ produced from the elements. Write the S° values. Each of the S° values must be multiplied by the number of moles, *n*, necessary to balance the equation.

$$\begin{array}{lcccccc} & 2C(s) & +\ 3H_2(g) & +\ \frac{1}{2}O_2(g) & \rightarrow & C_2H_5OH(g) & \\ n\Delta S_f^{\circ}: & 2(5.74) & 3(130.57) & \frac{1}{2}(205.03) & & 1(282.6) & \text{all in J/K} \end{array}$$

Keeping in mind that we *lose the substances on the left and gain those on the right*,

$$\begin{aligned} \Delta S^{\circ} &= -(\text{sum of the reactants}) \qquad\qquad + (\text{sum of products}) \\ \Delta S^{\circ} &= -[2(5.74) + 3(130.57) + \tfrac{1}{2}(205.03)] + [1(282.6)] \\ \Delta S^{\circ} &= -223.1\ \text{J/K} \cdot \text{mol} \end{aligned}$$

Now, from *(16-12)*,

$$\begin{aligned} \Delta H_f^{\circ} &= \Delta G_f^{\circ} + T\Delta S_f^{\circ} \\ &= -168.57\ \text{kJ/mol} + (298.15\ \text{K})(-0.2231\ \text{kJ/K} \cdot \text{mol}) = -235.09\ \text{kJ/mol} \end{aligned}$$

Note that Gibbs free energy is listed as a single entry for each substance in Table 16-1, but entropy must be calculated by taking the difference of the tabulated absolute entropies of the substance and its elements from which it is made.

16.5. (*a*) What is the ΔG° at 25°C for this reaction?

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

(*b*) What is ΔG at 25°C under conditions where the partial pressures of H_2, CO_2, H_2O, and CO are 10, 20, 0.02, and 0.01 atm, respectively?

(*a*) The first step is to record the free energy values under each substance in the balanced equation.

$$\begin{array}{lccccc} & H_2(g) & +\ CO_2(g) & \rightleftharpoons\ H_2O(g) & + & CO(g) \\ n\Delta G_f^{\circ}: & 0 & 1(-394.37) & 1(-228.59) & & 1(-137.15) \end{array}$$

Then, the calculation of ΔG° is done in the same manner as that of ΔH° (Problem 7.12).

$$\Delta G = (0 - 394.37) - (-228.59 - 137.15) = 28.63\ \text{kJ}$$

(*b*) The calculation for ΔG° for the reaction including the partial pressures depends on

$$\begin{aligned} \Delta G &= \Delta G^{\circ} + RT \ln Q \\ &= (28.63\ \text{kJ}) + (8.314 \times 10^{-3}\ \text{kJ/K})(298.15\ \text{K}) \left[\ln \frac{P(H_2O)P(CO)}{P(H_2)P(CO_2)} \right] \\ &= \left[28.63 + 5.708 \log \frac{(0.02)(0.01)}{(10)(20)} \right] \text{kJ} = \left[28.63 + 5.708 \log 10^{-6} \right] \text{kJ} = [(28.63 - 6(5.708)]\ \text{kJ} \\ &= (28.63 - 34.25)\ \text{kJ} = -5.62\ \text{kJ} \end{aligned}$$

Note that the reaction, although not possible under standard conditions, becomes possible ($G < 0$) under this set of experimental conditions. Note the conversion from natural to common logarithms is by the factor of 2.3026.

16.6. Calculate the absolute entropy of $CH_3OH(g)$ at 25°C.

Although there is no S^o entry in Table 16-1 for CH_3OH, the ΔG_f^o value for this substance listed in Table 16-1, the ΔH_f^o value listed in Table 7-1, and the S^o values for the constituent elements may be combined to yield the desired value. From (*16-12*),

$$\Delta S_f^o = \frac{\Delta H_f^o - \Delta G_f^o}{T} = \frac{(-200.7 + 162.0)\,\text{kJ/K}\cdot\text{mol}}{298.15\,\text{K}} = -129.8\,\text{J/mol}$$

From the equation for the formation of 1 mol of CH_3OH under standard conditions,

$$C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(g)$$

we can write

$$\begin{aligned}-129.8\,\text{J/K} &= (1\,\text{mol})[S^o(CH_3OH)] - (1\,\text{mol})[S^o(C)] - (2\,\text{mol})[S^o(H_2)] - \left(\frac{1}{2}\,\text{mol}\right)[S^o(O_2)] \\ &= (1\,\text{mol})[S^o(CH_3OH)] - [5.7 + 2(130.6) + \frac{1}{2}(205.0)]\,\text{J/K}\end{aligned}$$

Solving for $S^o(CH_3OH)$, we received 239.6 J/K · mol

16.7. Estimate the boiling point of PCl_3.

The boiling point is the temperature at which G^o for the following reaction is zero.

$$PCl_3(l) \rightleftharpoons PCl_3(g)$$

The reaction is not spontaneous at 25°C, where, according to Table 16-1,

$$\Delta G^o = (1\,\text{mol})[\Delta G_f^o\,(PCl_3, g)] - (1\,\text{mol})[\Delta G_f^o\,(PCl_3, l)] = -267.8 + 272.4 = +4.6\,\text{kJ}$$

If we assume that ΔH^o and ΔS^o are both independent of temperature between 25°C and the boiling point, then the temperature dependence of ΔG^o is given by the factor T in (*16-10*). Further, if ΔH^o and ΔS^o are known from the data at 25°C, T can be calculated to satisfy the condition of ΔG^o equals zero.

$$\Delta G^o = \Delta H^o - T\Delta S = 0 \qquad \text{or} \qquad \text{T}_{\text{b.p.}} = \frac{\Delta H^o}{\Delta S^o}$$

Now,

$$\Delta S^o = (1\,\text{mol})[S^o(g)] - (1\,\text{mol})[S^o(l)] = 311.7 - 217.1 = +94.6\,\text{J/K}$$

and, from Table 7-1,

$$\Delta H^o = (1\,\text{mol})[\Delta H_f^o(g)] - (1\,\text{mol})[\Delta H_f^o(l)] = -287.0 - (-319.7) = +32.7\,\text{kJ}$$

Then, after converting so that the values are in the same units (we chose J, not kJ),

$$\text{T}_{\text{b.p.}} = \frac{\Delta H^o}{\Delta S^o} = \frac{32.7 \times 10^3\,\text{J}}{94.6\,\text{J/K}} = 346\,\text{K}$$

or an estimated temperature of 73°C. The observed boiling point, 75°C, is very close to the estimated.

EQUILIBRIUM

16.8. For the gaseous reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

explain the effect on the equilibrium of (*a*) increased temperature; (*b*) increased pressure; (*c*) higher concentration of Cl_2; (*d*) higher concentration of PCl_5; and (*e*) presence of a catalyst.

(*a*) The effect of the increase in temperature is to shift the equilibrium in the direction that absorbs heat. Table 7-1 can be used to determine that the forward reaction as written is endothermic,

$$\begin{aligned}\Delta H &= (1\ \text{mol})[\Delta H_f^\circ(PCl_3)] + (1\ \text{mol})[\Delta H_f^\circ(Cl_2)] - (1\ \text{mol})[\Delta H_f^\circ(PCl_5)]\\ &= -287.0 + 0 - (-374.9) = +87.9\ \text{kJ}\end{aligned}$$

So, increasing the temperature will cause the dissociation of PCl_5.

(*b*) When the pressure of a system at equilibrium is increased, the equilibrium point is displaced in the direction of the smaller volume. One volume each of PCl_3 and Cl_2 (2 gas volumes) forms one volume of PCl_5. The pressure increase will shift the reaction to the left.

(*c*) Increasing the concentration will shift the equilibrium in the direction that will reduce that concentration in the effort to re-establish the equilibrium. The shift will be to the right.

(*d*) Using the same line of logic in (*c*), the shift will be to the left.

(*e*) Since catalysts speed up both the forward and reverse reactions to the same extent and do not favor either direction, there is no difference in the equilibrium.

16.9. What conditions would you suggest for the manufacture of ammonia by the Haber process?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -22\ \text{kcal}$$

From the sign of ΔH, the forward reaction is exothermic (gives off heat) and we know that the forward reaction is favored. However, we can shift the equilibrium to the right by dropping the temperature, except that reactions tend to progress more slowly at low temperatures. A catalyst would help increase the rate of reaction, but by itself the catalyst would not increase the output of ammonia.

We can shift the reaction to the right by increasing the concentration of N_2 or H_2, or both reactants. A shift to the right will also occur if NH_3 is removed. We can also cause a shift to the right by running the reaction at high pressure (left, 4 volumes; right, 2 volumes). If the reaction were to be run at high pressure and high temperature (to increase the rate of reaction), the shift to the right would be expected.

16.10. All reactants and products are gases.

(*a*) Calculate ΔG° and K_p for this reaction at 25°C:

$$2NO_2 \rightleftharpoons N_2O_4$$

(*b*) Calculate ΔG° and K_p for the reverse reaction:

$$N_2O_4 \rightleftharpoons 2NO_2$$

(*c*) Calculate the ΔG° and K_p for the forward reaction (*a*) written with different coefficients:

$$NO_2 \rightleftharpoons \frac{1}{2}N_2O_4$$

(*d*) Repeat calculation (*a*) for a standard state pressure of 1 bar (a little above 1 atm). For $NO_2(g)$, ΔG_f° is 51.32 kJ/mol, and for $N_2O_4(g)$ it is 97.89 kJ/mol (both are at 1 bar).

(*a*)
$$\Delta G^{\circ} = (1\,\text{mol})[\Delta G_f^{\circ}(\text{N}_2\text{O}_4)] - (2\,\text{mol})[\Delta G_f^{\circ}(\text{NO}_2)]$$
$$= 97.82 - 2(51.30) = -4.78\,\text{kJ}$$

Since $\Delta G^{\circ} = -RT \ln K_p$ and by rearrangement,

$$\log K = \frac{-\Delta G^{\circ}}{2.303RT} = \frac{4.78 \times 10^3\,\text{J}}{(2.303)(8.3145\,\text{J/K})(298.2\,\text{K})} = 0.837$$
$$Kp = 6.87$$

(*b*)
$$\Delta G^{\circ} = (2\,\text{mol})[\Delta G_f^{\circ}(\text{NO}_2)] - (1\,\text{mol})[\Delta G_f^{\circ}(\text{N}_2\text{O}_4)]$$
$$= 2(5.30) - 97.82 = 4.78\,\text{kJ}$$

Since $\Delta G^{\circ} = -RT \ln K_p$ and by rearrangement,

$$\log K = \frac{-\Delta G^{\circ}}{2.303RT} = \frac{-4.78 \times 10^3\,\text{J}}{(2.303)(8.3145\,\text{J/K})(298.2\,\text{K})} = -0.837$$
$$K_p = 0.146$$

Parts (*a*) and (*b*) illustrate the general requirements that ΔG of a reverse reaction is the negative of ΔG for the forward reaction and K for a reverse reaction is the reciprocal of K (i.e., 1 divided by K) for the forward reaction.

(*c*)
$$\Delta G^{\circ} = \left(\frac{1}{2}\,\text{mol}\right)[\Delta G_f^{\circ}(\text{N}_2\text{O}_4)] - (1\,\text{mol})[\Delta G_f^{\circ}(\text{NO}_2)]$$
$$= \frac{1}{2}(97.82) - 51.30 = -2.39\,\text{kJ}$$

Since $\Delta G^{\circ} = -RT \ln K_p$ and by rearrangement,

$$\log K = \frac{-\Delta G^{\circ}}{2.303RT} = \frac{2.39 \times 10^3\,\text{J}}{(2.303)(8.3145\,\text{J/K})(298.2\,\text{K})} = 0.419$$

$$K_p = 2.62$$

Parts (*a*) and (*b*) illustrate the general result that ΔG for a reaction with halved coefficients is half the ΔG value for the standard coefficients. Further, K for the reaction with halved coefficients is the one-half power (i.e., square root) of the K for the standard reaction. Note that the value of the following ratio at equilibrium must be independent of the way we write the balanced equation:

$$\frac{P(\text{N}_2\text{O}_4)}{P^2(\text{NO}_2)}$$

Any equilibrium constant for the reaction must involve the two partial pressures in exactly this way. For part (*a*), K is equal to this ratio. For part (*c*), K is equal to the square root of this ratio.

(*d*)
$$\Delta G^{\circ} = (1\,\text{mol})[\Delta G_f^{\circ}(\text{N}_2\text{O}_4)] - (2\,\text{mol})[\Delta G_f^{\circ}(\text{NO}_2)]$$
$$= 97.89 - 2(51.32) = -4.75$$

Since $\Delta G^{\mathrm{o}} = -RT \ln K_p$ and by rearrangement,

$$\ln K_p = \frac{-\Delta G^{\mathrm{o}}}{2.303RT} = \frac{4.75 \times 10^3\ \mathrm{J}}{(8.3145\ \mathrm{J/K})(298.2\ \mathrm{K})} = 1.916$$

$$K_p = 6.79$$

Since 1 atm and 1 bar are close (1 atm = 1.013 bar), the differences are small, but not insignificant. K_p (bar) can also be calculated from K_p (atm) by simply converting units.

$$K_p(\mathrm{bar}) = \frac{P(\mathrm{atm})(\mathrm{N_2O_4}) \times 1.013}{[P(\mathrm{atm})(\mathrm{NO_2}) \times 1.013]^2} = \frac{K_p(\mathrm{atm})}{1.013} = \frac{6.87}{1.013} = 6.78$$

16.11. A quantity of PCl_5 was heated in a 12-L vessel at 250°C and reached the equilibrium below:

$$\mathrm{PCl_5}(g) \rightleftharpoons \mathrm{PCl_3}(g) + \mathrm{Cl_2}(g)$$

At equilibrium, the vessel contained 0.21 mol PCl_5, 0.32 mol PCl_3, and 0.32 mol Cl_2. (*a*) Calculate the equilibrium constant, K_p, for the dissociation of PCl_5 at 250°C when pressures are referred to the standard state of 1 atm. (*b*) What is ΔG^{o} for the reaction? (*c*) Estimate ΔG^{o} from the data in Tables 7-1 and 16-1, assuming constancy of ΔH^{o} and ΔS^{o}. (*d*) Calculate K_p from the original data using SI units and a standard state of 1 bar.

(*a*)

$$P(\mathrm{PCl_5}) = \frac{nRT}{V} = \frac{(0.21\ \mathrm{mol})[0.0821\ \mathrm{L \cdot atm/mol \cdot K})](523\ \mathrm{K})}{12\ \mathrm{L}} = 0.751\ \mathrm{atm}$$

$$P(\mathrm{Cl_2}) = P(\mathrm{PCl_3}) = \frac{(0.32)(0.0821)(523)}{12} = 1.145\ \mathrm{atm}$$

$$K_p = \frac{P(\mathrm{PCl_3})P(\mathrm{Cl_2})}{P(\mathrm{PCl_5})} = \frac{(1.145)(1.145)}{0.751} = 1.75$$

(*b*)

$$\Delta G^{\mathrm{o}} = -RT \ln K = -(8.3145\ \mathrm{J/K})(523\ \mathrm{K}) \ln 1.75 = -2.4\ \mathrm{kJ}$$

(*c*)

$$\Delta G^{\mathrm{o}}_{298} = -267.8 + 305.0 = +37.2\ \mathrm{kJ}$$

$$\Delta H^{\mathrm{o}}_{298} = -287.0 + 374.9 = +87.9\ \mathrm{kJ}$$

At 298.2 K,

$$\Delta G^{\mathrm{o}} = \Delta H^{\mathrm{o}} - T\Delta S \qquad \Delta S^{\mathrm{o}} = \frac{\Delta H^{\mathrm{o}} - \Delta G^{\mathrm{o}}}{T} = \frac{(78.9 - 37.2)(1000)}{298.2} = +170.0\ \mathrm{J/K}$$

At 523 K,

$$\Delta G^{\mathrm{o}}_{523} = 87.9 - \frac{(523)(170.0)}{1000} = 87.9 - 88.9 = -1.0\ \mathrm{kJ}$$

The estimate is close to the experimentally determined value based on the equilibrium measurement. This is despite the large temperature range over which ΔH^{o} and ΔS^{o} were assumed constant.

(*d*)
$$P(\mathrm{PCl_5}) = \frac{nRT}{V} = \frac{(0.21\,\mathrm{mol})(8.3124\,\mathrm{m^3\cdot Pa/mol\cdot K})(523\,\mathrm{K})(1\,\mathrm{bar}/10^5\mathrm{Pa})}{(12\,\mathrm{L})(1\,\mathrm{m^3}/10^3\,\mathrm{L})} = 0.761\,\mathrm{bar}$$
$$P(\mathrm{Cl_2}) = P(\mathrm{PCl_3}) = \frac{(0.32)(8.3145)(535)(10^3)}{12\times 10^5} = 1.160\,\mathrm{bar}$$
$$K_p\ (\mathrm{bar}) = \frac{(1.160)(1.160)}{0.761} = 1.77$$

16.12. When 1 mol of pure ethyl alcohol is mixed with 1 mol of acetic acid at room temperature, the equilibrium mixture contains $\frac{2}{3}$ mol each of ester and water. (*a*) What is the equilibrium constant? (*b*) What is ΔG^o for the reaction? (*c*) How many moles of ester are formed at equilibrium when 3 mol of alcohol are mixed with 2 mol of acid? All substances are liquids at the reaction temperature.

(*a*) A table is a convenient way of doing the bookkeeping for equilibrium problems. Use the balanced equation because the amounts included in the lines must reflect the coefficients in the balanced equation. The first line (1) shows the amounts of starting materials. The second line (2) records changes, including the signs (− for materials lost and + for those appearing). The third line (3) is the simple addition of the other two lines. Line (3) is used to calculate the value of the equilibrium constant for the reaction.

	alcohol $C_2H_5OH(l)$	+	**acid** $CH_3COOH(l)$	⇌	**ester** $CH_3COOC_2H_5(l)$	+	**water** $H_2O(l)$
(1) *n* at start:	1		1		0		0
(2) Change by reaction:	$-\frac{2}{3}$		$-\frac{2}{3}$		$+\frac{2}{3}$		$+\frac{2}{3}$
(3) *n* at equilibrium:	$1-\frac{2}{3}=\frac{1}{3}$		$1-\frac{2}{3}=\frac{1}{3}$		$\frac{2}{3}$		$\frac{2}{3}$

Let v = liters of mixture. (Since we have not been given information from which we can calculate volume, we can take 1 mol/L as the standard-state concentration.) The calculation of K becomes

$$K = \frac{[\text{ester}][\text{water}]}{[\text{alcohol}][\text{acid}]} = \frac{\left(\frac{\frac{2}{3}}{v}\right)\left(\frac{\frac{2}{3}}{v}\right)}{\left(\frac{\frac{1}{3}}{v}\right)\left(\frac{\frac{1}{3}}{v}\right)} = 4$$

Note that the concentration of water in this experiment is not so large compared with the other reaction components that it remains constant under the reaction conditions. Water's concentration becomes extremely large when water is the solvent, but that is not the case with this reaction as the reactants are pure materials. Water must be included in the calculations for K.

(*b*)
$$\Delta G^\mathrm{o} = -RT\ln K = -(8.3145\,\mathrm{J/K})(298.2\,\mathrm{K})[(2.303)(\log 4)] = -3.44\,\mathrm{kJ}$$

Because K is independent of the choice of standard-state concentration (the product of the exponents in the numerator equals the product of the exponents in the denominator), so is ΔG^o.

(*c*) Let x = number of moles of alcohol reacting. Note that the amount of alcohol lost during the reaction is *the same* as that of the acid reacted. That amount is *the same* as the ester gained and the water gained. These gains and losses are dictated by the balanced equation, 1:1:1:1 ratio in this case.

$$C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

(1) *n* at start:	3	1	0	0
(2) Change by reaction:	$-x$	$-x$	$+x$	$+x$
(3) *n* at equilibrium:	$3-x$	$1-x$	x	x

$$K = 4 = \frac{[\text{ester}][\text{water}]}{[\text{alcohol}][\text{acid}]} = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\left(\frac{3-x}{v}\right)\left(\frac{1-x}{v}\right)} = \frac{x^2}{3-4x+x^2} \qquad \text{or} \qquad 4 = \frac{x^2}{3-4x+x^2}$$

The above becomes $x^2 = 4(3 - 4x + x^2)$ or $3x^2 - 16x + 12 = 0$. This equation requires the quadratic formula to solve for x.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{16 \pm \sqrt{16^2 - 4(3)(12)}}{2(3)} = \frac{16 \pm 10.6}{6} = 4.4 \text{ or } 0.9$$

Of the two values provided by the quadratic formula, only one has physical meaning and can usually be chosen easily. Keep in mind that the value of x is substituted back into the third line (3) in the table. Since 4.4 cannot be subtracted from 3 (look at the alcohol column) and give us an amount that makes sense, 0.9 is the value we must use. So, the answer to the original question is: 0.9 mol ester produced.

Note that, in more complex problems, especially if the equation to be solved exceeds the abilities of the quadratic formula (cubed values and higher), it may be best to find the equilibrium concentrations by a method of successive approximations. You would select a consistent set of concentration values near where it is guessed the answer will be. Then, the calculations for K are performed and repeated until a sufficiently precise result is reached.

It is always a good idea to check your work. The check for (c) is to substitute back into the K expression.

$$K = \frac{(0.9)(0.9)}{(2.1)(0.1)} = 3.86 = 4 \qquad \text{(within the limits of precision of the calculation)}$$

Note that the number of moles of ester formed is greater than the number of moles of ester in (a), 0.9 compared with 0.67 $\left(\text{from } \frac{2}{3}\right)$. This result was to be expected because the increased concentration of alcohol, one of the reactants, will shift the reaction to the right. More alcohol can be added to increase the yield of ester. Regardless of the amount of alcohol added, only 1 mole of ester can be produced before running out of acid (1 mole provided). In reality, there is a good chance that the reaction will not proceed as indicated by the equation (common with organic reactions), resulting in less ester than predicted. If the alcohol and acid are cheap compared to the ester, the yield of ester could be increased by adding either alcohol or acid (the cheaper of the two).

16.13. In a 10-L evacuated chamber, 0.5 mol H_2 and 0.5 mol I_2 are reacted at 448°C.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

At the given temperature, and for a standard state of 1 mol/L, $K = 50$. (a) What is the total initial pressure in the chamber and the pressure at equilibrium? (b) How many moles of I_2 remain unreacted at equilibrium? (c) What is the partial pressure of each component in the equilibrium mixture?

(a) Before the reaction progresses, the total number of gas molecules is $0.5 + 0.5 = 1$. At equilibrium, there has been no change in the total number of moles. The total initial pressure and that at equilibrium are the same and can be calculated from the ideal gas law.

$$P(\text{total}) = \frac{n(\text{total})RT}{V} = \frac{(1\text{ mol})\left(0.0821\,\frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(721\text{ K})}{10\text{ L}} = 5.9\text{ atm}$$

(b) Let x be the number of moles iodine reacting.

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
(1) n at start:	0.5		0.5		0
(2) Change by reaction:	$-x$		$-x$		$+2x$
(3) n at equilibrium:	$0.5 - x$		$0.5 - x$		$2x$

Note that the reaction ratio of H_2:I_2:HI is 1:1:2 and that must be reflected in the K expression. Regardless of how complete or incomplete the reaction may be, 2 mol HI are always formed for each mol H_2 and/or I_2 that react.

Since the number of moles of reactant gas equals the number of moles of product gas, moles may be used in place of concentrations (as in Problem 16-12), and $K_p = K$.

$$K_p = 50 = \frac{(2x)^2}{(0.5 - x)(0.5 - x)} \qquad \text{or} \qquad \sqrt{50} = 7.1 = \frac{2x}{0.5 - x}$$

$$2x = 7.1(0.5 - x) \qquad \text{and} \qquad x = 0.39$$

The above calculation is substituted into line (3), $0.5 - 0.39$, providing the information that 0.11 moles of I_2 are in excess at equilibrium.

A check of the solution is

$$K = \frac{(2x)^2}{(0.5 - x)(0.5 - x)} = 50$$

(*c*)

$$P(I_2) = \frac{n(I_2)}{n(\text{total})} \times (\text{total pressure}) = \left(\frac{0.11}{1}\right)(5.9\ \text{atm}) = 0.65\ \text{atm}$$

$$P(H_2) = P(I_2) = 0.65\ \text{atm}$$

$$P(\text{HI}) = (\text{total pressure}) - [P(H_2) + P(I_2)] = 5.9 - 1.3 = 4.6\ \text{atm}$$

or

$$P(\text{HI}) = \frac{n(\text{HI})}{n(\text{total})} \times (\text{total pressure}) = \left(\frac{0.78}{1}\right)(5.9\ \text{atm}) = 4.6\ \text{atm}$$

16.14. Sulfide ion in alkaline solution reacts with solid sulfur to form polysulfide ions having the formulas S_2^{2-}, S_3^{2-}, S_4^{2-}, and so on. The equilibrium constant for the formation of S_2^{2-} is 12, for S_3^{2-} is 130, and both are formed from S and S^{2-}. What is the equilibrium constant for the formation of S_3^{2-} from S_2^{2-} and S?

To avoid confusion, let us refer to the equilibrium constants for the various reactions by subscripts. Also, we note that only the ion concentrations appear in the equilibrium constant equations because solids (sulfur, in this case) are omitted from the calculations.

$$\begin{aligned} S + S^{2-} &\rightleftharpoons S_2^{2-} \qquad & K_1 &= [S_2^{2-}]/[S^{2-}] = 12 \\ 2S + S^{2-} &\rightleftharpoons S_3^{2-} \qquad & K_2 &= [S_3^{2-}]/[S^{2-}] = 130 \\ S + S_2^{2-} &\rightleftharpoons S_3^{2-} \qquad & K_3 &= [S_3^{2-}]/[S_2^{2-}] \end{aligned}$$

The desired constant, K_3, expresses the equilibrium ratio of S_2^{2-} and S_3^{2-} concentrations in a solution in equilibrium with solid sulfur. Such a solution must also contain sulfide ion, S^{2-}, resulting from the dissociation of S_2^{2-} (the reverse of the first reaction). Since all four species (S, S^{2-}, S_2^{2-}, and S_3^{2-}) are present, all the equilibria represented above must be satisfied. The three equilibrium ratios are not all independent because:

$$\frac{[S_3^{2-}]}{[S_2^{2-}]} = \frac{[S_3^{2-}]/[S^{2-}]}{[S_2^{2-}]/[S^{2-}]} \qquad \text{or} \qquad K_3 = \frac{K_2}{K_1} = \frac{130}{12} = 11$$

The result, $K_2 = K_1 K_3$, is a general one for any case where one chemical equation (the second in this case) can be written as the sum of two other equations (the first and third).

16.15. At 27°C and 1 atm, N_2O_4 is 20% dissociated into NO_2. (*a*) Find K_p. (*b*) Calculate the percent dissociation at 27°C and a total pressure of 0.10 atm. (*c*) What is the extent of dissociation in a 69-g sample of N_2O_4 confined in a 20-L vessel at 27°C?

(*a*) When 1 mol N_2O_4 dissociates completely, 2 mol NO_2 are formed. Since this problem does not specify a particular size vessel or a particular weight of sample, we are free to choose 1 mol (92 g) as the starting amount of N_2O_4. For the given total pressure of 1 atm, the table set up with the reaction is

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
n at start:	1		0
Change by reaction:	−0.20		+0.40
n at equilibrium:	0.80		0.40
Then, Mole fractions:	0.80/(0.80 + 0.40)		0.40/(0.80 + 0.40)
	0.667		0.333
and, Partial pressure = (mole fraction)(1 atm)	0.667 atm		0.333 atm

We can now calculate K_p using the partial pressures.

$$K_p = \frac{P(\text{NO}_2)^2}{P(\text{N}_2\text{O}_4)} = \frac{(0.333)^2}{0.667} = 0.167$$

(*b*) Let a = fraction of N_2O_4 dissociated at equilibrium, 0.1 atm total pressure.

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
n at start:	1		0
Change by reaction:	$-a$		$+2a$
n at equilibrium:	$1 - a$		$2a$

Then, Mole fractions: $(1 - a)/(1 + a)$ $\quad$ $2a/(1 + a)$

and, Partial pressure = (mole fraction)(1 atm) $\quad$ $((1 - a)/(1 + a) \times 0.1)$ atm $\quad$ $(2a/1 + a \times 0.1)$ atm

From (*a*), $K_p = 0.167$. Substituting into the expression,

$$0.167 = K_p = \frac{P(\text{NO}_2)^2}{P(\text{N}_2\text{O}_4)} = \frac{\left(\dfrac{2a}{1+a} \times 0.1\right)^2}{\dfrac{1-a}{1+a} \times 0.1} = \frac{0.4a^2}{1 - a^2}$$

or $0.4a^2 = 0.167(1 - a^2)$. Solving, $a = 0.54$, which translates to 54% dissociated at 27°C and 1 atm.

Note that a larger fraction of the N_2O_4 is dissociated at 0.1 atm than at 1 atm. This is in agreement with Le Chatelier's principle as decreasing the pressure should favor the side with the greater volume (2NO, rather than N_2O_4).

(*c*) If the sample were all N_2O_4, it would contain 69 g/92 g/mol = 0.75 mol. Let a be the fraction dissociation. The table we set up is as follows:

		$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
n at start:		0.75		0
Change by reaction:		$-0.75a$		$+2(0.75a)$
n at equilibrium:		$0.75 - 0.75a$		$2(0.75a)$
	or	$0.75(1 - a)$		$150a$

Because the total pressure is unknown, it is simplest to calculate the partial pressure directly from Dalton's law (Chapter 5).

$$P(\text{N}_2\text{O}_4) = \frac{n(\text{N}_2\text{O}_4)RT}{V} = \frac{[0.75(1-a)\,\text{mol}]\left(0.0821\,\dfrac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{k}}\right)(300\,\text{K})}{20\,\text{L}} = 0.92(1 - a)\,\text{atm}$$

$$P(\text{NO}_2) = \frac{n(\text{NO}_2)RT}{V} = \frac{1.50a}{0.75(1-a)}[0.92(1-a)\,\text{atm}] = 1.84a\,\text{atm}$$

Then,

$$0.167 = K_p = \frac{P(\text{NO}_2)^2}{P(\text{N}_2\text{O}_4)} = \frac{(1.84a)^2}{0.92(1-a)} = \frac{3.68a^2}{1-a}$$

or

$$3.68a^2 + 0.167a - 0.167 = 0$$

The quadratic formula is required to solve for a.

$$a = \frac{-0.167 \pm \sqrt{(0.167)^2 + 4(0.167(3.68))}}{2(3.68)} = \frac{-0.167 \pm 1.577}{7.36} = -0.24 \text{ or } +0.19$$

The negative is discarded (negative matter?... not likely!). The extent of dissociation is 19%.

16.16. (*a*) Under what conditions will $CuSO_4 \cdot 5H_2O$ be efflorescent at 25°C? (*b*) How good a drying agent is $CuSO_4 \cdot 3H_2O$ at the same temperature? The reaction is:

$$CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4 \cdot 3H_2O(s) + 2H_2O(g)$$

K_p at 25°C is 1.086×10^{-4}. The vapor pressure of water at 25°C is 23.8 torr.

(*a*) An *efflorescent* salt is one that loses water to the atmosphere. This will occur if the water vapor pressure in equilibrium with the salt is greater than the water vapor pressure in the atmosphere. The mechanism by which $CuSO_4 \cdot 5H_2O$ could be efflorescent is that the salt would lose 2 molecules of water and simultaneously form 1 formula unit of $CuSO_4 \cdot 3H_2O$ for each unit of the original salt that dissociates. Then, the above equilibrium equation would apply since all three components would be present.

Since $CuSO_4 \cdot 5H_2O$ and $CuSO_4 \cdot 3H_2O$ are both solids,

$$K_p = P(H_2O)^2 = 1.086 \times 10^{-4}$$

Taking the square root of both sides,

$$P(H_2O) = 1.042 \times 10^{-2}\ \text{atm}$$

where $P(H_2O)$ is the partial pressure of water vapor (relative to the standard state pressure of 1 atm) in equilibrium with the two solids. A conversion to torr is necessary for the comparison:

$$(1.042 \times 10^{-2}\ \text{atm})(760\ \text{torr/atm}) = 7.92\ \text{torr}$$

Since the $P(H_2O)$ of 7.92 is less than the vapor pressure of water at the same temperature (23.8 torr), $CuSO_4 \cdot 5H_2O$ will not always effloresce. It will effloresce only on a dry day when the partial pressure of water in the air is less than 7.92 torr. This will occur when the relative humidity is less than

$$\frac{7.92\ \text{torr}}{23.8\ \text{torr}} = 0.33 \qquad \text{which is } 33.3\%$$

(*b*) $CuSO_4 \cdot 3H_2O$ could act as a drying agent by reacting with 2 molecules of water to form $CuSO_4 \cdot 5H_2O$. Because of the equilibrium partial pressure of water discussed above, $CuSO_4 \cdot 3H_2O$ cannot absorb water from the air below that partial pressure, 7.92 torr. Many other drying agents can reduce the partial pressure of water below 7.92 torr (Problem 16.44).

To find the conditions under which $CuSO_4 \cdot 3H_3O$ would be efflorescent, we would have to know the equilibrium constant for another reaction. This reaction shows the dehydration of $CuSO_4 \cdot 3H_2O$,

$$CuSO_4 \cdot 3H_2O(s) \rightleftharpoons CuSO_4 \cdot H_2O(s) + 2H_2O(g)$$

Supplementary Problems

Tables 7-1 and 16-1 are to be used for the solution of the problems below. The data in the tables are based on experimental measurements and are subject to reevaluation. That means that the tables in different books may have some entries that do not agree with those in this book. However, the problems in this book were written from Tables 7-1 and 16-1 and the answers were calculated from them.

THERMODYNAMICS

16.17. Calculate S° at 25°C for PCl_5.

Ans. 364 J/K · mol

16.18. Calculate ΔH_f° for $Cl_2O(g)$ at 25°C.

Ans. 80.2 kJ/mol

16.19. Predict the phase-transition temperature for the conversion of gray to white tin at one atmosphere using the thermodynamic data in Table 16-1.

Ans. 9°C (the observed value is 13°C)

16.20. Consider the production of water gas: $C(s,\ \text{graphite}) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$. (*a*) What is ΔG° for this reaction at 25°C? (*b*) Estimate the temperature at which $\Delta G^{\circ} = 0$.

Ans. (*a*) 91.44 kJ; (*b*) 982 K. The extrapolation for this estimate is extended over such a large temperature range that an appreciable error might be expected. The experimental value is 947 K, which is not all that far from the estimate.

16.21. The ΔG_f° for the formation of HI(g) from its gaseous elements is -10.10 kJ/mol at 500 K. When the partial pressure of HI is 10 atm and that of I_2 is 0.001 atm, what must the partial pressure of hydrogen be to reduce the magnitude of ΔG to 0 at the same temperature?

Ans. 7.8×10^2 atm

16.22. Under what conditions could the decomposition of $Ag_2O(s)$ into $Ag(s)$ and $O_2(g)$ proceed spontaneously at 25°C?

Ans. The partial pressure of oxygen must be kept below 0.090 torr.

16.23. The S° for silver is 42.72 J/K · mol (*a*) Estimate the minimum temperature at which the decomposition of $Ag_2O(s)$ will proceed spontaneously (refer to Problem 16.22) when the oxygen pressure is 1.00 atm. (*b*) Make the same estimate when the partial pressure of oxygen is 0.21 atm.

Ans. (*a*) 466 K; (*b*) 425 K

16.24. The effect of changing the standard state from 1 atm to 1 bar is to raise the molar entropies, S°, of all gaseous substances by 0.109 J/k · mol at 298.2 K. Convert ΔG_f° of (*a*) $CH_3OH(l)$; (*b*) $CH_3OH(g)$; (*c*) $H_2O(l)$; and (*d*) Sn(s, gray) to the standard state of 1 bar. Assume that within the precision of the tables in this text, ΔH_f° of all substances is unchanged by this small change in standard state.

Ans. (*a*) -166.28 kJ/mol; (*b*) -161.95 kJ/mol; (*c*) -237.14 kJ/mol; (*d*) 0.12 kJ/mol

16.25. Given: $N_2 + O_2 \rightleftharpoons 2NO$ state the effect on the reaction equilibrium of (*a*) increased temperature; (*b*) decreased pressure; (*c*) higher concentration of O_2; (*d*) lower concentration of N_2; (*e*) higher concentration of NO; (*f*) presence of a catalyst.

Ans. Favors (*a*) forward reaction; (*b*) neither reaction; (*c*) forward reaction; (*d*) reverse reaction; (*e*) reverse reaction; (*f*) neither reaction.

16.26. Predict the effect upon the following reaction equilibria of (*a*) increased temperature; (*b*) increased pressure:

1. $CO(g) + H_2(g) \rightleftharpoons CO_2(g) + H_2(g)$
2. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
3. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
4. $H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$
5. $2O_3(g) \rightleftharpoons 3O_2(g)$
6. $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$
7. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
8. $C(s) + H_2O(g) \rightleftharpoons H_2(g) + CO(g)$
9. $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$
10. $C(s,\ \text{diamond}) \rightleftharpoons C(s,\ \text{graphite})$*

*This equilibrium can only exist under very special conditions. Density of diamond = 3.5; density of graphite = 2.3 g/cm^3.

Ans. F = favors the forward reaction, B = favors backward (reverse) reaction.

1. (*a*) B, (*b*) neither
2. (*a*) B, (*b*) F
3. (*a*) F, (*b*) B
4. (*a*) F, (*b*) B
5. (*a*) B, (*b*) B
6. (*a*) B, (*b*) F
7. (*a*) F, (*b*) B
8. (*a*) F, (*b*) B
9. (*a*) B, (*b*) F
10. (*a*) B, (*b*) B

16.27. Assuming that ΔH° and ΔS° remain constant, derive from equation (*16-11*) an expression relating K_1 at temperature T_1 to K_2 at temperature T_2.

Ans. $\ln(K_2/K_1) = (\Delta H^{\circ}/R)(T_2 - T_1)/T_2T_1$

16.28. For the neutralization reaction:

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$$

The ΔH° is -55.8 kJ. For the ionization of water, which is the reverse of the above, the equilibrium constant at 25°C is: $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$. This is a very important constant (**Memorize it**!), which appears throughout Chapter 17. Using the result of Problem 16.27, calculate K_w at (*a*) 37°C, normal human body temperature, and at (*b*) 50°C.

Ans. (*a*) 2.4×10^{-14}; (*b*) 5.7×10^{-14}

EQUILIBRIUM

16.29. When α-D-glucose is dissolved in water, it undergoes a partial conversion to β-D-glucose, a sugar of the same molecular mass but slightly different physical properties. At 25°C, this conversion, called *mutarotation*, stops when 63.6% of the glucose is in the β-form. Assuming that equilibrium has been attained, calculate K and ΔG° for the reaction, α-D-glucose $\rightleftharpoons$ β-D-glucose, at 25°C.

Ans. 1.75, -1.38 kJ

16.30. The equilibrium constant is 0.09 for the reaction, H_3BO_3 + glycerin $\rightleftharpoons$ (H_3BO_3-glycerin). How much glycerin would be added per liter of 0.10 molar H_3BO_3 solution so that 60% of the H_3BO_3 is converted to the boric acid-glycerin complex?

Ans. 1.7 mol

16.31. The equilibrium,

$$p\text{-xyloquinone} + \text{methylene white} \rightleftharpoons p\text{-xylohydroquinone} + \text{methylene blue}$$

may be studied conveniently by observing the difference in color between methylene blue and methylene white. One mmol of methylene blue was added to a liter of solution that was 0.24 M *p*-xylohydroquinone and 0.0120 M *p*-xyloquinone. It was found that 4.0% of the added methylene blue was reduced to methylene white. What is the equilibrium constant for the reaction? *Note*: The equation is balanced with 1 mole of each of the four substances.

Ans. 4.8×10^2

16.32. When SO_3 is heated to a high temperature, it decomposes by

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

A sample of pure SO_3 was sealed in a large cylinder fitted with a piston and heated to a high temperature, T. The equilibrium ratio $SO_2:SO_3$ was 0.152 and the total pressure was 2.73 atm. If the piston is pushed in to cut the volume in half, what will be the new pressure? (*Note*: Because of the degree of the equations involved, a solution is most readily obtained by successive approximations.)

Ans. 5.40 atm

16.33. Consider the equilibrium described in the previous problem. Instead of pushing in the piston, a quantity of $SO_3(g)$ equal to that already present is injected. This addition momentarily doubles the concentration of SO_3. (*a*) What is the new SO_3 pressure when equilibrium is restored with no temperature change? (*b*) What is its ratio of the equilibrium pressure to that pressure momentarily present at the time of injection (before reaction)? (*c*) Calculate a similar ratio for SO_2.

Ans. (*a*) 4.26 atm; (*b*) 0.96; (*c*) 1.54

16.34. A saturated solution of iodine in water contains 0.33 g I_2 per liter. More than this can dissolve in a KI solution because of the following equilibrium:

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

A 0.100 M KI solution (0.100 M I^-) actually dissolves 12.5 g iodine per liter, most of which is converted to I_3^-. (*a*) Assuming that the concentration of I_2 in all saturated solutions is the same, calculate the equilibrium constant for the above reaction with 1 molar solutions as standard states. (*b*) What is the effect of adding water to a saturated solution of I_2 in the KI solution?

Ans. (*a*) 7.1×10^2; (*b*) The reverse reaction is favored.

16.35. Consider the reaction: $H_2(g)+I_2(g) \rightleftharpoons 2HI(g)$. When 46 g of I_2 and 1.00 g of H_2 are heated to 470°C, the equilibrium mixture contains 1.90 g of I_2. (*a*) How many moles of each gas are present at equilibrium? (*b*) Calculate the equilibrium constant.

Ans. (*a*) 0.0075 mol I_2, 0.32 mol H_2, 0.35 mol HI; (*b*) $K = 50$

16.36. Exactly 1 mol each of H_2 and I_2 are heated in a 30-L previously evacuated chamber to 470°C. Using the value of K from Problem 16.35, determine (*a*) how many moles of each gas are present at equilibrium; (*b*) the total pressure in the chamber; (*c*) the partial pressures of I_2 and of HI at equilibrium. (*d*) If one additional mole of H_2 is introduced into the equilibrium system, how many moles of the original iodine will remain unreacted?

Ans. (*a*) 0.22 mol; (*b*) 4.1 atm; (*c*) $P(H_2) = P(I_2) = 0.45$ atm, $P(HI) = 3.2$ atm; (*d*) 0.065 mol

16.37. Consider the reaction: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. Calculate the number of moles Cl_2 present at equilibrium when 1 mol PCl_5 is heated at 250°C in a 10-L vessel. At 250°C, $K = 0.041$ for this dissociation based on the 1 mol/L standard state.

Ans. 0.47 mol

16.38. PCl_5 is introduced into an evacuated chamber and comes to equilibrium (see Problem 16.37), at 250°C and 2.00 atm. The equilibrium gas contains 40.7% Cl_2 by volume.

(*a*1) What are the partial pressures of the gaseous components at equilibrium?

(*a*2) From these data, calculate K_p at 250°C on the basis of the 1 atm standard state for the reaction written in Problem 16.37.

If the volume of the gas mixture is increased so that it is at 0.200 atm at 250°C, calculate:

(*b*1) The percent of PCl_5 that would be dissociated at equilibrium.

(*b*2) The percent by volume of Cl_2 at equilibrium.

(*b*3) The partial pressure of Cl_2 at equilibrium.

Ans. (*a*1) $P(Cl_2) = P(PCl_3) = 0.814$ atm, $P(PCl_5) = 0.372$ atm; (*a*2) 1.78 (*b*1) 94.8%; (*b*2) 48.7%; (*b*3) 0.0974 atm

16.39. At 46°C, K_p for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.67 at 1 bar. (*a*) Calculate the percent dissociation of N_2O_4 at 46°C and a total pressure of 0.507 bar. (*b*) What are the partial pressures of N_2O_4 and NO_2 at equilibrium?

Ans. (*a*) 50%; (*b*) $P(N_2O_4) = 0.17$ bar, $P(NO_2) = 0.34$ bar

16.40. Consider the reaction: $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$. If nitrosyl bromide (NOBr) is 34% dissociated at 25°C and a total pressure of 0.25 bar, calculate K_p for the dissociation at this temperature based on 1 bar standard state.

Ans. 1.0×10^{-2}

16.41. At 986°C, the equilibrium constant for the reaction below is 0.63:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

A mixture of 1 mol of water vapor and 3 mol of CO is allowed to come to equilibrium at a total pressure of 2 atm. (*a*) How many moles H_2 are present at equilibrium? (*b*) What are the partial pressures of the gases at equilibrium?

Ans. (*a*) 0.68 mol; (*b*) $P(CO) = 1.16$ atm, $P(H_2O) = 0.16$ atm, $P(CO_2) = P(H_2) = 0.34$ atm

16.42. Consider the reaction: $SnO_2(s) + 2H_2(g) \rightleftharpoons 2H_2O(g,\ \text{steam}) + Sn(l)$.

(*a*) Calculate K_p at 900 K; the equilibrium steam-hydrogen mixture was 45% H_2 by volume.

(*b*) Calculate K_p at 1100 K; the equilibrium steam-hydrogen mixture was 24% H_2 by volume.

(*c*) Would you recommend higher or lower temperatures for more efficient reduction of tin?

Ans. (*a*) 1.5; (*b*) 10; (*c*) higher

16.43. The preparation of quicklime from limestone is $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$. Experiments carried out between 850°C and 950°C led to a set of K_p values fitting an *empirically determined* (resulting from experimentation) equation

$$\log K = 7.282 - \frac{8500}{T}$$

where T is the absolute temperature. If the reaction is carried out in quiet air, what temperature would be predicted from this equation for the complete decomposition of the limestone? In quiet air, assume it is necessary to build up the CO_2 pressure to 1 atm to ensure continual removal of the product.

Ans. 894°C

16.44. The moisture content of a gas is often expressed in terms of the *dew point*, the temperature to which the gas must be cooled before it becomes saturated with water vapor. At this temperature, water (liquid or solid depending on the ambient temperature) will be deposited on a solid surface.

The efficiency of $CaCl_2$ as a drying agent was measured by a dew-point experiment. Air at 0°C was allowed to pass slowly over large trays containing $CaCl_2$. The air was them passed through a glass vessel through which a copper rod was sealed. The rod was cooled by immersing the part of the rod outside the vessel in a dry ice bath. The temperature of the rod inside the glass vessel was measured by a thermocouple. As the rod was cooled slowly, the temperature at which the first crystals of frost were deposited was observed to be −43°C. The vapor pressure of ice at this temperature is 0.07 torr. Assuming that the $CaCl_2$ owes its *desiccating* (ability to remove water from a gas mixture) properties to the formation of $CaCl_2 \cdot 2H_2O$, calculate K_p at 0°C for the reaction,

$$CaCl_2 \cdot 2H_2O(s) \rightleftharpoons CaCl_2(s) + 2H_2O(g)$$

Ans. 8×10^{-9}

16.45. At higher temperatures, the following equilibria result from reactions in a mixture of carbon, oxygen, and their compounds:

$$\begin{array}{rl} C(s) + O_2(g) \rightleftharpoons CO_2(g) & K_1 \\ 2C(s) + O_2(g) \rightleftharpoons 2CO(g) & K_2 \\ C(s) + CO_2(g) \rightleftharpoons 2CO(g) & K_3 \\ 2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) & K_4 \end{array}$$

If it were possible to measure K_1 and K_2 independently, how could K_3 and K_4 be calculated?

Ans. $K_3 = K_2/K_1$ and $K_4 = K_1/K_3 = K_1^2/K_2$

16.46. Consider this reaction including urea, $CO(NH_2)_2$, $CO_2(g) + 2NH_3(g) \rightleftharpoons CO(NH_2)_2(s) + H_2O(g)$. The ΔG_f° for urea is −197.2 kJ/mol. (ΔG_f° for NH_3 is −16.7; refer to Table 16-1 for others.) (*a*) Calculate the ΔG for the reaction. (*b*) Is the direction of the reaction spontaneous as written?

Ans. (*a*) $\Delta G = +2.03$ kJ; (*b*) No, ΔG is negative for a spontaneous reaction.

CHAPTER 17

Acids and Bases

The general principles of chemical equilibrium (Chapter 16) apply to reactions of neutral molecules and to reactions of ions. Chemical equilibria are of special interest, not only because they are used in commercial processes, but also because many of the reactions involved in life are equilibrium reactions. As in Chapter 16, concentrations will be expressed in mol/L and will be referred to in the mathematical relationships by enclosing the substance in square brackets. Further, these chapters are dedicated to the discussion of aqueous solutions. In other words: if the solvent is not identified, it is to be taken as water.

ACIDS AND BASES

Arrhenius concept

According to the classical definition as formulated by Arrhenius, an *acid* is a substance that can yield H^+ in aqueous solution. *Strong acids* are those that ionize completely in water, such as $HClO_4$ and HNO_3. These acids ionize by means of

$$HClO_4 \rightarrow H^+ + ClO_4^- \qquad \text{and} \qquad HNO_3 \rightarrow H^+ + NO_3^-$$

Weak acids are those that do not ionize completely and the dissociation of these acids provides us with an equilibrium reaction. A couple of examples are $HC_2H_3O_2$ and HNO_2.

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^- \qquad \text{and} \qquad HNO_2 \rightleftharpoons H^+ + NO_2^-$$

An equilibrium constant can be calculated. Since the substance on the left of the written reaction is an acid and is behaving as one by releasing H^+, the equilibrium constant is given a special symbol, K_a. For acetic acid, the K_a is calculated by

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^- \qquad K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} \qquad (17\text{-}1)$$

Note that the K_a expression is set up in the same way as the K's in Chapter 16: *K_a is the product of the products divided by the product of the reactants*, as in (*17-1*) above. As with any K, pure solids and liquids (including liquid water, the solvent, in these solutions) are not included in the K expression.

Bases are those substances that ionize in water to release OH^- ions. NaOH is a *strong base*, ionizing completely in water to yield Na^+ and OH^- ions. However, even those hydroxide bases that do not dissolve well, such as $Ca(OH)_2$, do ionize completely to the extent they dissolve. A *weak base* is one that does not ionize completely. As with the acids, a K expression can be calculated, and that expression is referred to as K_b (the K for a base, as in (*17-4*) below).

An interesting situation that may occur when ammonia, NH_3, dissolves in water is that hydroxide ions, OH^-, appear in the solution and the concentration is measurable. The implication is that NH_4OH forms, then ionizes to yield ammonium and hydroxide ions. This is logical, but NH_4OH has not been detected in aqueous solution. Since the OH^- concentration is only a few percent of the ammonia concentration, NH_3 is considered a weak base.

Brönsted-Lowry concept

The Brönsted-Lowry definition of an acid takes into account the nature of the solvent. Although water does not ionize well, it does ionize to a small extent. The result is the appearance of H^+ and OH^- ions in an equilibrium equation, which is

$$\mathrm{HOH} \rightleftharpoons \mathrm{H^+ + OH^-}$$

A point of this reaction is the release of H^+ ions—the Brönsted-Lowry approach considers this the appearance of a *proton* from the *acid*. A Brönsted-Lowry acid is a proton donor. Note that the hydrogen ion is a proton, hydrogen's nucleus without the electron found in the atom. Then, a Brönsted-Lowry acid must contain a hydrogen. Of course, if the solvent were not to be water, this statement may not work because the cation released could be other than the hydrogen ion, but there might be other ions performing the same service (liquid ammonia autoionizes, Problem 17.3).

The *base* in the Brönsted-Lowry concept is any substance that can accept the proton; it can even be the solvent. A Brönsted-Lowry base has an electron pair (a lone pair) that will accept the proton. The point that needs to be stressed here is that the proton is involved in both the definition of an acid (*donates a proton*) and a base (*accepts a proton*).

The Brönsted-Lowry concept looks at the equilibrium reaction and ties the acid on the left to a base on the right, called a *conjugate acid-base pair* or, more simply, a *conjugate pair*. Suppose we were to consider an acid reacting with a compound in equilibrium with the acid's anion and the products, as

$$\mathbf{HA} + \mathrm{B} \rightleftharpoons \mathbf{A^-} + \mathrm{BH^+} \qquad (17\text{-}2)$$

The conjugate pair would contain the acid, HA, on the left and A^- on the right (bold participants). A^- is the result of acid's loss of its proton (H^+). This relationship can be read as "A^- is the conjugate base of the acid, HA." A^- is a base, because in the reverse reaction (reading from right to left), it will accept a proton (H^+) and become the starting compound, HA.

B is a base, because it will accept the proton, whereas BH^+ is an acid. BH^+ is an acid because, if the reaction is read from right to left, it will give up the proton (H^+). So, the relationship can be read as "B is the conjugate base of the acid, BH^+."

Note that HA and B are not necessarily neutral. They could be ions that are capable of acting as an acid or a base. This is one of the features of the Brönsted-Lowry concept that broadens the definitions of acids and bases over the Arrhenius concept—there are many more substances that can behave as acids or bases. Further, we can write the reaction including the solvent, water in this case, and the associated K_a.

$$\mathrm{HC_2H_3O_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{C_2H_3O_2^-}(aq) \qquad K_a = \frac{[\mathrm{H_3O^+}][\mathrm{C_2H_3O_2^-}]}{[\mathrm{HC_2H_3O_2}]} \qquad (17\text{-}3)$$

Notice that water is not included in the K_a; it is a pure liquid and is omitted, as discussed in Chapter 16.

In a way similar to (*17-3*), we can write the ionization of the weak base, ammonia, and its K_b.

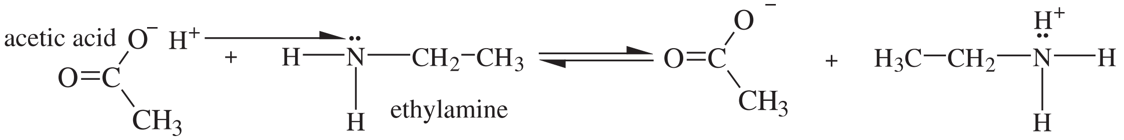
$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \qquad K_b = \frac{[\mathrm{NH_4^+}][\mathrm{OH^-}]}{[\mathrm{NH_3}]} \qquad (17\text{-}4)$$

Water can act as either an acid or a base, depending on the circumstances. This ability to act as either an acid or a base is referred to by stating that water is *amphoteric*. Water serves as a base in (*17-3*) and as an acid in (*17-4*). Note that the bare H^+ (a proton) becomes the *hydronium ion*, H_3O^+, which is a hydrated proton (H_3O^+ is $H^+ + H_2O$) because the bare proton does not really exist in solution. When we write the equilibrium constant expression for an aqueous equilibrium, we can use either the hydrogen ion, H^+, or the hydrated form, H_3O^+. Although the proton is hydrated in aqueous solution (as is the hydroxide), the use of H^+ and H_3O^+ is up to the style of the person working the problem and the problem itself. More often than not, leaving out water on both sides of the equation is used to keep the solutions to the problems visually simple. So long as water is in its standard state (liquid), it is not included in the K expression and, therefore, not necessary in the chemical equation.

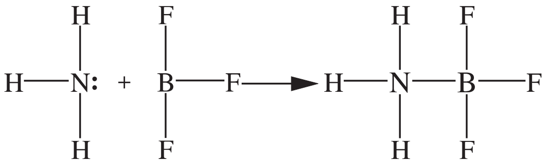
The strengths of acids can be compared in terms of their K_a's; the stronger the acid, the larger its K_a. This statement also applies to bases and their K_b's—the larger the K_b, the stronger the base. Also, the strengths of acids and bases are due to the magnitude of their respective K's in solvents other than water. For instance, HNO_3 is a strong acid in water and it is a weak acid in ethanol solvent—a K_a can be determined that is much smaller than that in water.

Lewis concept

Acids and bases, according to the Lewis concept, present an even more general picture than the two previous concepts. The Lewis *acid* is a structure which has an affinity for electron pairs—it can accept a share in a pair of electrons. A Lewis *base* is the structure that provides the electron pair. Notice the use of the word *structure*; this means that the Lewis acid or base does not necessarily have to be a compound. As a matter of fact, parts of a compound can function within the Lewis concept. An example of part of a compound acting is the amino group, $-NH_2$, which is included as the "amino" part of amino acids. There is an unshared pair of electrons on the nitrogen which can be shared, making the amino group a base. Additionally, by the definition, the hydrogen ion is the acid, not the acetic acid molecule.



Some other possible Lewis acids can be transition-metal ions, which can react with ligands (bases) to form complexes. Other substances that are short electrons are like BF_3, which can react with a base like NH_3 to form a compound, as below:



IONIZATION OF WATER

Since water is *amphiprotic* (meaning it can act as both an acid by releasing H^+ and as a base by releasing OH^-), every aqueous solution is characterized by *autoionization*, the process in which one H_2O molecule transfers a proton to another water molecule. The autoionization of water always occurs, whether or not there are other acids or bases in solution. A special K is assigned to the reaction:

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad K_w = [H^+][OH^-] \tag{17-5}$$

This is an example of a reaction in which we chose to write H^+ instead of H_3O^+, which is an acceptable procedure. As mentioned above, since water is the solvent, we know that all ions are hydrated and can take that for granted while writing the simpler form of the ion (H^+, instead of H_3O^+). Regardless, if water is included in the written reaction, it is *not* included in the K_w expression as it is a pure liquid. In this book, the problems involving concentrations of nonelectrolytes do not exceed 1 M and the concentrations of electrolytes do not exceed 0.1 M. For solutions containing larger concentrations of ions, the same laws of equilibrium apply if proper correction is made for the electrical interactions between ions, which is not covered in this book. Instead, examples have been chosen for which the numerical solutions should be correct to within 10 percent, even without such corrections.

At 25°C, $K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$; this value should be memorized (another factor related to water). In pure water (*no* solutes present), the concentrations of H^+ and OH^- must be equal. Therefore, at 25°C,

$$[H^+] = [OH^-] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}\text{M}$$

We can define a *neutral solution* as one in which $[H^+] = [OH^-] = \sqrt{K_w}$. The value of K_w varies with temperature; for instance, at 0°C, $K_w = 0.34 \times 10^{-7}$; however, most problems are written at 25°C or assuming 25°C when the temperature is not specified.

An *acid solution* is one that has a $[H^+]$ greater than 10^{-7} M. A *basic solution* is one in which the $[H^+]$ is less than 10^{-7} M. Having a hydrogen ion concentration less than 10^{-7} means that the hydroxide ion concentration is greater than 10^{-7} M. It is important to note that *as the hydrogen ion concentration decreases, the hydroxide ion increases*, and, of course, the reverse is true.

The acidity or *alkalinity* (basic extent) of a solution is often expressed by its *pH*, defined as

$$\text{pH} = -\log[H^+] \qquad \text{or} \qquad [H^+] = 10^{-\text{pH}}$$

We prefer to use the left-hand definition in this book, $\text{pH} = -\log[H^+]$. Similarly, we can define as

$$\text{pOH} = -\log[OH^-]$$

Taking the -log of both sides of (17-5), we find that the two measures are related by

$$\text{pH} + \text{pOH} = -\log K_w = 14.00 \qquad (\text{at } 25°\text{C}) \tag{17-6}$$

Note: These notations become more understandable if you consider that *p* stands for "take the negative log" of whatever follows. The following variable can be $[H^+]$, $[OH^-]$, for even K, as we will see shortly.

Table 17-1 summarizes the pH and pOH scales at 25°C.

The value of pK_a is a convenient expression for the expression of acid strength (pK_b for a base). pK_a is defined as $-\log K_a$. An example is an acid with the ionization constant of 10^{-4}; it will have a pK_a of 4. Similarly, $pK_b = -\log K_b$ for base values.

Table 17-1

$[H^+]$		$[OH^-]$	pH	pOH	Comment
1	$= 10^0$	10^{-14}	0	14	Strongly acidic
0.1	$= 10^{-1}$	10^{-13}	1	13	
0.001	$= 10^{-3}$	10^{-11}	3	11	
0.00001	$= 10^{-5}$	10^{-9}	5	9	Weakly acidic
0.0000001	$= 10^{-7}$	10^{-7}	7	7	Neutral
0.000000001	$= 10^{-9}$	10^{-5}	9	5	Weakly basic*
0.00000000001	$= 10^{-11}$	10^{-3}	11	3	
0.0000000000001	$= 10^{-13}$	10^{-1}	13	1	
0.00000000000001	$= 10^{-14}$	10°	14	0	Strongly basic

**Basic* and *alkaline* are terms with the same definition.
Note: An uncertainty of +10% $[H^+]$ corresponds to an uncertainty of 0.04 pH units.

HYDROLYSIS

A salt containing at least one ion which is conjugate to a weak acid or base undergoes a reaction with water of an acid-base nature. Let us look at $NaC_2H_3O_2$, a salt produced from a strong base, NaOH, and a weak acid, $HC_2H_3O_2$. The acetate ion in sodium acetate is conjugate to the acetic acid, a weak acid. The acetate ion is a base and can accept a proton from an acid or from the solvent (water):

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^- \qquad K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} \qquad (17\text{-}7)$$

The above reaction is called *hydrolysis* (literally, *splitting water*). As a result of this process, a solution of sodium acetate in water is basic because an excess of OH^- is produced; the OH^- released from the above reaction is added to pure water (neutral). Note that the reaction (*17-5*) is the sum of the reactions (*17-3*) and (*17-7*). The equilibrium constants for these three reactions must then be related as follows (see Problem 16.14):

$$K_w = K_a K_b \qquad \text{rearranged to} \qquad K_b = \frac{K_w}{K_a} \qquad (17\text{-}8)$$

An equation of the type (*17-8*) applies to the hydrolysis of any species which is the conjugate base to an acid having an ionization constant K_a. Some examples are CN^-, HS^-, SCN^-, NO_2^-. Since hydrolysis involves a reverse of acid dissociation, the tendency toward hydrolysis runs opposite to the tendency of the conjugate acid toward ionization. The weaker the acid, the greater the difficulty of removing a proton from the acid, and the easier for its anion (its conjugate base) to attach a proton from water (that is, to hydrolyze). This relationship appears mathematically as the inverse proportionality between K_a of the acid and K_b of the conjugate base. Acetic acid is a *moderately weak* acid, and the acetate ion hydrolyzes to a *slight* extent. HCN is a *very weak acid* and the cyanide ion, CN^-, hydrolyzes to a *great* extent. Chloride ion, on the other hand, does not undergo the hydrolysis reaction at all. The reason is that its conjugate acid, HCl, is a *strong acid* and cannot exist to any appreciable extent in dilute aqueous solution because Cl^- is an extremely weak base.

There is a clear example of a cation behaving as an acid. NH_4^+ is quite capable of losing a proton (the fourth hydrogen, which is really a hydrogen nucleus, H^+), and the conjugate base, NH_3, appears. Because of this situation, a solution of ammonium chloride, NH_4Cl, would be acidic.

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

K_a for NH_4^+ can be obtained from K_b for NH_3, its conjugate base, by rearranging equation (*17-8*).

$$K_a = \frac{K_w}{K_b}$$

Many heavy metal cations hydrolyze to some extent in aqueous solution in a reaction characterized by an equilibrium constant, K_a. As an example,

$$Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+ \qquad K_a = \frac{[Fe(OH)^{2+}][H^+]}{[Fe^{3+}]} \qquad (17\text{-}9)$$

This reaction is sometimes written with the hydrated forms of ions to show that the hydrated ferric ion, like the neutral acids, demonstrates its acidity by loss of a proton.

$$Fe(H_2O)_6^{3+} \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H^+$$

The two equations, (*17-9*) and the one directly above, are equivalent.

BUFFER SOLUTIONS AND INDICATORS

There are conditions under which a solution is resistant to a change in pH. For instance, distilled (or deionized) water, if totally neutral when produced, has a pH of 7.00. However, if that water is stored in containers that let in the smallest amount of air, the pH of the "pure" water drops into the acid range. A pH of 6.0 is not uncommon in the supposedly pure water used in laboratories. If it were possible to treat the water so that the H^+ that appears when CO_2 dissolves and reacts could be neutralized, the pH of the water would remain at or near 7.00. CO_2 and H_2O react as follows; H^+ end up in the solution:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \qquad \text{and} \qquad H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

A *buffer solution* (or a *buffered* solution) is a solution that is resistant to change when small amounts of acid or bases are added. Such a solution contains relatively large amounts of both a weak acid (or weak base) and its strong salt (one that ionizes very well). If a small amount of a strong acid (or base) is added to a buffer, most of the added H^+ (or OH^-) will combine with an equivalent amount of the weak base (or acid) of the buffer to form the conjugate acid (or base) of that weak base (or acid). The result is that the hydrogen ion and hydroxide concentrations in the solution display very little change.

Any pair of weak acid and base can be used to form a buffer solution, so long as each can form its conjugate base or acid in aqueous solution.

EXAMPLE 1 A particularly simple and common case of the buffer solution is one in which the weak acid and weak base are conjugates of each other. We could choose acetic acid as the weak acid and the acetate ion is, then, the weak base. Since relatively large amounts of each are needed, it would not be possible to use just a solution of the acid because the ionization equilibrium favors the acid to a large extent. However, we can still make an acid-acetate buffer by these methods:

1. Dissolve a relatively large amount of acetic acid and an acetate salt in water. The salt must be a *strong salt*, one that ionizes to a large extent, if not completely. $NaCH_2H_3O_2$ and $KCH_2H_3O_2$ are good choices for salts as they are strong salts, ionizing completely, and are inexpensive (an important point).
2. Dissolve a relative large amount of acetic acid in water. *Partially* neutralize the acid by adding some strong base, like NaOH. The amount of acetate formed will be equivalent to the amount of strong base added. The amount of acetic acid left in solution will be the starting amount minus the amount converted to acetate.
3. Dissolve a relatively large amount of an acetate salt in water, preferably a strong salt. *Partially* neutralize the acetate by adding some strong acid, like HCl. The amount of acetic acid formed will be equivalent to the amount of strong acid added. The amount of acetate ion left in solution will be the starting amount minus the amount converted to acetic acid.

The ratio of acetic acid to acetate in solution can be chosen to provide a desired $[H^+]$ or pH for the buffer solution. Usually, the ratio is kept within the limits of 10 and 0.1. Let us look at the equilibrium reaction for this system and the associated calculation for K_a:

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} \qquad \text{by rearrangement} \qquad [H^+] = K_a \times \frac{[HC_2H_3O_2]}{[C_2H_3O_2^-]}$$

The rearrangement above can be expressed in a generalized form:

$$[H^+] = K_a \times \frac{[\text{acid}]}{[\text{conjugate base}]} \tag{17-10}$$

Taking the logarithms of (*17-10*) and reversing the signs yields a convenient form:

$$\text{pH} = \text{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

An *indicator* is used to give a visual indication of the pH of a solution. Like a buffer, it is a conjugate acid-base pair; however, indicators are used in such small amounts (a couple of drops) that the pH of the solution is not affected. The pH of the solution determines the ratio of the acid form to the conjugate base form of the indicator. Each form of the indicator has a definite color, so it is easy to see the change from the acid to the conjugate base as the dominant form in solution—that is the indicator of the pH of that solution. If the acid dissociation of the indicator is written as follows:

$$\mathrm{HIn} \rightleftharpoons \mathrm{H^+In^-} \qquad \text{then,} \qquad [\mathrm{H^+}] = K_{a(\text{indicator})} \times \frac{[\mathrm{HIn}]}{[\mathrm{In^-}]} \tag{17-11}$$

If the ratio exceeds about 10:1, the color will appear to be purely that of HIn, the acid form. If the ratio is less than roughly 0.1, the color will be purely that of the base form, $\mathrm{In^-}$. There is a change from color to color generally through a mixing or blending of colors. As an example, if the extreme colors are yellow and blue, the intermediate will be a gradual change from yellow-green through green to blue-green. The gradual change occurs over a 100-fold range in $[\mathrm{H^+}]$, about 2 pH units, with the $\mathrm{p}K_a$ near the center of the range. A variety of indicators is known, each with its own $\mathrm{p}K_a$ and range of color change. (Note that the greater the difference in color intensity between the acid and base forms, the further off-center will be $\mathrm{p}K_a$.)

WEAK POLYPROTIC ACIDS

If multiple ionizations are possible, as in H_2S, H_2CO_3, and H_3PO_4, each stage of ionization has its own equilibrium constant, K_1, K_2, etc. The subscripts are numbers representing the ionization in stages starting with the ionization of the molecule (K_1) and continuing in order (1, 2, 3, etc.). H_2S ionizes in steps:

$$\text{Primary ionization:} \qquad \mathrm{H_2S} \rightleftharpoons \mathrm{H^+ + HS^-} \qquad K_1 = \frac{[\mathrm{H^+}][\mathrm{HS^-}]}{[\mathrm{H_2S}]} \tag{17-12}$$

$$\text{Secondary ionization:} \qquad \mathrm{HS^-} \rightleftharpoons \mathrm{H^+ + S^{2-}} \qquad K_2 = \frac{[\mathrm{H^+}][\mathrm{S^{2-}}]}{[\mathrm{HS^-}]} \tag{17-13}$$

The secondary ionization constant of polyprotic acids is always smaller than the primary ($K_2 < K_1$); the tertiary, K_3, is even smaller; and so on.

We should make it clear at this point that $[\mathrm{H^+}]$ is the actual concentration of hydrogen ions *in solution*, regardless of the source. In an aqueous mixture containing more than one acid, the different acids all contribute to the hydrogen ion concentration, but there is only one value of $[\mathrm{H^+}]$ in any given solution. That value must simultaneously satisfy the equilibrium conditions for all the different acids present. Although it may seem complex to solve a problem in which there are lots of equilibria, simplifications can be made when all sources but one make a small enough contribution that it can be insignificant (less than 10 percent in this book) to the total concentration of the ion.

In the case of polyprotic acids, K_1 is often so much greater than K_2 that only the K_1 equilibrium need be considered to calculate $[\mathrm{H^+}]$ in a solution of the acid. Examples where this assumption may and may not be made will be given in specific Solved Problems with the reasoning included.

Another problem of interest is the calculation of the concentration of the divalent ion (2^-) in a solution of a weak polyprotic acid, when the total $[\mathrm{H^+}]$ is essentially due to a stronger acid present in the solution or to a buffer. In such a case, the concentration of the divalent ion can best be calculated by multiplying the expressions for K_1 and K_2. Again, illustrating with H_2S, we find the following:

$$K_1K_2 = \frac{[\mathrm{H^+}][\mathrm{HS^-}]}{[\mathrm{H_2S}]} \times \frac{[\mathrm{H^+}][\mathrm{S^{2-}}]}{[\mathrm{HS^-}]} = \frac{[\mathrm{H^+}]^2[\mathrm{S^{2-}}]}{[\mathrm{H_2S}]} \tag{17-14}$$

TITRATION

When a base is added in small increments to a solution of acid, the pH of the solution rises on each addition of base. When the pH is plotted against the amount of base added, the steepest rise occurs at the *equivalence* *point* (when the acid is exactly neutralized). This region of steepest rise is called the *end point*, and the whole process of base addition and determination at the end point is called *titration*. The graph showing the change of pH during the titration is called a *titration curve*. Example 2 discusses the titration curve with reference to Fig. 17-1*a* and 17-1*b*.

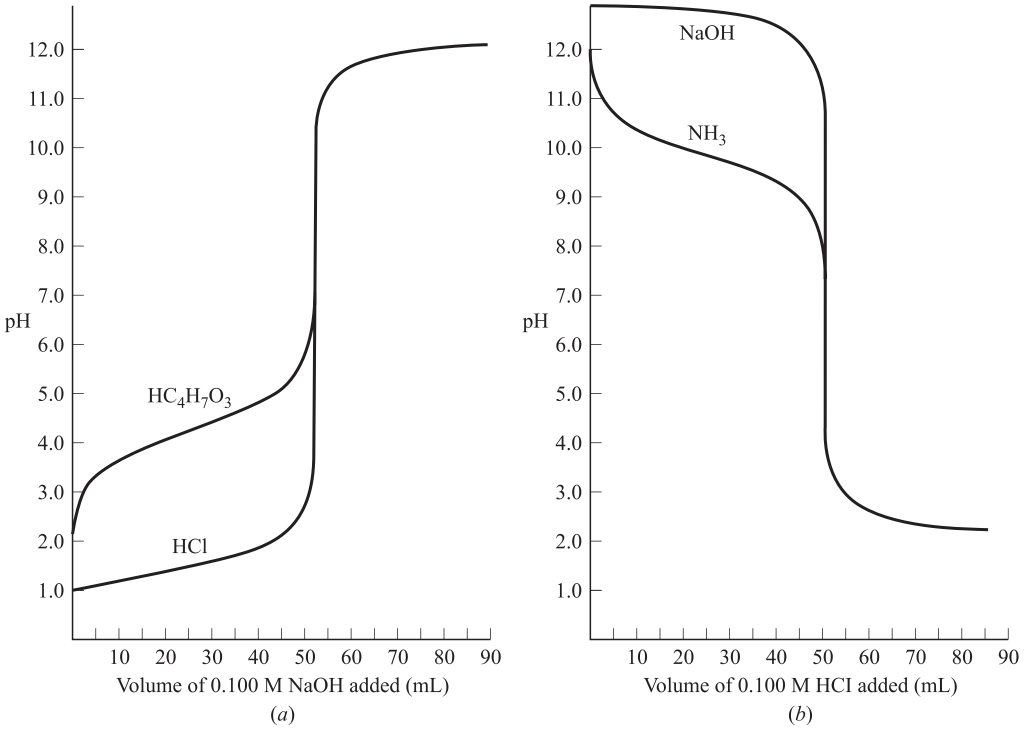


Fig. 17-1

EXAMPLE 2 Figure 17-1*a* shows the titration of one strong acid and one weak acid, separately, with a strong base. Figure 17-1*b* shows the titration of one strong base and one weak base, separately, with a strong acid. All four titrations are performed at 25°C. All reagents are 0.100 M so that the end point always occurs on the addition of exactly 50.0 mL of *titrant* (known concentration solution added during titration). The strong acid is HCl and the weak acid is $HC_4H_7O_3$; the strong base is NaOH and the weak base is NH_3. *Note*: $HC_4H_7O_3$ is β-hydroxybutyric acid.

All curves display a very sharp rise or fall in pH at the end point. When HCl is titrated (Fig. 17-1*a*), the pH rises slowly until very near the end point. The rise at the end point is much greater than for $HC_4H_7O_3$, which starts at a higher pH, has an initial rapid rise, reverses its curvature, and eventually undergoes the very sharp rise typical of the end point. Beginning slightly beyond the end point, the two curves are identical. The titration curves for NaOH and NH_3 (Fig. 17-1*b*) are almost mirror images of those for HCl and $HC_4H_7O_3$ with decreasing pH. There is no practical reason for using a weak reagent as a titrant. If, for instance, NH_3 were to be used in place of NaOH in Fig. 17-1*a*, the curve would level off beyond the end point at least 3 pH units lower, making the end point more difficult to spot.

The points along a titration curve can be calculated by methods previously discussed in this chapter. Basically, there are four regions making up a titration curve. Consider the titration of acid with strong base.

1. Starting point: 0% neutralization.

   In the case of the strong acid, $[H^+]$ in the initial solution is simply the molar concentration of the acid. In the case of a weak acid, $[H^+]$ is calculated by the method used to determine the extent of ionization of any weak acid in terms of its ionization constant and molar concentration.

2. Approach to the end point: 5% to 95% neutralization.

   For the case of the strong acid, the neutralization reaction is as follows.

$$H^+ + OH^- \rightarrow H_2O$$

This reaction may be assumed to go to completion to the extent of the amount of base added. The amount of unreacted H^+ is then the difference between the initial amount of H^+ and the amount neutralized. To determine $[H^+]$, allowance is made for the dilution effect of increasing the total volume of solution on the addition of base (also a solution).

For the case of a weak acid, the neutralization reaction may be written as

$$HC_4H_7O_3 + OH^- \rightarrow C_4H_7O_3^- + H_2O$$

The amount of hydroxybutyrate ion, $C_4H_7O_3^-$, is equal to the amount of base added. The amount of acid, $HC_4H_7O_3$, that has not ionized is the difference between the initial amount and the amount neutralized. Then,

$$[H^+] = K_{a(HC_4H_7O_3)} \times \frac{[HC_4H_7O_3]}{[C_4H_7O_3^-]}$$

The above is Equation (17-10); solutions in this region of a weak acid titration are buffers.

3. The end point: 100% neutralization.

   The pH at the end point is the same as for a solution of a salt containing the ions remaining at neutralization, NaCl or $NaC_4H_7O_3$. NaCl solutions are neutral (pH = 7); however, $NaC_4H_7O_3$ hydrolyzes and the pH can be evaluated by solving the hydrolysis equilibria. The $HC_4H_7O_3$–NaOH titration has a pH greater than 7 at the end point because of the hydrolysis of the hydroxybutyrate ion.

4. Extension beyond the end point: Over 105% neutralization.

   With NaOH as the titrant, the excess OH^- beyond that needed for neutralization accumulates in the solution. The $[OH^-]$ is calculated in terms of this excess and the total volume of the solution $[H^+]$ can then be calculated from the K_w relationship, which is as follows:

$$[H^+] = \frac{K_w}{[OH^-]}$$

   It makes no difference whether the acid titrated was weak or strong.

   Points within 5% of the starting point or 5% of the end point can be calculated by the same equilibria, but some of the simplifying assumptions made above would no longer be valid.

Polyprotic acids, like H_3PO_4, may have two or more distinct end points corresponding to neutralization of the first, second, and subsequent hydrogens. In such a case, each end point would occur at a different pH.

The calculations for the titration curves of bases with strong acid (Fig. 17-1*b*) are done by similar methods.

The end point of a titration, the region of the steepest rise in the titration curve, can be determined experimentally if an instrument is available for measuring the pH after each addition of base. A simpler means is to introduce into the solution a small amount of an indicator chosen so that its range lies within the steep vertical portion of the curve. This ensures a sharp color change at the end point.

Solved Problems

ACIDS AND BASES

17.1. Write the formulas for the conjugate bases of the following acids: (*a*) HCN; (*b*) HCO_3^-; (*c*) $N_2H_5^+$; (*d*) C_2H_5OH; (*e*) HNO_3.

In each case, the conjugate base is derived from the acid when it loses a proton (H^+) from the highly electronegative oxygen, rather than from carbon. If there is no oxygen, as in (*a*) and (*c*), the proton will be lost from the most electronegative element to which it is bonded (the carbon and nitrogen, respectively, in these cases). (*a*) CN^-; (*b*) CO_3^{2-}; (*c*) N_2H_4; (*d*) $C_2H_5O^-$; (*e*) NO_3^-

17.2. Write the formulas for the conjugate acids of the following bases: (*a*) $HC_2H_3O_2$; (*b*) HCO_3^-; (*c*) C_5H_5N; (*d*) $N_2H_5^+$; (*e*) OH^-.

In each case, the conjugate acid is formed from the base by the addition of a proton. The proton is added to oxygen in (*a*) or to nitrogen in (*c*) and (*d*), all of which have unshared pairs available to which the proton is attracted. In (*a*), the proton is added to the carbonyl oxygen ($-C{=}O$).

(*a*) $HC_2H_3O_2^+$. This species might form in liquid acetic acid on the addition of a strong acid.

(*b*) H_2CO_3. HCO_3^- can serve as both an acid [Problem 17.1(*b*)] and a base.

(*c*) $C_5H_5NH^+$.

(*d*) $N_2H_6^{2+}$. Bases, like acids, can be multifunctional. The second proton is accepted by N_2H_4, but only with great difficulty.

(*e*) H_2O.

17.3. Liquid NH_3, like water, is an amphiprotic solvent. Write the equation for its autoionization.

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

$$(2H_2O \rightleftharpoons H_2O^+ + OH^-) \qquad \text{Included for comparison.}$$

Note that, as NH_3 replaces H_2O, the ammonium ion occupies the same position as H^+ in the autoionization of water. And, of course, the amide ion takes the place of the hydroxide ion.

17.4. Aniline, $C_6H_5NH_2$, is a weak organic base in aqueous solutions. Suggest a solvent in which aniline would become a strong base.

The solvent needed to do the job is one that has appreciably stronger acid properties than water. One such solvent, in which aniline is a strong base, is liquid acetic acid or any other acidic solvent with greater acid properties than water.

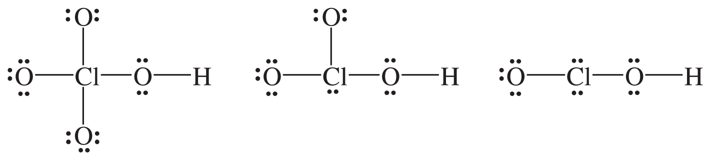
17.5. NH_4ClO_4 and $HClO_4 \cdot H_2O$ both crystallize in the same orthorhombic structure, having unit-cell volumes of 0.395 and 0.370 nm^3, respectively. How do you account for the similarity in crystal structure and crystal dimensions?

Both are ionic substances with lattice sites occupied by cations and anions. In perchloric acid monohydrate, the cation is H_3O^+ and there are no water *molecules* of hydration. The cations in the two crystals, H_3O^+ and NH_4^+, should occupy nearly equal amounts of space because they are *isoelectronic* (having the same number of electrons).

Historical note: The data in this problem have been cited as one of the proofs for the existence of the hydronium ion, H_3O^+.

17.6. (*a*) Give an explanation for the decreasing acid strength in the series $HClO_4$, $HClO_3$, $HClO_2$. (*b*) What would be the relative basic strengths of ClO_4^-, ClO_3^-, ClO_2^-? (*c*) Keeping in mind the discussion of (*a*), how do you account for the fact that there is very little difference in acid strength in the series H_3PO_4, H_3PO_3, H_3PO_2?

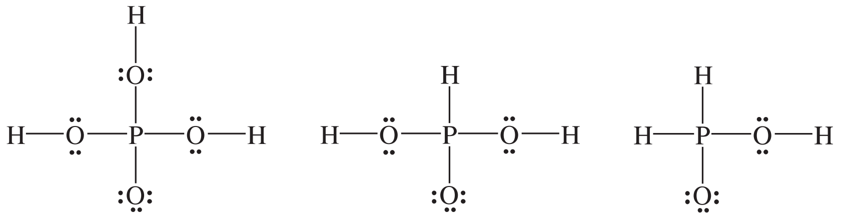
(*a*) The Lewis structures are



Since oxygen is more electronegative than chlorine, each terminal oxygen tends to withdraw electrons from the chlorine and, in turn, from the O—H bond. This withdrawal leads to an increasing tendency for the proton (H^+) to dissociate. In general, the greater the number of terminal oxygens in an oxygen-containing acid with the same central atom, the stronger the acid.

(*b*) Members of a conjugate acid-base pair stand in complementary relationship to each other—the stronger an acid, the weaker its conjugate base. This results in the order of decreasing basic strength, which is $ClO_2^- > ClO_3^- > ClO_4^-$ (reversed for increasing acid strength).

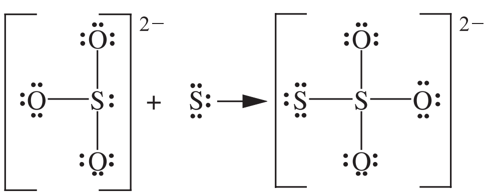
(*c*) The hydrogens in these acids are not all bonded to oxygens. The Lewis structures are



The number of terminal oxygen atoms, one, is exactly the same in all three acids, so that, according to (*a*), no great differences in acidity are expected. Since the electronegativities of P and H are almost the same, there is no tendency for the phosphorus-bonded H to ionize, nor to influence the ionization of the oxygen-bonded H's.

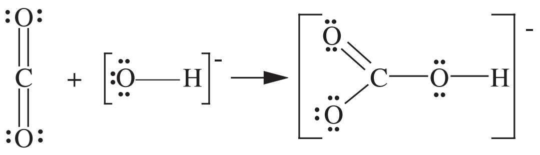
17.7. How do you account for the formation of $S_2O_3^{2-}$ from SO_3^{2-} and S in terms of Lewis acid theory?

The sulfur atom is electron-deficient and can be regarded as an acid. SO_3^{2-} is the base, for which an octet structure can be written with an unshared pair proving its base character.



17.8. In combustion analysis of organic compounds, solid NaOH is used to absorb the CO_2 from the combustion gases. Account for this reaction in terms of Lewis acid-base theory.

Because the oxygen in the OH^- ion has three unshared pairs of unshared electrons, it is a Lewis base. Understanding how CO_2 functions as an acid relies on noting that the carbon in CO_2 is *sp* hybridized, but by reverting to sp^2 hybridization, as in HCO_3^-, an orbital is made available to accept the base pair.



IONIZATION OF ACIDS AND BASES

17.9. At 25°C, a 0.0100 M NH_3 solution is 4.1% ionized. Assuming no volume changes, calculate (*a*) the concentration of OH^- and NH_4^+ ions; (*b*) the concentration of molecular ammonia; (*c*) the ionization constant of aqueous ammonia; (*d*) $[OH^-]$ after 0.0090 mol NH_4Cl is added to 1 L of the above solution; (*e*) $[OH^-]$ of a solution prepared by dissolving 0.010 mol NH_3 and 0.0050 mol HCl per liter.

$$NH_3 + H_2O \rightleftharpoons [NH_4^+] + OH^-$$

The label on a solution refers to the stoichiometric or weight composition, not the concentration of any particular component in an ionic equilibrium. In other words, 0.0100 M NH_3 means that the solution was produced from 0.0100 mol ammonia and the necessary water to make a liter of solution. It does not mean that the concentration of the un-ionized ammonia in the solution, $[NH_3]$, is 0.0100.

(*a*)
$$[NH_4^+] = [OH^-] = (0.041)(0.0100) = 0.00041 \text{ M}$$

(*b*)
$$[NH_3] = 0.0100 - 0.00041 = 0.0096 \text{ M}$$

(*c*)
$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.00041)(0.00041)}{0.0096} = 1.75 \times 10^{-5}$$

(*d*) Since the base is so slightly ionized, we may assume that (1) the $[NH_4^+]$ is completely derived from NH_4Cl and that (2) the $[NH_3]$ at equilibrium is the same as the stoichiometric molar concentration of the base. Then,

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \qquad \text{rearranged to} \qquad [OH^-] = \frac{K_b[NH_3]}{[NH_4^+]} = \frac{(1.75 \times 10^{-5})(0.0100)}{0.0090} = 1.94 \times 10^{-5}$$

The addition of NH_4Cl holds back the ionization of NH_3. This action reduces greatly the $[OH^-]$ of the solution. This action of shifting the reaction by means of two sources of the same ion is called the *common-ion effect*.

Alternate method: There were a lot of assumptions made in the above solutions, but there is a way to work without making assumptions. The technique involves writing the reaction and then making a table below that equation holding the information given in the problem so that the answers can be derived by direct, mathematical means. Water is a pure liquid in this reaction and is not included in K.

	NH_3	$+ \; H_2O \rightleftharpoons [NH_4^+]$	$+ \; OH^-$
$[NH_3]$ at the start	0.0100	0	0
$[NH_4^+]$ at start	0	0.0090	0
Change by reaction	$-x$	$+x$	$+x$
Equilibrium concentrations	$0.0100 - x$	$0.0090 + x$	x

$$[OH^-] = \frac{K_b[NH_3]}{[NH_4]} \qquad \text{by substitution} \qquad [OH^-] = x = \frac{(1.75 \times 10^{-5})(0.0100 - x)}{0.0090 + x}$$

This yields a quadratic equation, which can be solved by the usual methods. Clearing fractions and ignoring for the moment the rules of significant digits,

$$x^2 + 0.0090175x - 1.75 \times 10^{-7} = 0$$

The quadratic equation must be used for the solution for x as follows:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad \text{by substitution} \qquad x = \frac{-0.0090175 \pm \sqrt{(0.0090175)^2 - 4(1)(-1.75 \times 10^{-7})}}{2(1)}$$

and, since one possible answer is negative, the other value, $x = 1.94 \times 10^{-5}$, is the only logical choice.

Clearly, making simplifying assumptions provides for a large reduction in labor for this problem and others. However, for many students, the table provides a good system of bookkeeping and helps when putting together the solution. Once x has been found, substituting into the last line above will provide the concentrations of all species present. Recall that water is the solvent and, since it is a pure liquid, its concentration is constant and not included in the K expression.

(*e*) Since HCl is a strong acid, the 0.0050 mol of HCl will react completely with the 0.0050 mol of NH_3 to form 0.0050 mol $[NH_4^+]$. Of the original 0.0100 mol of NH_3, only half will remain as ammonia that is not ionized.

$$[OH^-] = \frac{K_b[NH_3]}{[NH_4]} \qquad \text{by substitution} \qquad x = \frac{(1.75 \times 10^{-5})(0.0050)}{0.0050} = 1.75 \times 10^{-5}$$

Check of assumption: The amount of NH_4^+ contributed by the dissociation of NH_3 must be equal to the amount of OH^-, or 1.75×10^{-5} mol/L. This is quite small compared with the 0.0050 mol/L formed by the neutralization of NH_3 with HCl.

17.10. Calculate the molarity at which an acetic acid solution is 2.0% ionized. K_a at 25°C for $HC_2H_3O_2$ is 1.75×10^{-5}.

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

Let x be the molar concentration of acetic acid. Then,

$$[H^+] = [C_2H_3O_2^-] = 0.020x \qquad \text{and} \qquad [HC_2H_3O_2] = x - 0.020x \approx x$$

The approximation is well within 10%, which allows us to ignore $0.020x$.

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} \qquad \text{or} \qquad 1.75 \times 10^{-5} = \frac{(0.020x)(0.020x)}{x}$$

Solving:

$$(0.020)^2 x = 1.75 \times 10^{-5} \qquad \text{or} \qquad x = 0.044$$

17.11. Calculate the percent ionization of a 1.00 M HCN (hydrocyanic acid); K_a of HCN is 4.93×10^{-10}.

$$HCN \rightleftharpoons H^+ + CN^-$$

Since H^+ and CN^- are present in the solution only as a result of the ionization, their concentrations must be equal. Assume that $[H^+]$ from the ionization of water is not significant.

Let $x = [H^+] = [CN^-]$. Such being the case, $[HCN] = 1.00 - x$. Let us assume that x will be very small compared to 1.00, so that $[HCN] = 1.00$, which should be within the allowed error of 10%. Then,

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \qquad \text{or} \qquad 4.93 \times 10^{-10} = \frac{x^2}{1.00} \qquad \text{then} \qquad x = 2.22 \times 10^{-5}$$

$$\text{Percent ionization} = \frac{\text{ionized HCN}}{\text{total HCN}} \times 100 = \frac{2.22 \times 10^{-5}\ \text{mol/L}}{1.00\ \text{mol/L}} \times 100\% = 0.00222\%$$

Check of assumptions: (1) $(x = 2.22 \times 10^{-5})$ is very small compared with 1.00; (2) the $[H^+]$ in neutral water is only 1×10^{-7}, which is less than 1% of x. Also, the ionization of water is suppressed even more by the presence of the acid because the added hydrogen ion from the acid shifts the ionization of water toward the water ($H_2O \rightleftharpoons H^+ + OH^-$).

17.12. The $[H^+]$ in a 0.020 M solution of benzoic acid is 1.1×10^{-3}. Calculate K_a for the acid, $HC_7H_5O_2$.

$$HC_7H_5O_2 \rightleftharpoons H^+ + C_7H_5O_2^-$$

Since the hydrogen ion and benzoate ion come only from the ionization of the acid, their concentrations are equal. The contribution of H^+ by the ionization of water is insignificant.

$$[H^+] = [C_7H_5O_2^-] = 1.1 \times 10^{-3} \qquad [HC_7H_5O_2] = 0.020 - (1.1 \times 10^{-3}) = 0.019$$

$$K_a = \frac{[H^+][C_7H_5O_2^-]}{[HC_7H_5O_2]} = \frac{(1.1 \times 10^{-3})^2}{0.019} = 6.4 \times 10^{-5}$$

17.13. The ionization constant for formic acid, HCO_2H, is 1.77×10^{-4}. What is the percent ionization of a 0.00100 M solution of formic acid?

Let $x = [H^+] = [HCO_2^-]$. Then $[HCO_2H] = 0.00100 - x$. Assume, as in Problem 17.11, that the percent ionization is less than 10% and that the formic acid concentration, $0.00100 - x$, may be approximated as 0.00100. Then,

$$K_a = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{x^2}{0.00100} = 1.77 \times 10^{-4} \qquad \text{or} \qquad x = 4.2 \times 10^{-4}$$

In checking the assumption, we see that x is *not* insignificant compared with 0.0010. Therefore, the assumption and the solution based on it *must be rejected* and the full quadratic form of the equation must be solved. (Refer to Problem 17.9 for the techniques involved.)

$$\frac{x^2}{0.00100 - x} = 1.77 \times 10^{-4}$$

Solving: $x = 3.4 \times 10^{-4}$. Note that we rejected the negative root, -5.2×10^{-4} (negative concentration?).

$$\text{Percent ionization} = \frac{\text{ionized } HCO_2H}{\text{total } HCO_2H} \times 100\% = \frac{3.4 \times 10^{-4}}{0.00100} \times 100\% = 34\%$$

This exact solution (34% ionization) shows that the solution based on the original assumption was almost 25% too high.

The pitfall introduced by this problem is making the assumption as to the significance of x in $0.00100 - x$ and, after calculations, finding that the assumption was incorrect. Then, we had to do the work all over again with x included. There is a way of getting around such false assumptions called the *five percent rule*. This rule states that x may be omitted as being insignificant if x is less than 5% of the number it is being subtracted from (or added to). In other words, the value of x is so small that it doesn't make any difference if it is or is not subtracted from (or added to) the number. Notice that the chemical equation produces 2 ions in this problem. If, since these two ions are multiplied together (squared, if they are the same concentration), we were to take the square root of K, it would approximate the value of x. If that value, the square root of K_a, is less than 5% of the number it is being subtracted from, it is insignificant. The square root of K_a, $(1.77 \times 10^{-4})^{1/2}$, is 0.0133 and 5% of 0.00100 is 0.00005. Since the square root of K_a is larger than the 5% approximation, it cannot be ignored.

17.14. What concentration of acetic acid is needed to give a $[H^+]$ of 3.5×10^{-4}? K_a is 1.75×10^{-5}.

Let x be the number of moles acetic acid per liter.

$$[H^+] = [C_2H_3O_2^-] = 3.5 \times 10^{-4} \qquad \text{and} \qquad [HC_2H_3O_2] = x - (3.5 \times 10^{-4})$$

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} \qquad \text{or} \qquad 1.75 \times 10^{-5} = \frac{(3.5 \times 10^{-4})^2}{x - (3.5 \times 10^{-4})} \qquad \text{or} \qquad x = 7.3 \times 10^{-3}\ \text{M}\ HC_2H_3O_2$$

17.15. A 0.100 M solution of an acid (density = 1.010 g/mL) is 4.5% ionized. Calculate the freezing point of the solution. The molar mass of the acid is 300.

Since we are dealing with a freezing-point change, we must know the molality of the solution, and we can use any volume of solution for the calculations—using 1 L is convenient.

$$\text{Mass of 1 L of solution} = (1000\ \text{mL})(1.010\text{g/mL}) = 1010\ \text{g solution}$$

$$\text{Mass of solute in 1 L of solution} = (0.100\text{mol})(300\ \text{g/mol}) = 30\ \text{g acid}$$

$$\text{Mass of water in1 L of solution} = 1010\ \text{g} - 30\ \text{g} = 980\ \text{g}\ H_2O$$

$$\text{Molality of solution} = \frac{0.100\ \text{mol acid}}{0.980\ \text{kg water}} = 0.102\ \text{mol/kg} = 0.102\ \text{m}$$

If the acid were not ionized at all, the freezing-point lowering (Chapter 14) would be

$$\Delta T_f = km \qquad \text{or} \qquad \Delta T_f = 1.86 \times 0.102 = 0.190°\text{C}$$

However, because of the ionization, the total number of dissolved particles is greater than 0.102 mol per kg solvent. The freezing-point depression is determined by the total number of dissolved particles, regardless of whether they are charged (ions) or uncharged (molecules).

Let a = fraction ionized. For every mole of acid added to the solution, there will be $(1 - a)$ moles of un-ionized acid at equilibrium, a moles of H^+, and a moles of anion base conjugate to the acid. This gives us a total of $(1 + a)$ moles of dissolved particles. Then, the molality with respect to all dissolved particles is $(1 + a)$ times the molality calculated without regard to ionization.

$$\Delta T_f = (1 + a)km \qquad \text{or} \qquad \Delta T_f = 1.045 \times 1.86 \times 0.102 = 0.198^\circ\text{C}$$

The freezing point of the solution is -0.198°C.

17.16. A solution was made up to be 0.0100 M $HC_2H_2O_2Cl$, chloroacetic acid, and also 0.0020 M $NaC_2H_2O_2Cl$. K_a for chloroacetic acid is 1.40×10^{-3}. Calculate $[H^+]$.

Instead of making the 10% assumption, as has been done in most of the problems above, let us apply the 5% rule. Solving this problem is made easier by recording the reaction involved and doing the bookkeeping under the reactions, as was introduced in Problem 17.9

	$HC_2H_2O_2Cl \rightleftharpoons$	H^+	$+$	$C_2H_2O_2Cl^-$
At the start	0.0100	0		0.0020 (from the salt)
Change by reaction	$-x$	$+x$		$+x$
Equilibrium	$0.0100 - x$	x		$0.0020 + x$

The 0.0020 anion added in the first line recognizes that sodium salts ionize completely in aqueous solution. We now have to substitute into the K_a expression, but do we have to add x on the right and subtract x on the left? The square root of K_a is 0.037, which is larger than 5% of 0.0020 (0.0001) on the right and also larger than 5% of 0.0100 on the left. This means that we cannot ignore the value of x anywhere in this setup. Then,

$$\frac{[H^+][C_2H_2O_2Cl^-]}{[HC_2H_2O_2Cl]} = K_a \qquad \text{or} \qquad \frac{(x)(0.0020 + x)}{0.0100 - x} = 1.40 \times 10^{-3}$$

After solving this equation in the $ax^2 + bx + c = 0$ format and applying the quadratic formula, we find that the hydrogen ion concentration is 2.4×10^{-3} M.

Note that, had we made the assumption that x was not significant, we would have discovered that it could not be left out and would have been required to redo the problem, doubling the work.

17.17. Calculate $[H^+]$ and $[C_2H_3O_2^-]$ in a solution that is 0.100 M $HC_2H_3O_2$ and 0.050 M HCl. K_a for acetic acid is 1.75×10^{-5}.

HCl contributes so much more H^+ than acetic acid that we can take $[H^+]$ as equal to the molar concentration of the HCl, 0.050; this is another example of the common-ion effect.

Then, if $[C_2H_3O_2^-] = x$, we have $[HC_2H_3O_2] = 0.100 - x$, which we can assume is 0.100.

$$[C_2H_3O_2^-] = \frac{[HC_2H_3O_2]K_a}{[H^+]} = \frac{(0.100)(1.75 \times 10^{-5})}{0.050} = 3.5 \times 10^{-5}$$

Check of assumption: (1) The contribution of acetic acid to $[H^+]$, x, is quite small compared with 0.050; (2) x is definitely small compared with 0.100.

17.18. Calculate $[H^+]$, $[C_2H_3O_2^-]$, and $[CN^-]$ in a solution that is 0.100 M in $HC_2H_3O_2$ ($K_a = 1.75 \times 10^{-5}$) and 0.200 M in HCN ($K_a = 4.93 \times 10^{-10}$).

This problem is similar to the preceding one; one of the acids, acetic, completely dominates the other in terms of contribution to the total $[H^+]$ of the solution. We base this assumption on the fact that the K_a for acetic acid is so much greater than the one for hydrocyanic acid. We will check the assumption after solving the problem. Let us start by treating the acetic acid as if the hydrocyanic were not present.

Let $[H^+] = [C_2H_3O_2^-] = x$; then, $[HC_2H_3O_2] = 0.100 - x$, and this is taken to be 0.100 because of the small expected value of x. Actually, the five percent rule tells us that the value of x is approximately 0.0042, which is less than 5% of 0.100, which is 0.005, telling us that x can be omitted.

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} \qquad \text{or} \qquad 1.75 \times 10^{-5} = \frac{x^2}{0.100} \qquad \text{or} \qquad x = 1.32 \times 10^{-3}$$

Check of assumption: x is very small compared to 0.100.

Now we treat the HCN equilibrium established at a value of $[H^+]$ determined by the acetic acid, 1.32×10^{-3}. Let $[CN^-] = y$; then $[HCN] = 0.200 - y \approx 0.200$, because the square root of K_a is so small compared to 0.200 that it is not significant. And

$$y = [CN^-] = \frac{K_a[HCN]}{[H^+]} = \frac{(4.93 \times 10^{-10})(0.200)}{1.32 \times 10^{-3}} = 7.5 \times 10^{-8}$$

Check of assumption: (1) y is small compared with 0.200; (2) the amount of H^+ contributed by HCN is equal to the amount of CN^- formed (7.5×10^{-8} mol/L) and is small compared with the amount of H^+ contributed by $HC_2H_3O_2$ (1.32×10^{-3} mol/L).

17.19. Calculate $[H^+]$ in a solution that is 0.100 M HCOOH ($K_a = 1.77 \times 10^{-4}$) and 0.100 M HOCN ($K_a = 3.3 \times 10^{-4}$).

This is a case in which two weak acids both contribute to $[H^+]$; however, neither one is a much larger contributor than the other. Both need to be considered for their contributions. Let us do the bookkeeping for both equilibria and see where that leads us.

	HCOOH	$\rightleftharpoons$	H^+	+	HCO_2^-	HOCN	$\rightleftharpoons$	H^+	+	OCN^-
Initial conc.	0.100		0		0	0.100		0		0
Change by rxn.	$-x$		$+x$		$+x$	$-y$		$+y$		$+y$
Equilibrium conc.	$0.100 - x$		$x + y$		x	$0.100 - y$		$x + y$		y
Approx. equil.	0.100		$x + y$		x	0.100		$x + y$		y

The final line is based on the assumption that x and y are both small compared to 0.100 at the 10% level.

$$\frac{x(x+y)}{0.100} = 1.77 \times 10^{-4} \qquad \text{and} \qquad \frac{y(x+y)}{0.100} = 3.3 \times 10^{-4}$$

Dividing the HOCN equation by the HCOOH equation,

$$\frac{y}{x} = \frac{3.3}{1.77} = 1.86 \qquad \text{or} \qquad y = 1.86x$$

Subtracting the HCOOH equation from the HOCN equation,

$$\frac{y(x+y) - x(x+y)}{0.100} = 1.5 \times 10^{-4} \qquad \text{or} \qquad y^2 - x^2 = 1.5 \times 10^{-5}$$

Substitute $y = 1.86x$ into the last equation and solving: $x = 2.5 \times 10^{-3}$. Then

$$y = 1.86x = 4.6 \times 10^{-3} \qquad \text{and} \qquad [H^+] = x + y = 7.1 \times 10^{-3}$$

Check of assumptions: The values of x and y are not much less than 10% of 0.100, which is pressing the 10% limit of error generally allowed in this chapter. Note that, if the five percent rule were to be applied, there would be a great deal more calculation involved due to the necessary use of the quadratic formula. The point is that you need to be aware of how much error is allowed and stick to that limit.

IONIZATION OF WATER

17.20. Calculate the $[H^+]$ and the $[OH^-]$ in 0.100 M $HC_2H_3O_2$ which is 1.31% ionized.

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \text{and} \qquad K_w = [H^+][OH^-]$$

From acetic acid,

$$[H^+] = (0.0131)(0.100) = 1.31 \times 10^{-3}$$

$$[OH^-] = \frac{1.00 \times 10^{-14}}{[H^+]} = \frac{1.00 \times 10^{-14}}{1.31 \times 10^{-3}} = 7.6 \times 10^{-12}$$

Note that $[H^+]$ is calculated as if the $HC_2H_3O_2$ were the only contributor, whereas $[OH^-]$ is based on the ionization of water. If water ionizes to supply OH^-, it must supply an equal amount of H^+ at the same time. Implied in this solution is the assumption that water's contribution to $[H^+]$, 7.6×10^{-12} mol/L, is negligible compared with that of the $HC_2H_3O_2$. Actually, this assumption is valid in all but the most dilute acid solutions. In calculating $[OH^-]$, water is the only source and it therefore cannot be overlooked.

17.21. Determine the $[OH^-]$ and the $[H^+]$ in a 0.0100 M ammonia solution which is 4.1% ionized.

$$[OH^-] = (0.041)(0.0100) = 4.1 \times 10^{-4}$$

$$[H^+] = \frac{1.00 \times 10^{-14}}{[OH^-]} = \frac{1.00 \times 10^{-14}}{4.1 \times 10^{-4}} = 2.4 \times 10^{-11}$$

In this problem, we have made the assumption that the contribution of water to $[OH^-]$ (equal to $[H^+]$, or 2.4×10^{-11} M) is negligible compared with that of NH_3. K_w is used to calculate $[H^+]$, since water is the only supplier of H^+. In general, $[H^+]$ for acidic solutions can be calculated without regard to the water equilibrium; then K_w is used to calculate $[OH^-]$. Conversely, $[OH^-]$ for basic solutions can usually be calculated without regard to the water equilibrium; then, K_w is used to calculate $[H^+]$.

17.22. Express the following H^+ concentrations in terms of pH: (*a*) 1×10^{-3} M, (*b*) 5.4×10^{-9} M.

(*a*) $\text{pH} = -\log[H^+] = 3$, (*b*) $\text{pH} = -\log[H^+] = 8.27$.

Enter the molar concentration into your calculator, then press the log button. Remember to reverse the sign of the answer because taking the $-\log\ [H^+]$ is the same as $-1 \times \log[H^+]$.

17.23. Calculate the pH values (100% ionization) of (*a*) 4.9×10^{-4} N acid, (*b*) 0.0016 N base.

(*a*) 3.31; (*b*) $14 = \text{pH} + \text{pOH}$ is the relationship needed for this calculation. Recall that *p* means "take the negative log" of whatever follows. Then, $\text{pH} = 14 - \text{pOH}$, and the hydroxide ion concentration comes directly from the problem. So, $\text{pH} = 14 - 2.8 = 11.2$.

17.24. Change the following pH values to $[H^+]$ values: (*a*) 4, (*b*) 3.6.

(*a*) Since $\text{pH} = -\log[H^+]$ then,

$$-\text{pH} = \log[H^+]$$

Taking the antilog of both sides will prove the answer. Then,

$$\text{antilog} - 4 = [H^+] \qquad (\text{the antilog key is } 10^x)$$

$$[H^+] = 0.0001$$

(*b*) Using the same technique as in (*a*), $[H^+] = 2.5 \times 10^{-4}$.

17.25. What is the pH of (*a*) 5.0×10^{-8} M HCl, (*b*) 5.0×10^{-10} M HCl?

(*a*) If we were to consider only the contribution of the HCl to the acidity of the solution, $[\mathrm{H^+}]$ would be 5.0×10^{-8} and the pH would be greater than 7, which is a pH indicating a base. We have to take into account the contribution of water to the total acidity, something we have not done in previous problems because the acids and bases way overshadowed water's effect. The bookkeeping is

	H_2O	$\rightleftharpoons$	H^+	$+$	OH^-
From the HCl			5×10^8		
Change by ionization of water			$+x$		$+x$
At equilibrium			$5 \times 10^8 + x$		x

$$K_w = [\mathrm{H^+}][\mathrm{OH^-}] = (5.0 \times 10^{-8} + x)(x) = 1.00 \times 10^{-14}$$

From the quadratic equation: $x = 7.8 \times 10^{-8}$. Then, $[\mathrm{H^+}] = (5.0 \times 10^{-8} + x) = 1.28 \times 10^{-7}$, and

$$\mathrm{pH} = -\log(1.28 \times 10^{-7}) = 6.89$$

(*b*) Although the method of (*a*) could be used here, the problem can be simplified by noting that HCl is so dilute as to make only a small contribution to $[\mathrm{H^+}]$ as compared with the ionization of water. We may therefore write directly: $[\mathrm{H^+}] = 1.00 \times 10^{-7}$ and pH 7.00.

HYDROLYSIS

17.26. Calculate the extent of hydrolysis in a 0.0100 M solution of NH_4Cl. K_b for NH_3 is 1.75×10^{-5}.

$$\mathrm{NH_4^+ NH_3 + H^+}$$

$$K_a = \frac{[\mathrm{NH_3}][\mathrm{H^+}]}{[\mathrm{NH_4^+}]} = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

By the reaction equation, equal amounts of NH_3 and H^+ are formed. Let $x = [\mathrm{NH_3}] = [\mathrm{H^+}]$.

$$[\mathrm{NH_4^+}] = 0.0100 - x \approx 0.0100$$

and

$$K_a = \frac{[\mathrm{NH_3}][\mathrm{H^+}]}{[\mathrm{NH_4^+}]} \quad \text{becomes} \quad 5.7 \times 10^{-10} = \frac{x^2}{0.0100} \quad \text{then} \quad x = 2.4 \times 10^{-6}$$

Check of approximation: x is very small compared with 0.0100.

$$\text{Fraction hydrolyzed} = \frac{\text{amount hydrolyzed}}{\text{total amount}} = \frac{2.4 \times 10^{-6}\ \text{mol/L}}{0.0100\ \text{mol/L}} = 1.4 \times 10^{-4} \quad \text{or} \quad 0.24\%$$

17.27. Calculate $[\mathrm{OH^-}]$ in a 1.00 M solution of NaOCN; K_a for HOCN is 3.5×10^{-4}.

$$\mathrm{OCN^- + H_2O \rightleftharpoons HOCN + OH^-}$$

$$K_b = \frac{[\mathrm{HOCN}][\mathrm{OH^-}]}{[\mathrm{OCN^-}]} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{3.5 \times 10^{-4}} = 2.9 \times 10^{-11}$$

Since the source of the OH^- and HOCN is the hydrolysis reaction, they must exist in equal concentrations. Let $x = [OH^-] = [HOCN]$. Then

$$[OCN^-] = 1.00 - x \approx 1.00$$

and

$$K_b = 2.9 \times 10 = \frac{x^2}{1.00} \qquad \text{becomes} \qquad x = [OH^-] = 5.4 \times 10^{-6}$$

Check of approximation: x is very small compared with 1.00.

17.28. The acid ionization (hydrolysis) constant of Zn^{2+} is 3.3×10^{-10}. (*a*) Calculate the pH of 0.0010 M $ZnCl_2$. (*b*) What is the basic dissociation constant of $Zn(OH)^+$?

(*a*) $$Zn^{2+} + H_2O \rightleftharpoons Zn(OH)^+ + H^+ \qquad K_a = \frac{[Zn(OH)^+][H^+]}{[Zn^{2+}]} = 3.3 \times 10^{-10}$$

Let $x = [Zn(OH)^+] = [H^+]$. Then, $[Zn^{2+}] = 0.0010 - x \approx 0.0100$, and

$$\frac{x^2}{0.0100} = 3.3 \times 10^{-10} \qquad \text{or} \qquad x = [H^+] = 5.7 \times 10^{-7}$$

$$\text{pH} = -\log(5.7 \times 10^{-7}) = -\log\ 10^{-6.24} = 6.24$$

Check of approximation: x is very small compared with 0.0010.

(*b*) $$Zn(OH)^+ \rightleftharpoons Zn^{2+} + OH^- \qquad K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.3 \times 10^{-10}} = 3.0 \times 10^{-5}$$

17.29. Calculate the extent of hydrolysis and the pH of 0.0100 M $NH_4C_2H_3O_2$. K_a for $HC_2H_3O_2$ is 1.75×10^{-5} and K_b for NH_3 is also 1.75×10^{-5}.

The problem illustrates a situation where both the cation and anion hydrolyze.

$$\text{For } NH_4^+: \qquad K_a = \frac{K_w}{K_{b(NH_3)}} = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

$$\text{For } C_2H_3O_2^-: \qquad K_b = \frac{K_w}{K_{a(HC_2H_3O_2)}} = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

By coincidence, the hydrolysis constants for these two ions are identical. The production of H^+ by NH_4^+ hydrolysis must, therefore, exactly equal the production of OH^- by $C_2H_3O_2^-$ hydrolysis. The H^+ and OH^- formed by hydrolysis neutralize each other to maintain the original water equilibrium. The solution is neutral, $[H^+] = [OH^-] = 1.00 \times 10^{-7}$; the pH is 7.00.

For NH_4^+ hydrolysis,

$$\frac{[NH_3][H^+]}{[NH_4^+]} = K_a = 5.7 \times 10^{-10}$$

Let $x = [NH_3]$. Then $0.0100 - x = [NH_4^+]$ and

$$\frac{x(1.00 \times 10^{-7})}{0.0100 - x} = 5.7 \times 10^{-10} \qquad \text{or} \qquad x = 5.7 \times 10^{-5}$$

$$\text{Percent } NH_4^+ \text{ hydrolyzed} = \frac{5.7 \times 10^{-5}}{0.0100} \times 100\% = 0.57\%$$

The percent hydrolysis of acetate must also be 0.57% because the equilibrium constant for the hydrolysis is the same as for NH_4^+.

In comparing the results of this problem with Problem 17.26, note that the percent hydrolysis of NH_4^+ is greater in the presence of a hydrolyzing anion (like acetate). The reason is that the removal of some of the products of the two hydrolyses, H^+ and OH^-, by the water equilibrium reaction ($H_2O \rightleftharpoons H^+ + OH^-$) allows both hydrolyses to proceed to an increasing extent.

17.30. Calculate the pH in 0.100 M NH_4OCN. K_b for NH_3 is 1.75×10^{-5} and K_a for HOCN is 3.5×10^{-4}.

As in Problem 17.29, both cation and anion hydrolyze. Since NH_3 is a weaker base than HOCN is an acid, NH_4^+ hydrolyzes more than OCN^-, and the pH of the solution is less than 7. In order to preserve electrical neutrality, there cannot be an appreciable difference between $[NH_4^+]$ and $[OCN^-]$. (If there is a slight difference, it can be accounted for by the $[H^+]$ or $[OH^-]$.) Therefore, $[NH_3]$ must be practically equal to [HOCN], and we will assume that they are for this problem.

Let $x = [NH_3] = [HOCN]$; then, $0.100 - x = [NH_4^+] = [OCN^-]$.

$$\text{For } [NH_4^+]: \qquad K_a = \frac{[NH_3][H^+]}{[NH_4^+]} = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

and

$$[H^+] = (5.7 \times 10^{-10})\left(\frac{0.100 - x}{x}\right) \tag{1}$$

$$\text{For } OCN^-: \qquad K_b = \frac{[HOCN][OH^-]}{[OCN^-]} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{3.5 \times 10^{-4}} = 2.9 \times 10^{-11}$$

and

$$[OH^-] = (2.9 \times 10^{-11})\left(\frac{0.100 - x}{x}\right) \tag{2}$$

Dividing (*1*) by (*2*),

$$\frac{[H^+]}{[OH^-]} = \frac{5.7 \times 10^{-10}}{2.9 \times 10^{-11}} = 19.7 \tag{3}$$

Also, $[H^+]$ and $[OH^-]$ must satisfy the K_w relationship:

$$[H^+][OH^-] = K_w = 1.00 \times 10^{-14} \tag{4}$$

Multiplying (*3*) by (*4*), we obtain:

$$[H^+]^2 = 19.7 \times 10^{-14} \qquad [H^+] = 4.4 \times 10^{-7} \qquad pH = -\log[H^+] = 6.36$$

Check of assumption: Our assumption that $[NH_3] = [HOCN]$ is valid only if $[H^+]$ and $[OH^-]$ are much smaller than $[NH_3]$ and [HOCN]. We will solve for x, the $[NH_3]$ or [HOCN]. From (*1*),

$$x = \frac{(5.7 \times 10^{-10})(0.100 - x)}{[H^+]} = \frac{(5.7 \times 10^{-10})(0.100 - x)}{4.4 \times 10^{-7}} \approx 1.3 \times 10^{-4} \tag{5}$$

Both $[H^+]$ and $[OH^-]$ are small compared with x.

It appears from the solution to this problem that the pH is independent of the concentration of NH_4OCN, and this is true at sufficiently high concentrations. However, x decreases with the initial concentration, as is shown in (*5*), so that, at much lower concentrations, the simplifying assumptions are no longer valid. *Note*: The problem can still be solved by insisting on conservation of electrical charge, but the solution becomes very complicated.

POLYPROTIC ACIDS

17.31. Calculate $[H^+]$ of 0.10 M H_2S. K_1 and K_2 for H_2S are 1.0×10^{-7} and 1.2×10^{-13}.

By far, most of the H^+ results from the primary ionization: $H_2S \rightleftharpoons H^+ + S^-$ because K_1 is so much larger than K_2.

Let $x = [H^+] = [HS^-]$. Then, $[H_2S] = 0.10 - x \approx 0.10$.

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]} \qquad \text{or} \qquad 1.0 \times 10^{-7} = \frac{x^2}{0.10} \qquad \text{or} \qquad x = 1.0 \times 10^{-4}$$

Check of assumptions: (1) x is definitely small compared with 0.10. (2) For the above value of $[H^+]$ and $[HS^-]$, the extent of the second dissociation is given by

$$[S^-] = \frac{K_2[HS^-]}{[H^+]} = \frac{(1.2 \times 10^{-13})(1.0 \times 10^{-4})}{(1.0 \times 10^{-4})} = 1.2 \times 10^{-13}$$

The extent of the second dissociation is so small that it does not either lower $[HS^-]$ or raise $[H^+]$ as calculated from the first dissociation significantly. Notice that in a solution of a polyprotic acid the concentration of the conjugate base resulting from the second dissociation is equal to K_2. This result is general whenever the extent of the second dissociation is less than 5% (an application of the five percent rule).

17.32. Calculate the concentration of $C_8H_4O_4^-$ (*a*) in 0.010 M $H_2C_8H_4O_4$, (*b*) in a solution which is 0.10 M $H_2C_8H_4O_4$ and 0.020 M HCl. The ionization constants for $H_2C_8H_4O_4$, phthalic acid, are

$$H_2C_8H_4O_4 \rightleftharpoons H^+ + HC_8H_4O_4^- \qquad K_1 = 1.3 \times 10^{-3}$$
$$HC_8H_4O_4^- \rightleftharpoons H^+ + C_8H_4O_4^- \qquad K2 = 3.9 \times 10^{-6}$$

(*a*) If there were no second dissociation, the $[H^+]$ could be calculated on the basis of K_1.

$$\frac{x^2}{0.010 - x} = 1.3 \times 10^{-3} \qquad \text{or} \qquad x = [H^+] = [HC_8H_4O_4^-] = 3.0 \times 10^{-3}$$

Note that it was necessary to solve the quadratic to obtain x. If we assume that the second dissociation does not appreciably affect $[H^+]$ or $[HC_8H_4O_4^-]$, then

$$[C_8H_4O_4^{2-}] = \frac{K_2[HC_8H_4O_4^-]}{[H^+]} = \frac{(3.9 \times 10^{-6})(3.0 \times 10^{-3})}{3.0 \times 10^{-3}} = 3.9 \times 10^{-3}$$

Check of assumption: The extent of the second dissociation relative to the first is sufficiently small to validate the assumption as follows:

$$\frac{3.9 \times 10^{-6}}{3.0 \times 10^{-3}} = 1.3 \times 10^{-3} \qquad \text{or} \qquad 0.13\%$$

(*b*) The $[H^+]$ in solution may be assumed to be essentially all from the HCl. Also, this large common-ion concentration reduces the ionization of phthalic acid, so that we assume that $[HC_8H_4O_4^-] = 0.010$. The most convenient equation to use is the K_1K_2 equation, since all the concentrations for this equation are known, except for one.

$$\frac{[H^+]^2[C_8H_4O_4^{2-}]}{[H_2C_8H_4O_4]} = K_1K_2 = (1.3 \times 10^{-3})(3.9 \times 10^{-6}) = 5.1 \times 10^{-9}$$

$$[C_8H_4O_4^{2-}] = \frac{(5.1 \times 10^{-9})[H_2C_8H_4O_4]}{[H^+]^2} = \frac{(5.1 \times 10^{-9})(0.010)}{(0.020)^2} = 1.3 \times 10^{-7}$$

Check on assumption: Solving for the first dissociation,

$$[HC_8H_4O_4^-] = \frac{K_1[H_2C_8H_4O_4]}{[H^+]} = \frac{(1.3 \times 10^{-3})(0.010)}{0.020} = 6.5 \times 10^{-4}$$

The amount of H^+ contributed by this dissociation, 6.5×10^{-4} mol/L, is less that 10% of the amount contributed by HCl (0.020 mol/L). The amount of the H^+ contributed by the second dissociation is still less.

17.33. Calculate the extent of hydrolysis of 0.005 M K_2CrO_4. The ionization constants of H_2CrO_4 are $K_1 = 0.18$, $K_2 = 3.2 \times 10^{-7}$.

Just as in the ionization of polyprotic acids, so in the hydrolysis of their salts, the reaction proceeds in successive stages. The extent of the second stage is generally very small compared with the first. This is particularly true in this case, where H_2CrO_4 is quite a strong acid with respect to its first ionization and much weaker in the second ionization. The equation of interest is

$$CrO_4^{2-} + H_2O \rightleftharpoons HCrO_4^- + OH^-$$

which indicates that the conjugate acid of the hydrolyzing CrO_4^{2-} is $HCrO_4^-$. As the ionization constant for $HCrO_4^-$ is K_2, the basic hydrolysis constant for the reaction is K_w/K_2.

$$\frac{[OH^-][HCrO_4^-]}{[CrO_4^{2-}]} = K_b = \frac{K_w}{K_2} = \frac{1.0 \times 10^{-14}}{3.2 \times 10^{-7}} = 3.1 \times 10^{-8}$$

Let $x = [OH^-] = [HCrO_4^-]$. Then, $[CrO_4^{2-}] = 0.005 - x \approx 0.005$ and

$$\frac{x^2}{0.005} = 3.1 \times 10^{-8} \qquad \text{or} \qquad x = 1.2 \times 10^{-5}$$

$$\text{Fraction hydrolysis} = \frac{1.2 \times 10^{-5}}{0.005} = 2.4 \times 10^{-3} \qquad \text{or} \qquad 0.24\%$$

Check assumption: x is quite small compared with 0.005.

17.34. What is the pH of 0.0050 M Na_2S? For H_2S, $K_1 = 1.0 \times 10^{-7}$ and $K_2 = 1.2 \times 10^{-13}$.

As in Problem 17.33, the first stage of hydrolysis, leading to HS^-, by far overshadows the second stage.

$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$$

$$K_b = \frac{[HS^-][OH^-]}{[S^{2-}]} = \frac{K_w}{K_2} = \frac{1.0 \times 10^{-14}}{1.2 \times 10^{-13}} = 8.3 \times 10^{-2}$$

Because of the large value for K_b, it cannot be assumed that the equilibrium concentration of S^{2-} is approximately 0.0050 mol/L. In fact, the hydrolysis is so extensive that most of the S^{2-} is converted to HS^-.

Let $x = [S^{2-}]$, then $[HS^-] = [OH^-] = 0.0050 - x$, and

$$\frac{(0.0050 - x)^2}{x} = 8.3 \times 10^{-2} \qquad \text{then} \qquad x = 2.7 \times 10^{-4}$$

$$[OH^-] = 0.0050 - 2.7 \times 10^{-4} = 0.0047$$

$$\text{pOH} = -\log(4.77 \times 10^{-4}) = 2.33 \qquad \text{and} \qquad \text{pH} = 14.00 - 2.33 = 11.67$$

Check of assumption: Consider the second stage of hydrolysis:

$$HS^- + H_2O \rightleftharpoons H_2S + OH^- \qquad K_b = \frac{K_w}{K_1} = \frac{1.00 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7}$$

Solve for $[H_2S]$ by assuming the values of $[OH^-]$ and $[HS^-]$ already calculated above.

$$[H_2S] = \frac{K_b[HS^-]}{[OH^-]} = \frac{(1.0 \times 10^{-7})(4.7 \times 10^{-3})}{4.7 \times 10^{-3}} = 1.0 \times 10^{-7}$$

The extent of the second hydrolysis compared with the first, (1.6×10^{-7}) to (4.7×10^{-3}), is very small.

17.35. Calculate $[H^+]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$, and $[PO_4^{3-}]$ in 0.0100 M H_3PO_4. K_1, K_2, and K_3 are 7.52×10^{-3}, 6.23×10^{-8}, and 4.5×10^{-13}, respectively.

We begin by assuming that H^+ comes mostly from the first stage of dissociation and that the concentration of any anion formed by one stage of an ionization is not appreciably lowered by the second state of ionization.

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad K_1 = 7.52 \times 10^{-3}$$

Let $[H^+] = [H_2PO_4^-] = x$. Then $[H_3PO_4] = 0.0100 - x$, and

$$\frac{x^2}{0.0100 - x} = 7.5 \times 10^{-3} \qquad \text{or} \qquad x = 0.0057$$

We next take the above values for $[H^+]$ and $[H_2PO_4^-]$ to solve for $[HPO_4^{2-}]$.

$$H_2PO_4^- \rightleftharpoons H^+ + [HPO_4^{2-}] \qquad K_1 = 6.23 \times 10^{-8}$$

$$[HPO_4^{2-}] = \frac{K_2[H_2PO_4^-]}{[H^+]} = \frac{(6.23 \times 10^{-8})(0.0057)}{0.0057} = 6.23 \times 10^{-8}$$

Check of assumption: The extent of the second dissociation compared with the first is very small, 6.23×10^{-8} compared to 5.7×10^{-3}.

The next step would be to perform the same calculations using K_3 and the associated reaction, but we note that K_3 is very small as compared with K_2, the point being that the values that would be calculated are expected to be of little significance in comparison to the results of the previous K values.

17.36. What is the pH of 0.0100 M $NaHCO_3$? K_1 and K_2 for H_2CO_3 are 4.3×10^{-7} and 5.61×10^{-11}.

(*Note*: H_2CO_3 in aqueous solution is in equilibrium with dissolved CO_2, the majority species. The value of K_1 given here is based on the total concentration of both of these neutral species. Since there is no effect on the stoichiometry or charge balance, the problem can be worked as if all the neutral species were in the form H_2CO_3.)

This problem is somewhat similar to Problem 17.30 because there is one reaction tending to make the solution acid (the K_2 acid dissociation of HCO_3^- to yield H^+) and another reaction tending to make the solution basic (the hydrolysis of HCO_3^-).

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad K_2 = 5.61 \times 10^{-11} \qquad (1)$$

$$HCO_3^- + H_2O \rightleftharpoons OH^- + H_2CO_3 \qquad K_b = \frac{K_w}{K_1} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8} \qquad (2)$$

We notice that the hydrolysis constant for reaction (*2*) is related to K_1, because both hydrolysis and the K_1 equilibrium involve H_2CO_3 and HCO_3^-. We see that the equilibrium constant for (*2*) is greater than that for (*1*); then, the pH is definitely going to exceed 7.

We assume that, after the self-neutralization of both, $[H^+]$ and $[OH^-]$ were so small as to have no appreciable effect on the ionic charge balance. Therefore, electrical neutrality can be preserved only by maintaining a fixed total anionic charge among the various carbonate species. This is true since the cationic charge remains at 0.0100 M, which is the concentration of Na^+, regardless of the acid-base equilibria. In other words, for every negative charge removed by the conversion of HCO_3^- to H_2CO_3, another negative charge is created by converting HCO_3^- to CO_3^{2-}.

This leads to the following conditions:

$$[H_2CO_3] = [CO_3^{2-}] = x \qquad \text{and} \qquad [HCO_3^-] = 0.0100 - 2x \approx 0.0100$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{[H^+]x}{0.0100} = 5.61 \times 10^{-11} \tag{3}$$

$$K_b = \frac{[OH^-][H_2CO_3]}{[HCO_3^-]} = \frac{[OH^-]x}{0.0100} = 2.3 \times 10^{-8} \tag{4}$$

Multiplying (*3*) and (*4*), while recalling that $[H^+][OH^-] = 1.00 \times 10^{-14}$, we have

$$\frac{(1.00 \times 10^{-14})x^2}{(0.0100)^2} = (5.61 \times 10^{-11})(2.3 \times 10^{-8}) \qquad \text{or} \qquad x = 1.14 \times 10^{-4}$$

Provisional check: $2x$ is small compared with 0.0100.

We return now to (*3*).

$$[H^+] = \frac{(5.61 \times 10^{-11})[HCO_3^-]}{[CO_3^{2-}]} = \frac{(5.61 \times 10^{-11})(0.0100)}{1.14 \times 10^{-4}} = 4.9 \times 10^{-9}$$

$$\text{pH} = -\log[H^+] = -\log(4.9 \times 10^{-9}) = 8.31$$

Final check: Both $[H^+]$ and $[OH^-]$ are small compared with x and will have no appreciable effect on the electrical charge balance.

Alternatively, $[H^+]$ could have been calculated from K_1 only; the result would have been the same.

BUFFER SOLUTIONS, INDICATORS, AND TITRATION

17.37. A buffer solution of pH 8.50 is desired. (*a*) Starting with 0.0100 mol KCN and the usual inorganic reagents of the laboratory, how would you prepare 1 L of the buffer solution? K_a for HCN is 4.93×10^{-10}. (*b*) By how much would the pH change after the addition of 5×10^{-5} mol $HClO_4$ to 100 mL of the buffer? (*c*) By how much would the pH change after the addition of 5×10^{-5} mol NaOH to 100 mL of the buffer? (*d*) By how much would the pH change after the addition of 5×10^{-5} mol NaOH to 100 mL pure water?

(*a*) To find the desired $[H^+]$:

$$\log[H^+] = -\text{pH} = -8.50$$

Taking the antilog of both sides:

$$[H^+] = 3.2 \times 10^{-9}$$

The buffer solution could be prepared by mixing CN^- (weak base, using a strong salt, such as KCN as it ionizes completely) with HCN (weak acid) in the proper proportions to satisfy the K_a for HCN.

$$HCN \rightleftharpoons H^+ + CN^- \qquad K_a = 4.93 \times 10^{-10} = \frac{[H^+][CN^-]}{[HCN]}$$

and, by rearrangement and solving,

$$\frac{[CN^-]}{[HCN]} = \frac{K_a}{[H^+]} = \frac{4.93 \times 10^{-10}}{3.2 \times 10^{-9}} = 0.154 \tag{1}$$

The ratio of CN^- to HCN (0.154:1) can be attained if some of the CN^- is neutralized with a strong acid, like HCl, to form an equivalent amount of HCN. The total cyanide available for both forms is 0.0100 mol. Let $x = [\text{HCN}]$; then $[\text{CN}^-] = 0.0100 - x$. Substituting in (*1*) directly above,

$$\frac{0.0100 - x}{x} = 0.154 \qquad \text{then} \qquad x = 0.0087 \qquad \text{and} \qquad 0.0100 - x = 0.0013$$

The buffer solution can be prepared by dissolving 0.0100 mol KCN and 0.0087 mol HCl in sufficient water to make up 1 L of solution.

(*b*) 100 mL of the buffer contains

$$(0.0087\ \text{mol/L}(0.100\ \text{L}) = 8.7 \times 10^{-4}\ \text{mol HCN}$$

and

$$(0.0013\ \text{mol/L})(0.100\ \text{L}) = 1.3 \times 10^{-4}\ \text{mol CN}^-$$

The addition of 5×10^{-5} mol of strong acid converts more CN^- to HCN. The amount of HCN will be

$$(8.7 \times 10^{-4}) + (0.5 \times 10^{-4}) = 9.2 \times 10^{-4}\ \text{mol HCN}$$

and the amount of CN^- will be

$$(1.3 \times 10^{-4}) - (0.5 \times 10^{-4}) = 0.8 \times 10^{-4}\ \text{mol CN}^-$$

Only the ratio of the two concentrations is needed.

$$[\text{H}^+] = K_a\frac{[\text{HCN}]}{[\text{CN}^-]} = (4.93 \times 10^{-10})\left(\frac{9.2}{0.8}\right) = 5.7 \times 10^{-9}$$
$$\text{pH} = -\log[\text{H}^+] = -\log(5.7 \times 10^{-9}) = 8.24$$

The drop in pH caused by the addition of the acid is 8.50 − 8.24, or 0.26 pH units.

(*c*) The addition of 5×10^{-5} mol of a strong base will convert an equivalent amount of HCN to CN^-.

HCN: Resulting amount $= (8.7 \times 10^{-4}) - (0.5 \times 10^{-4}) = 8.2 \times 10^{-4}$ mol

CN^-: Resulting amount $= (1.3 \times 10^{-4}) - (0.5 \times 10^{-4}) = 1.8 \times 10^{-4}$ mol

$$[\text{H}^+] = K_a\frac{[\text{HCN}]}{[\text{CN}^-]} = (4.93 \times 10^{-10})\left(\frac{8.2}{1.8}\right) = 2.2 \times 10^{-9}$$
$$\text{pH} = -\log[\text{H}^+] = -\log(2.2 \times 10^{-9}) = 8.66$$

The rise in pH caused by the addition of the base is 8.66 − 8.50, or 0.16 pH units.

(*d*)

$$[\text{OH}^-] = \frac{5 \times 10^{-5}\ \text{mol}}{0.100\ \text{L}} = 5 \times 10^{-4}$$
$$\text{pOH} = -\log[\text{OH}^-] = -\log(5 \times 10^{-4}) = 3.30$$

and

$$\text{pH} = 14 - \text{pOH} = 14.00 - 3.30 = 10.70$$

Pure water has a pH of 7.00. The rise caused by the addition of the base is 10.70 − 7.00, or 3.70 pH units. Note that this rise is quite large when compared to the rise due to addition to the buffer solution. Recall that the buffer is capable of absorbing hydrogen and/or hydroxide ions with little change; pure water cannot do that.

17.38. If 0.00010 mol H_3PO_4 were to be added to a solution well buffered at pH 7.00, what are the relative proportions for the four forms: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}? $K_1 = 7.52 \times 10^{-3}$, $K_2 = 6.23 \times 10^{-8}$, and $K_3 = 4.5 \times 10^{-13}$.

In the previous problem, we expected some pH change, but in this problem we can assume that the pH is not changed by the addition of the very small amount of phosphoric acid mentioned because it is "well buffered," meaning that it is extremely resistant to pH change. Then, if $[H^+]$ is fixed, the ratio of two of the desired concentrations can be calculated from each of the ionization constant equations.

$\frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = K_1$	$\frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = K_2$	$\frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = K_3$
$\frac{[H_3PO_4]}{[H_2PO_4^-]} = \frac{[H^+]}{K_1}$	$\frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = \frac{[H^+]}{K_2}$	$\frac{[HPO_4^{2-}]}{[PO_4^{3-}]} = \frac{[H^+]}{K_3}$
$\frac{[H_3PO_4]}{[H_2PO_4^-]} = \frac{1.00\times10^{-7}}{7.52\times10^{-3}}$	$\frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = \frac{1.00\times10^{-7}}{6.23\times10^{-8}}$	$\frac{[HPO_4^{2-}]}{[PO_4^{3-}]} = \frac{1.00\times10^{-7}}{4.5\times10^{-13}}$
$\frac{[H_3PO_4]}{[H_2PO_4^-]} = 1.33 \times 10^{-5}$	$\frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = 1.61$	$\frac{[HPO_4^{2-}]}{[PO_4^{3-}]} = 2.2 \times 10^{-5}$

Since the ratio $[H_3PO_4]/[H_2PO_4^-]$ is very small and the ratio $[HPO_4^{2-}]/[PO_4^{3-}]$ is very large, practically all of the material will exist as $H_2PO_4^-$ and HPO_4^{2-}. The sum of the amounts of these two ions will be practically equal to 0.00010 mol. If the total volume is 1 L, the sum of these two ion concentrations will be 0.00010 M.

Let $x = [HPO_4^{2-}]$; then $[H_2PO_4^-] = 0.00010 - x$. Then

$$\frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = 1.61 \qquad \text{by substitution} \qquad \frac{0.00010 - x}{x} = 1.61$$

$$\text{Solving} \qquad x = [HPO_4^{2-}] = 3.8 \times 10^{-5}$$

$$[H_2PO_4^-] = 0.00010 - x = 6.2 \times 10^{-5}$$

$$[H_3PO_4] = (1.33 \times 10^{-5})[H_2PO_4^-] = (1.33 \times 10^{-5})(6.2 \times 10^{-5}) = 8.2 \times 10^{-10}$$

$$[PO_4^{3-}] = \frac{[HPO_4^{2-}]}{2.2 \times 10^5} = \frac{3.8 \times 10^{-5}}{2.2 \times 10^5} = 1.7 \times 10^{-10}$$

A total volume of 1 L was selected for convenience in illustrating the relative concentrations. However, the same *ratios* of concentrations would be valid for any reasonable choice of total volume.

17.39. K_a for $HC_2H_3O_2$ is 1.75×10^{-5}. A 40.0-mL sample of 0.0100 M acetic acid is titrated with 0.0200 M NaOH. Calculate the pH after the addition of (*a*) 3.0 mL; (*b*) 10.0 mL; (*c*) 20.0 mL; (*d*) 30.0 mL of NaOH solution.

We can keep track of the changing amounts of various species and the increasing volume by a bookkeeping system, such as Table 17-2.

Note that the amount of acetic acid neutralized (amount of $C_2H_3O_2^-$) follows the amount of OH^- added, up to complete neutralization. Additional OH^-, having no more acid to neutralize, accumulates in the solution. Up to the end point, the amount of $HC_2H_3O_2$ remaining is obtained by simply subtracting the amount of $C_2H_3O_2^-$ from the initial amount of $HC_2H_3O_2$. At the end point and beyond, however, $[HC_2H_3O_2]$ cannot be set equal to zero, but must be deduced from the hydrolysis equilibrium.

(*a*) and (*b*). The numerical values for the concentrations are not needed for these parts of the problem; however, the ratio of the conjugate acid to base is required.

	(*a*)	(*b*)
$[H^+] = \frac{K_a[HC_2H_3O_2]}{[C_2H_3O_2^-]}$	$\frac{(1.75 \times 10^{-5})(3.40)}{0.60} = 9.9 \times 10^{-5}$	$\frac{(1.75 \times 10^{-5})(2.00)}{2.00} = 1.75 \times 10^{-5}$
$pH = -\log [H^+]$	4.00	4.76

Table 17-2

		(*a*)	(*b*)	(*c*)	(*d*)
Amount of base added/L	0	0.0300	0.0100	0.0200	0.0300
Total volume in L	0.0400	0.0430	0.0500	0.0600	0.0700
$n(HC_2H_3O_2)$ before neutralization	4.00×10^{-4}	4.00×10^{-4}	4.00×10^{-4}	4.00×10^{-4}	4.00×10^{-4}
$n(OH^-)$ added (Row 1 × 0.0200 M)	0.00×10^{-4}	0.60×10^{-4}	2.00×10^{-4}	4.00×10^{-4}	6.00×10^{-4}
$n(C_2H_3O_2^-)$ formed	0.0×10^{-4}	0.60×10^{-4}	2.00×10^{-4}	4.00×10^{-4}	4.00×10^{-4}
$n(HC_2H_3O_2)$ remaining	4.00×10^{-4}	3.40×10^{-4}	2.00×10^{-4}	x	y
$n(OH^-)$ excess					2.00×10^{-4}

(c)

$$[C_2H_3O_2^-] = \frac{4.00 \times 10^{-4\,\mathrm{mol}}}{0.0600\,\mathrm{L}} = 6.7 \times 10^{-3}\,\mathrm{M}$$

The solution at the end point is the same as 6.7×10^{-3} M $Na_2C_2H_3O_2$; consider its hydrolysis:

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$$

Let $[HC_2H_3O_2] = [OH^-] = x$, and $[C_2H_3O_2^-] = 6.7 \times 10^{-3} - x \approx 6.7 \times 10^{-3}$. Then

$$\frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = \frac{x^2}{6.7 \times 10^{-3}} = K_b = \frac{1.00 \times 10^{-14}}{1.75 \times 10^{-5}} \qquad \text{or} \qquad x = 1.96 \times 10^{-6}$$

Check of assumption: x is quite small compared with 6.7×10^{-3}.

$$\mathrm{pOH} = -\log[OH^-] = -\log(1.9 \times 10^{-6}) = 5.72$$

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14 - 5.72 = 8.28$$

(d) From the extra OH^- beyond that needed to neutralize all the acetic acid, we know that

$$[OH^-] = \frac{2.0 \times 10^{-4}\,\mathrm{mol}}{0.070\,\mathrm{L}} = 2.9 \times 10^{-3}\,\mathrm{mol/L}$$

$$\mathrm{pOH} = -\log[OH^-] = -\log\ 2.9 \times 10^{-3} = 2.54 \qquad \text{and} \qquad \mathrm{pH} = 14.00 - 2.54 = 11.46$$

17.40. Calculate a point on the titration curve for the addition of 2.0 mL of 0.0100 M NaOH to 50.0 mL of 0.0100 M chloroacetic acid, $HC_2H_2O_2Cl$. $K_a = 1.40 \times 10^{-3}$.

The simplifying assumption made in Problem 17.39 just won't work in this problem. If the amount of chloroacetate ion formed were to be equivalent to the amount of NaOH added, we would have

Amount OH^- added = (0.0020 L)(0.010 mol/L) = 2.0×10^{-5} mol

Total volume = 0.0520 L

$$[C_2H_2O_2Cl^-] = \frac{2.0 \times 10^{-5}\,\mathrm{mol}}{0.0520\,\mathrm{L}} = 3.8 \times 10^{-4}\,\mathrm{M} \tag{1}$$

$$[HC_2H_2O_2Cl] = \frac{(0.0500\,\mathrm{L})(0.0100\,\mathrm{mol/L})}{0.0520\,\mathrm{L}} - 3.8 \times 10^{-4}\,\mathrm{M} = 9.2 \times 10^{-3}\,\mathrm{M} \tag{2}$$

$$[H^+] = \frac{K_a[HC_2H_2O_2Cl]}{[C_2H_2O_2Cl^-]} = \frac{(1.40 \times 10^{-3})(9.2 \times 10^{-3})}{3.8 \times 10^{-4}} = 3.4 \times 10^{-2}\,\mathrm{M} \tag{3}$$

This answer simply won't work because the $[H^+]$ cannot possibly be more than the beginning molar concentration of the acid. Apparently the amount of chloroacetate ion is greater than the equivalent amount of base added. This fact is related to the relatively strong acidity of the acid and to the appreciable ionization of the acid, even before the titration begins. Mathematically, this is taken into account by an equation of electroneutrality, according to which there must be equal numbers of cations and anions in solution.

$$[H^+] + [Na^+] = [C_2H_2O_2Cl^-] + [OH^-] \tag{4}$$

It is safe to drop the $[OH^-]$ in (*4*) in this case because it is so much smaller than any of the others. $[Na^+]$ is obtained from the amount of NaOH added (complete ionization) and the total volume of solution.

$$[Na^+] = \frac{2.0 \times 10^{-5}}{0.0520} = 3.8 \times 10^{-4} \tag{5}$$

Chloroacetate ion can be calculated from (*4*) and (*5*) while omitting $[OH^-]$ from consideration.

$$[C_2H_2O_2Cl^-] = 3.8 \times 10^{-4} + [H^+] \tag{6}$$

The undissociated acid concentration is the total molar concentration of acid minus $[C_2H_2O_2Cl^-]$.

$$[HC_2H_2O_2Cl] = \frac{(0.0100)(0.0500)}{0.0520} - (3.8 \times 10^{-2} + [H^+]) = 9.2 \times 10^{-3} - [H^+] \tag{7}$$

Note that (*6*) and (*7*) differ from (*1*) and (*2*) only in the inclusion of the $[H^+]$ terms.

Now, we may return to the ionization equilibrium for the acid.

$$[H^+] = \frac{K_a[HC_2H_2O_2Cl]}{[C_2H_2O_2Cl^-]} = \frac{(1.40 \times 10^{-3})(9.2 \times 10^{-3} - [H^+])}{3.8 \times 10^{-4} + [H^+]}$$

The solution to the quadratic equation is $[H^+] = 2.8 \times 10^{-3}$, and $\text{pH} = -\log [H^+] = 2.55$.

The complication treated in this problem occurs whenever, during a partial neutralization, $[H^+]$ or $[OH^-]$ cannot be neglected in comparison with the concentrations of other ions in solution. This is likely to be the case near the beginning of the titration of an acid which is only moderately weak.

17.41. An acid-base indicator has a K_a of 3.0×10^{-5}. The acid form is red and the basic form is blue. (*a*) By how much must the pH change in order to change from 75% red to 75% blue? (*b*) For which of the titrations shown in Fig. 17-1*a* and 17.1*b* would this indicator be a good choice?

(*a*)
$$[H^+] = \frac{K_a[\text{acid}]}{[\text{base}]}$$

75%; red: $[H^+] = \frac{(3.0 \times 10^{-5})(75)}{25} = 9.0 \times 10^{-5}$ $\quad$ pH = 4.05

75% blue: $[H^+] = \frac{(3.0 \times 10^{-5})(25)}{75} = 1.0 \times 10^{-5}$ $\quad$ pH = 5.00

The change in pH is 5.00 − 4.05 = 0.95 pH units.

(*b*) The indicator changes color between pH 4 and pH 5 (Fig. 17-1*b*). With the use of HCl, the pH is falling rapidly in this range; the indicator would be suitable for both of them. In the titration of HCl with NaOH in Fig. 17-1*a*, the pH is rising rapidly in this range; the indicator can be used. The indicator, however, would not be suitable for the $HC_4H_7O_3$ titration, which would change from red to blue long before the end point is reached.

Supplementary Problems

Notes:

1. The numerical values tabulated for equilibrium constants differ in various books. The values selected for this book are internally consistent, and the calculated answers are based on values given here. The temperature is assumed to be 25°C, unless there is a specific statement to the contrary.
2. Some of the problems at the end of the sections on Acids and Bases, Hydrolysis, Polyprotic Acids, and Buffers involve multiple equilibria. They may be omitted in a simplest treatment of ionic equilibria.

ACIDS AND BASES

17.42. A certain reaction is catalyzed by acids. The catalytic activity for 0.1 M solutions of acids in water was found to decrease in the order: HCl, HCOOH, $HC_2H_3O_2$. The same reaction takes place in anhydrous ammonia, but the three acids all have the same catalytic effect in 0.1 M solutions. Explain.

Ans. The order of catalytic activity in water is the same as the order of acidity. In anhydrous ammonia, a stronger base than water (i.e., a more efficient proton acceptor), all three acids are strong.

17.43. The amino acid glycine exists predominantly in the form $^+NH_3CH_2COO^-$. Write the formulas for (*a*) the conjugate base and (*b*) the conjugate acid of glycine.

Ans. (*a*) $NH_2CH_2COO^-$; (*b*) $^+NH_3CH_2COOH$

17.44. In the reaction of BeF_2 with $2F^-$ to form BeF_4^{2-}, which reactant is the Lewis acid and which is the Lewis base?

Ans. BeF_2 is the acid and F^- is the base.

17.45. The conjugate acid of nitric acid loses a water molecule in certain solvents. Explain how the resulting entity can still act as an acid in the Lewis sense.

Ans. $H_2NO_3^+$ would be the conjugate acid of nitric acid (the result of $HNO_3 + H^+$). Then, $H_2NO_3^+ \rightarrow H_2O + NO_2^+$ (refer below for nitrite)

$$:\ddot{O}=\overset{+}{N}=\ddot{O}:$$

Nitrogen can go from *sp* to sp^3 hybridization providing an empty orbital for a base pair. (Note similar behavior of CO_2 in Problem 17.8.)

17.46. Is acetic acid a weaker or stronger acid in the following solvents as compared to water? (*a*) hydrazine, N_2H_4; (*b*) sulfur dioxide, SO_2; (*c*) methanol, CH_3OH; (*d*) liquid hydrogen cyanide, HCN; (*e*) liquid sulfuric acid, H_2SO_4.

Ans. (*a*) stronger; (*b*) weaker; (*c*) weaker; (*d*) weaker; (*e*) weaker

17.47. The self-ionization constant for pure formic acid, $K = [HCOOH_2^+][HCOO^-]$, has been estimated as 10^{-6} at room temperature. What percentage of formic acid molecules in pure formic acid, HCOOH, are converted to formate ion? The density of formic acid is 1.22 g/mL.

Ans. 0.004%

17.48. Calculate the ionization constant of formic acid, HCOOH, which ionizes 4.2% in 0.10 M solution.

Ans. 1.8×10^{-4}

17.49. A solution of acetic acid is 1.0% ionized. What must be the molar concentration of acetic acid and the $[H^+]$ of the solution? K_a of $HC_2H_3O_2$ is 1.75×10^{-5}.

Ans. 0.17M $HC_2H_3O_2$, 1.7×10^{-3} M H^+

17.50. The ionization constant of ammonia in water is 1.75×10^{-5}. Determine (*a*) the degree of ionization and (*b*) the $[OH^-]$ of a 0.08 M solution of NH_3.

Ans. (*a*) 1.5%; (*b*) 1.2×10^{-3} M OH^-

17.51. Chloroacetic acid, a monoprotic acid, has a K_a of 1.40×10^{-3}. Calculate the freezing point of a 0.10 M solution of this acid. Assume that the numerical value of the molar and molal concentrations are the same.

Ans. −0.21°C

17.52. Determine the $[OH^-]$ of a 0.0500 M solution of ammonia to which has been added sufficient NH_4Cl to make the total $[NH_4^+]$ equal to 0.100.K_b for ammonia is 1.75×10^{-5}.

Ans. 8.8×10^{-6}

17.53. Find the value of the $[H^+]$ in a liter of solution in which are dissolved 0.080 mol $HC_2H_3O_2$ and 0.100 mol $NaC_2H_3O_2$. K_a for acetic acid is 1.75×10^{-5}.

Ans. 1.4×10^{-5}

17.54. A 0.025 M solution of monobasic acid had a freezing point of −0.060°C. What are K_a and pK_a for the acid? Assume that at this low concentration, molality is equal to molarity.

Ans. 3.0×10^{-3}, 2.52

17.55. What is $[NH_4^+]$ in a solution of 0.0200 M NH_3 and 0.0100 M KOH? K_b for NH_3 is 1.75×10^{-5}.

Ans. 3.5×10^{-5}

17.56. What molarity of NH_3 provides 1.5×10^{-3} M OH^-? K_b for NH_3 is 1.75×10^{-5}.

Ans. 0.13 M

17.57. What is $[HCOO^-]$ in a solution that is both 0.015 M HCOOH and 0.020 M HCl? K_a for HCOOH is 1.8×10^{-4}.

Ans. 1.4×10^{-4}

17.58. What are $[H^+]$, $[C_3H_5O_3^-]$, and $[OC_6H_5^-]$ in a solution that is 0.030 M $HC_3H_5O_3$ and 0.100 M HOC_6H_5? K_a-values for $HC_3H_5O_3$ and HOC_6H_5 are 3.1×10^{-5} and 1.05×10^{-10}, respectively.

Ans. $[H^+] = 9.6 \times 10^{-4}$, $[C_3H_5O_3^-] = 9.6 \times 10^{-4}$, $[OC_6H_5^-] = 1.1 \times 10^{-8}$

17.59. Find the value of $[OH^-]$ in a solution made by dissolving 0.0050 mol each of ammonia and pyridine in enough water to make 200 mL of solution. K_b for ammonia and pyridine are 1.75×10^{-5} and 1.78×10^{-9}, respectively. What are the concentrations of ammonium and pyridinium ions?

Ans. $[OH^-] = [NH_4^+] = 6.6 \times 10^{-4}$, [pyridinium ion] $= 6.7 \times 10^{-8}$

17.60. Consider a solution of a monoprotic weak acid with acidity constant K_a. Calculate the minimum concentration, C, for which the percent ionization is less than 10%.

Ans. $C = 90\, K_a$

17.61. What is the percent ionization of 0.0065 M chloroacetic acid? $K_a = 1.40 \times 10^{-3}$.

Ans. 37%

17.62. What concentration of dichloroacetic acid gives a $[H^+]$ of 8.5×10^{-3}? $K_a = 3.32 \times 10^{-2}$.

Ans. 1.07×10^{-2} M

17.63. Calculate $[H^+]$ in a 0.200 M dichloroacetic acid solution that is also 0.100 M sodium dichloroacetate. K_a for dichloroacetic acid is 3.32×10^{-2}.

Ans. 0.039

17.64. How much solid sodium dichloroacetate should be added to a liter of 0.100 M dichloroacetic acid to reduce the hydrogen ion concentration to 0.030 M? K_a for dichloroacetic acid is 3.32×10^{-2}. Assume no change in concentration on the addition of the solid.

Ans. 0.047 mol

17.65. Calculate $[H^+]$ and $[C_2HO_2Cl_2^-]$ in solution that is 0.0100 M HCl and 0.0100 M $HC_2HO_2Cl_2$. K_a for $HC_2HO_2Cl_2$ (dichloroacetic acid) is 3.32×10^{-2}.

Ans. 0.0167, 0.0067

17.66. Calculate $[H^+]$, $[C_2H_3O_2^-]$, and $[C_7H_5O_2^-]$ in a solution that is 0.0200 M $HC_2H_3O_2$ and 0.0100 M $HC_7H_5O_2$. K_a for $HC_2H_3O_2$ is 1.75×10^{-5}; K_a for $HC_7H_5O_2$ is 6.46×10^{-5}.

Ans. 1.00×10^{-3}, 3.5×10^{-4}, 6.5×10^{-4}

17.67. Liquid ammonia (*am*) ionizes to a slight extent. The ion product, $[NH_4^+][NH_2^-]$, at −50°C has a K_{am} of 10^{-30}. How many amide ions, NH_2^-, are present per mm^3 of pure liquid ammonia?

Ans. 6.0×10^2

17.68. Calculate the molar concentration of ammonium ions in a liter of liquid ammonia at −50°C (see previous problem), in which 10.0 grams each of NH_4Cl and sodium amide ($NaNH_2$) were dissolved.

Ans. 1.4×10^{-29} M

IONIZATION OF WATER

17.69. Assuming complete ionization, what are the pH and pOH of the following solutions? (*a*) 0.00345 N acid; (*b*) 0.000775 N acid; (*c*) 0.00868 N base.

Ans. (*a*) pH = 2.46, pOH = 11.54; (*b*) 3.11, 10.89; (*c*) 11.95, 2.05

17.70. Convert the following pH values to $[H^+]$ values: (*a*) 4; (*b*) 7; (*c*) 2.50; (*d*) 8.26.

Ans. (*a*) 10^{-4}; (*b*) 10^{-7}; (*c*) 3.2×10^{-3}; (*d*) 5.5×10^{-9}

17.71. The $[H^+]$ of an HNO_3 solution is 1×10^{-3}, and the $[H^+]$ of an NaOH solution is 1×10^{-12}. What are the molar concentration and pH of each solution?

Ans. 0.001 M HNO_3, pH = 3; 0.01 M NaOH, pH = 12

17.72. (*a*) Calculate $[H^+]$ and $[OH^-]$ in an 0.0010 M solution of a monobasic acid which is 4.2% ionized. (*b*) What is the pH of the solution? (*c*) What are K_a and pK_a for the acid?

Ans. (*a*) $[H^+] = 4.2 \times 10^{-5}$, $[OH^-] = 2.4 \times 10^{-10}$; (*b*) pH = 4.38; (*c*) $K_a = 1.8 \times 10^{-6}$, $pK_a = 5.74$

17.73. (*a*) Calculate $[OH^-]$ and $[H^+]$ in a 0.10 N solution of a weak base which is 1.3% ionized. (*b*) What is the pH of the solution?

Ans. (*a*) $[OH^-] = 1.3 \times 10^{-3}$, $[H^+] = 7.7 \times 10^{-12}$; (*b*) pH = 11.11

17.74. (*a*) What is the pH of a solution containing 0.010 mol HCl per liter? (*b*) Calculate the change in pH if 0.020 mol $NaC_2H_3O_2$ is added to a liter of this solution. K_a of $HC_2H_3O_2$ is 1.75×10^{-5}.

Ans. (*a*) Initial pH = 2.0; (*b*) Final pH = 4.76

17.75. The value of K_w at the physiological temperature (normal human body temperature, 37°C) is 2.4×10^{-14}. What is the pH of the neutral point of water at this temperature, where there are equal numbers of H^+ and OH^-?

Ans. 6.81

17.76. Calculate the pH of 1.0×10^{-7} M NaOH. What percentage of the added base was neutralized by the H^+ present in the water and what percentage remained to make the solution basic?

Ans. 7.21; 38% was neutralized; 62% remained

17.77. (*a*) What is the pH of 7.0×10^{-8} M $HC_2H_3O_2$? (*b*) What is the concentration of un-ionized acetic acid? K_a is 1.75×10^{-5} (*Hint*: Assume complete ionization of the acetic acid in solving for $[H^+]$.)

Ans. (*a*) 6.85; (*b*) 5.6×10^{-10}

17.78. Calculate $[OH^-]$ in a 0.0100 M $C_6H_5NH_2$ (aniline). K_b for the basic dissociation is 4.3×10^{-10}. What is the $[OH^-]$ in a 0.0100 M solution of aniline hydrochloride, which contains the ion $C_6H_5NH_3^+$?

Ans. 2.1×10^{-6}, 2.1×10^{-11}

17.79. Calculate the percent hydrolysis in a 0.0100 M solution of KCN. K_a for HCN is 4.93×10^{-10}.

Ans. 4.5%

17.80. The basic ionization constant for hydrazine, N_2H_4, is 9.6×10^{-7}. What would be the percent hydrolysis of 0.100 M N_2H_5Cl, a salt containing the acid ion conjugate to hydrazine base?

Ans. 0.032%

17.81. Calculate the pH of a moderately concentrated solution of pyridinium acetate, $(C_5H_5NH)(C_2H_3O_2)$. K_a for acetic acid is 1.75×10^{-5} and for pyridinium ion is 5.6×10^{-6}.

Ans. 5.00

17.82. A 0.25 M solution of pyridinium chloride, $C_5H_6N^+Cl^-$, was found to have a pH of 2.93. What is K_b for the basic dissociation of pyridine, C_5H_5N?

Ans. 1.8×10^{-9}

17.83. K_a for the acid ionization of Fe^{3+} to $Fe(OH)^{2+}$ and H^+ is 6.5×10^{-3}. What is the maximum pH value which could be used so that at least 95% of the total iron(III) in a dilute solution is in the Fe^{3+} form?

Ans. 0.91

17.84. A 0.010 M solution of $PuO_2(NO_3)_2$ was found to have a pH of 3.80. What is the hydrolysis constant, K_a, for PuO_2^{2+}, and what is K_b for PuO_2OH^+?

Ans. $K_a = 2.5 \times 10^{-6}$, $K_b = 4.0 \times 10^{-9}$

17.85. Calculate the pH of 1.00×10^{-3} M sodium phenolate, $NaOC_6H_5$. K_a for HOC_6H_5 is 1.28×10^{-10}.

Ans. 10.39

17.86. Calculate $[H^+]$ and $[CN^-]$ in 0.0100 M NH_4CN. K_a for HCN is 4.93×10^{-10} and K_b for NH_3 is 1.75×10^{-5}.

Ans. 5.3×10^{-10}, 4.8×10^{-3}

POLYPROTIC ACIDS

17.87. Calculate the $[H^+]$ of a 0.050 M H_2S solution. K_1 of H_2S is 1.0×10^{-7}.

Ans. 7.1×10^{-5}

17.88. What is $[S^{2-}]$ in a 0.0500 M H_2S solution. K_2 of H_2S is 1.2×10^{-13}.

Ans. 1.2×10^{-13}

17.89. What is $[S^{2-}]$ in a solution that is 0.050 M H_2S and 0.0100 M HCl? Refer to previous two problems.

Ans. 6.0×10^{-18}

17.90. (*a*) Calculate the $[HS^-]$ in the solution in the preceding problem. (*b*) If sufficient ammonia were added to buffer the solution at pH = 4.37, what would be the concentrations of S^{2-} and HS^-?

Ans. (*a*) 5.0×10^{-7}; (*b*) $[S^{2-}] = 3.3 \times 10^{-13}$, $[HS^-] = 1.2 \times 10^{-4}$

17.91. K_1 and K_2 for oxalic acid, $H_2C_2O_4$, are 5.9×10^{-2} and 6.4×10^{-5}, respectively. What is $[OH^-]$ in 0.0050 M $Na_2C_2O_4$?

Ans. 8.8×10^{-7}

17.92. Malonic acid is a dibasic acid having $K_1 = 1.49 \times 10^{-3}$ and $K_2 = 2.03 \times 10^{-6}$. Calculate the concentration of the divalent malonate ion in (*a*) 0.0010 M malonic acid, (*b*) a solution that is 0.00010 M malonic acid and 0.00040 M HCl.

Ans. (*a*) 2.0×10^{-6}; (*b*) 3.2×10^{-7}

17.93. What is the pH of a 0.010 M solution of H_3PO_4. $K_1 = 7.52 \times 10^{-3}$, $K_2 = 6.23 \times 10^{-8}$.

Ans. 2.24

17.94. (*a*) Calculate $[H^+]$ in a 0.0060 M H_2SO_4 solution. The first ionization of H_2SO_4 is complete and the second ionization has a K_a of 1.20×10^{-2}. (*b*) What is the sulfate concentration in this solution?

Ans. (*a*) $[H^+] = 9.4 \times 10^{-3}$; (*b*) $[SO_4^{2-}] = 3.4 \times 10^{-3}$

17.95. Ethylenediamine, $NH_2C_2H_4NH_2$, is a base that can add one or two protons. The successive pK_b values for the reaction of the neutral base and that of the monovalent (+1) cation with water are 3.288 and 6.436, respectively. In a 0.0100 M solution of ethylenediamine, what are the concentrations of the singly charged cation and of the doubly charged cation?

Ans. 2.03×10^{-3} mol/L, 3.66×10^{-7} mol/L

17.96. Suppose 0.0100 mol NaOH were added to a liter of the solution in the preceding problem. What would the concentrations of singly charged and doubly charged cations be after the addition?

Ans. 5.1×10^{-4} M, 1.88×10^{-8} M

17.97. Suppose that, instead of 0.0100 mol NaOH, 0.0100 mol HCl had been added to the solution in the previous problem. Calculate the molar concentrations of the singly charged cation, doubly charged cation, and neutral ethylenediamine.

Ans. 0.010; 2.7×10^{-4}; 2.7×10^{-4}

17.98. The pK_1 and pK_2 for pyrophosphoric acid are 0.85 and 1.49. Neglecting the third and fourth dissociations of this tetraprotic acid, what would be the concentration of the doubly charged anion in a 0.050 M solution of the acid?

Ans. 1.5×10^{-2} M

17.99. What is $[CO_3^{2-}]$ in a 0.00100 M Na_2CO_3 solution after the hydrolysis reactions have come to equilibrium? K_1 and K_2 for H_2CO_3 are 4.30×10^{-7} and 5.61×10^{-11}.

Ans. 6.6×10^{-4}

17.100. Calculate the pH of 0.050 M NaH_2PO_4 and of 0.00200 M Na_3PO_4. K_1, K_2, and K_3 of H_3PO_4 are 7.52×10^{-3}, 6.23×10^{-8}, and 4.5×10^{-12}.

Ans. 4.7, 11

17.101. Citric acid is a polyprotic acid with pK_1, pK_2, and pK_3 equal to 3.15, 4.77, and 6.39, respectively. Calculate the concentrations of H^+, the singly charged anion, the doubly charged anion, and the triply charged anion in 0.0100 M citric acid.

Ans. 2.3×10^{-3} M; 2.3×10^{-3} M; 1.7×10^{-5} M; 2.9×10^{-9} M

17.102. The amino acid glycine, NH_2CH_2COOH, is basic because of its —NH_2 group and acidic because of its —COOH group. By a process equivalent to base dissociation, glycine can gain an additional proton to form $^+NH_3CH_2COOH$. The resulting cation may be considered to be a diprotic acid, since one proton from the —COOH group and one proton from the positively charged —NH_3 group may be lost. The pK_a values for these processes are 2.35 and 9.78. In a 0.0100 M solution of neutral glycine, what is the pH and what percent of the glycine is in the cationic form at equilibrium?

Ans. 6.14, 0.016%

BUFFER SOLUTIONS, INDICATORS, AND TITRATIONS

17.103. A buffer solution was prepared by dissolving 0.0200 mol propionic acid and 0.0150 mol sodium propionate in enough water to make 1 L of solution. (*a*) What is the pH of the buffer? (*b*) What would be the pH change if 1.0×10^{-5} mol HCl were added to 10 mL of the buffer? (*c*) What would be the pH change if 1.0×10^{-5} mol NaOH were added to 10 mL of the buffer? K_a for propionic acid is 1.34×10^{-5}.

Ans. (*a*) 4.75; (*b*) −0.05; (*c*) +0.05

17.104. The base imidazole had a K_b of 1.11×10^{-7}. (*a*) In what amounts should 0.0200 M HCl and 0.0200 M imidazole be mixed to make 100 mL of a buffer at pH 7.00? (*b*) If the resulting buffer is diluted to 1 L, what is the pH of the dilute buffer?

Ans. (*a*) 34 mL acid, 66 mL base; (*b*) 7.00

17.105. In the titration of HCl with NaOH represented in Fig. 17-1*a*, calculate the pH after the addition of a total of 20.0, 30.0, and 60.0 mL of NaOH.

Ans. 1.37; 1.60; 11.96

17.106. In the titration of β-hydroxybutyric acid, $HC_4H_7O_3$, with NaOH (Fig. 17-1*a*), calculate the pH after the addition of a total of 20.0, 30.0, and 70.0 mL of NaOH. pK_a for $HC_4H_7O_3$ is 4.70.

Ans. 4.52; 4.88; 12.22

17.107. In the titration of NH_3 with HCl (Fig. 17-1*b*), calculate the total volume of the HCl solution needed to bring the pH to 10.00 and to 8.00. K_b for NH_3 is 1.75×10^{-5}.

Ans. 7.4 mL, 47.3 mL

17.108. Bromcresol green, a dye, has a pK_a value of 4.95. For which of the four titrations shown in Fig. 17-1 would bromcresol green be a suitable end-point indicator?

Ans. HCl vs. NaOH, NaOH, vs. HCl, NH_3 vs. HCl

17.109. Bromphenol blue is an indicator with a K_a value of 5.84×10^{-5}. What percentage of this indicator is in its basic form at a pH of 4.84?

Ans. 80%

17.110. Calculate the pH and $[NH_3]$ at the end point in the titration of NH_3 with HCl, at the concentrations indicated in Fig. 17-1*b*. K_b for NH_3 is 1.75×10^{-5}.

Ans. 5.28, 5.3×10^{-6}

17.111. If 0.00200 mol of citric acid is dissolved in 1 L of a solution buffered at pH 5.00 (without changing the volume), what will be the equilibrium concentrations of citric acid, its singly charged anion, the doubly charged anion, and the triply charged anion? Use the p*K* values from Problem 17.101.

Ans. 5.0×10^{-6} M; 3.6×10^{-4} M; 6.1×10^{-4} M; 2.5×10^{-5} M

17.112. If 0.000500 mol $NaHCO_3$ is added to a large volume of a solution buffered at pH 8.00, how much material will exist in each of the three forms, H_2CO_3, HCO_3^-, and CO_3^{2-}? For H_2CO_3, K_1 is 4.30×10^{-7} and K_2 is 5.61×10^{-11}.

Ans. 1.14×10^{-5} mol; 4.86×10^{-4} mol; 2.73×10^{-6} mol

17.113. A buffer solution of pH 6.71 can be prepared by using solutions of NaH_2PO_4 and Na_2HPO_4. If 0.0050 mol NaH_2PO_4 is weighed out, how much Na_2HPO_4 must be used to make 1 L of the solution? Take *K* values from Problem 17.100.

Ans. 0.0016 mol

17.114. How much NaOH must be added to 1 L of 0.010 M H_3BO_3 to make a buffer solution of pH 10.10? H_3BO_3 is a monoprotic acid with $K_a = 5.8 \times 10^{-10}$.

Ans. 0.0088 mol.

17.115. A buffer solution was prepared by dissolving 0.050 mol formic acid and 0.060 mol sodium formate in enough water to make 1 L of solution. K_a for formic acid is 1.77×10^{-4}. (*a*) Calculate the pH of the solution. (*b*) If this solution were to be diluted to ten times its volume, what would be the pH? (*c*) If the solution in (*b*) were to be diluted to ten times *its* volume, what would be the pH?

Ans. (*a*) 3.83; (*b*) 3.85; (*c*) 4.00

17.116. Consider the titration curve of a 0.100 M solution of a weak acid, HA, for which $K_a = 2.00 \times 10^{-4}$, using 0.100 M strong base. Calculate the pH at (*a*) the beginning (before any base); (*b*) the half-way point; (*c*) the end point of the titration.

Ans. (*a*) 2.35; (*b*) 3.70; (*c*) 8.20

17.117. The three points determined in the preceding problem were easy to calculate. They enable one to make a good sketch of the titration curve. Other intermediate values, e.g., 10%, 75%, etc., are also easy to calculate, but it may be more challenging to calculate points very near the beginning and end. Determine the pH in this titration (*a*) after 1% of the base is added, and (*b*) after 99% addition.

Ans. (*a*) 2.41; (*b*) 5.7

CHAPTER 18

Complex Ions; Precipitates

COORDINATION COMPLEXES

Coordination complexes and coordination compounds, introduced in Chapter 9, are composed of a central metal atom or ion (usually a transition metal) to which there are groups attached (*ligands*). The ligands may be either neutral or carry a charge; however, the net charge will be a simple sum of the component charges. The net charge may be neutral (a compound) or not (a *complex ion* or the more formal *coordination entity*). Some of the compounds of complex ions are so stable that salts can be prepared from them that show no appreciable amounts of the separate constituents. An example is the ferricyanide ion, $[Fe(CN)_6]^{3+}$, solutions of which are quite different in properties from those of Fe^{3+} or of CN^-. More commonly, the complex is not so stable and, in solution, is partly dissociated into its components. In such a case, there is an equilibrium constant which, after the reaction is written, is calculated in the same manner as any other equilibrium constant (the product of the product divided by the product of the reactants). This constant, of course, will also determine the relative concentrations of the participants in the reaction when they are not known in advance. An example is $[FeBr]^{2+}$, which may be formed or dissociated easily, depending on slight modifications of experimental conditions.

$$Fe^{3+} + Br^- \rightleftharpoons [FeBr]^{2+} \qquad K_s = \frac{\{[FeBr]^{2+}\}}{[Fe^{3+}][Br^-]}$$

K_s is the *stability constant*. The larger the value, the more stable is the complex.

Note: *Square brackets,* [], *are written around the complex ion, but they are also normally used to indicate molarity. Notice that we used* { }, *which are square brackets capitalized, to indicate molarity of the complex ion so that we may continue to write the ion in the traditional manner. (Square brackets within square brackets is very confusing.)*

In some cases, several ligands can be in a complex, but the reactions producing the complex occur one at a time. A separate equilibrium equation is written for each *successive* ligand addition as follows:

$$Cd^{2+} + CN^- \rightleftharpoons [CdCN]^+ \qquad K_1 = \frac{\{[CdCN]^+\}}{[Cd^{2+}][CN^-]}$$

$$[CdCN]^+ + CN^- \rightleftharpoons Cd(CN)_2 \qquad K_2 = \frac{[Cd(CN)_2]}{\{[CdCN]^+\}[CN^-]}$$

Equations can also be written for the addition of the third and fourth cyanide, with constants K_3 and K_4. In addition to the stepwise formation equilibria, we can write a single overall equation for the formation of a complex containing several ligands from the free cation and ligands (actually a summation of the other chemical equilibria). Further, $K_s = K_1K_2K_3K_4$.

$$\mathrm{Cd^{2+}} + 4\mathrm{CN^-} \rightleftharpoons [\mathrm{Cd(CN)_4}]^{2-} \qquad K_s = \frac{\{[\mathrm{CdCN)_4}]^{2-}\}}{[\mathrm{Cd^{2+}}][\mathrm{CN^-}]^4}$$

Equilibria between a complex ion and its components are sometimes written in reverse.

$$[\mathrm{Cd(CN)_4}]^{2-} \rightleftharpoons \mathrm{Cd^{2+}} + 4\mathrm{CN^-} \qquad K_d = \frac{[\mathrm{Cd^{2+}}][\mathrm{CN^-}]^4}{\{[\mathrm{CdCN)_4}]^{2-}\}}$$

The *dissociation constant*, K_d, is the reciprocal of the overall stability constant, K_s.

Other symbols commonly used in texts and tables of data are

Used as or for K_s:	K_f	or	K_{form}	(formation constant)
Used as or for K_d:	K_{diss}	or	K_{inst}	(instability constant)

SOLUBILITY PRODUCT

Consider the equilibrium between solid AgCl and its dissolved ions in a saturated solution. In these equations, (*s*) is the solid state, (*l*) is the liquid state, and (*aq*) refers to the substance in aqueous solution.

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq)$$

The expression for the equilibrium constant is the same as in past chapters: the product of the products divided by the product of the reactants. Pure solids and liquids are omitted from the calculations.

$$K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}]$$

Solubility product is the special name given to this constant and it uses K_{sp} as the symbol. Since the left of the equation is the undissociated solid substance and the various ions are on the right, the value of the constant is only the product of the products. Some selected solubility products are shown below:

$$K_{sp} \text{ of } \mathrm{BaCO_3} = [\mathrm{Ba^{2+}}][\mathrm{CO_3^{2-}}] \qquad K_{sp} \text{ of } \mathrm{CaF_2} = [\mathrm{Ca^{2+}}][\mathrm{F^-}]^2 \qquad K_{sp} \text{ of } \mathrm{Bi_2S_3} = [\mathrm{Bi^{3+}}]^2[\mathrm{S^{2-}}]^3$$

In each of these expressions, the exponents are derived from the balanced equation in the usual manner. As in previous chapters, the temperature will be taken as 25°C unless otherwise stated.

APPLICATIONS OF SOLUBILITY PRODUCT TO PRECIPITATION

Precipitation

The solubility product can be used to explain and predict the degree of completeness of precipitation reactions. We can substitute the initial concentrations into the K_{sp} expression and compare the result, often times referred to as the *ion product* or Q, to the value of K_{sp}.

1. If the value obtained is the same as K_{sp}, the solution is saturated.
2. If the value obtained is less than K_{sp}, the solution is not saturated and precipitation does not occur.
3. If the value obtained is greater than K_{sp}, the solution is of higher concentration than it can hold and precipitation occurs to bring the concentration to K_{sp} value.

EXAMPLE 1 When some NaF is added to a saturated solution of CaF_2, the $[F^-]$ is greatly increased and the product of the ion concentrations, $[Ca^{2+}][F^-]^2$, may temporarily exceed the value of the solubility product. To restore equilibrium, some Ca^{2+} unites with twice the amount (moles) of F^- to form solid CaF_2, until the product, $[Ca^{2+}][F^-]^2$, for the ions remaining in solution again conforms to the value of the solubility product. Note that in this case the final value of $[F^-]$ is much greater than twice that of $[Ca^{2+}]$, since NaF yields a large contribution to the total $[F^-]$.

The ion concentrations that appear in the expression for the solubility product refer only to the simple ions *in solution*, and do not include the material in the precipitate because solids are not included in K expressions. Additional equilibria may exist between the simple ions and complexes *in solution*, as in the case of soluble complexes forming. Such equilibria would be governed by their own stability constants.

Solution of precipitates

The product of the concentrations of any two ions (raised to the appropriate powers) in a solution is called the *ion product*, Q, which is similar to the Q (*reaction quotient*) of Chapter 16. Whenever the Q calculated from known solubility data is less than the value of its solubility product, the solution is not saturated.

EXAMPLE 2 Suppose HCl (supplies H^+) is added to a saturated solution of $Mg(OH)_2$ in equilibrium with some undissolved solute. The H^+ removes nearly all the OH^- in solution to form water. This greatly decreases the $[OH^-]$ and more $Mg(OH)_2$ dissolves so that the ion concentration product can again come to the value of K_{sp} for $Mg(OH)_2$. If all the $Mg(OH)_2$ dissolves, there is no longer an equilibrium between the ionic solid (it is all gone) and the solution; Q will be less than K_{sp}.

Prevention of precipitates

To prevent the precipitation of a slightly soluble salt, some substance must be added which will keep the concentration of one of the ions so low that the solubility product of the salt is not reached.

EXAMPLE 3 H_2S will not precipitate FeS from a strongly acid (HCl) solution of Fe^{2+}. The large $[H^+]$ furnished by the hydrochloric acid stalls the ionization of H_2S (common-ion effect) and reduces the $[S^{2-}]$ to so low a value that the solubility product of FeS is not reached.

Solved Problems

COMPLEX IONS

18.1. One liter of solution was prepared containing 0.00100 mol silver ion (Ag^+) and 1.00 mol NH_3. What is the concentration of free Ag^+ in the solution at equilibrium? K_d for $[Ag(NH_3)_2]^+$ is 6.0×10^{-8}.

Most of the silver, approximately 0.00100 mol, will be in the form of the complex ion, $[Ag(NH_3)_2]^+$. The concentration of free NH_3 at equilibrium is practically unchanged from 1.00 mol/L, since only 0.00200 mol of NH_3 would be used up to form 0.0010 mol of complex.

$$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$$

$$K_d = \frac{[Ag^+][NH_3]^2}{\{[Ag(NH_3)_2]^+\}} \qquad \text{or} \qquad 6.0 \times 10^{-8} = \frac{[Ag^+](1.00)^2}{0.00100}$$

Solving: $[Ag^+] = 6.0 \times 10^{-11}$, which means an equilibrium concentration of 6.0×10^{-11} mol/L (or M).

18.2. The K_1 for forming a complex of NH_3 with Ag^+ is 2.0×10^3. (*a*) With reference to Problem 18.1, what is the concentration of $[Ag(NH_3)]^+$? (*b*) What is K_2 for this system?

(*a*) K_1 refers to the following reaction and calculation:

$$\mathrm{Ag}^+ + \mathrm{NH_3} \rightleftharpoons [\mathrm{Ag(NH_3)}]^+ \qquad K_1 = \frac{\{[\mathrm{Ag(NH_3)}]^+\}}{[\mathrm{Ag}^+][\mathrm{NH_3}]}$$

Then, from Problem 18.1:

$$\{[\mathrm{Ag(NH_3)}]^+\} = K_1([\mathrm{Ag}^+][\mathrm{NH_3}]) = (2.0 \times 10^3)(6.0 \times 10^{-11})(1.00) = 1.2 \times 10^{-7}$$

This problem is actually a check on an assumption made in Problem 18.1, which is that practically all the dissolved silver was in the complex $[\mathrm{Ag(NH_2)_2}]^+$. If concentration of $[\mathrm{Ag(NH_3)}]^+$ had turned out to be greater than about 1×10^{-4} M, the assumption would have been shown to be incorrect.

(*b*) K_1, K_2, and K_d are interrelated as follows:

$$K_2 = \frac{\{[\mathrm{Ag(NH_3)_2}]^+\}}{\{[\mathrm{Ag(NH_3)}]^+\}[\mathrm{NH_3}]} = \frac{\{[\mathrm{Ag(NH_3)_2}]^+\}/[\mathrm{Ag}^+][\mathrm{NH_3}]^2}{\{[\mathrm{Ag(NH_3)}]^+\}/[\mathrm{Ag}^+][\mathrm{NH_3}]} = \frac{1/K_d}{K_1}$$

$$K_2 = \frac{1}{K_1 K_d} = \frac{1}{(2.0 \times 10^3)(6.0 \times 10^{-8})} = 8.3 \times 10^3$$

18.3. How much $\mathrm{NH_3}$ should be added to a solution of 0.00100 M $\mathrm{Cu(NO_3)_2}$ in order to reduce $[\mathrm{Cu}^{2+}]$ to 10^{-13}? K_d for $[\mathrm{Cu(NH_3)_4}]^{2+}$ is 4.35×10^{-13}. Assume that there is no copper complex with other than four ammonias.

$$[\mathrm{Cu(NH_3)_4}]^{2+} \rightleftharpoons \mathrm{Cu}^{2+} + 4\mathrm{NH_3} \qquad K_d = \frac{[\mathrm{Cu}^{2+}][\mathrm{NH_3}]^4}{\{[\mathrm{Cu(NH_3)_4}]^{2+}\}} = 4.35 \times 10^{-13}$$

Since the sum of the concentrations of copper in the complex and in the free ionic state must equal 0.00100 mol/L, and since the amount of free ion is very small, the concentration of the complex is taken to be 0.00100 mol/L.

Let $x = [\mathrm{NH_3}]$. Then,

$$\frac{(10^{-13})(x^4)}{0.00100} = 4.35 \times 10^{-13} \qquad \text{or} \qquad x^4 = 4.35 \times 10^{-3} \qquad \text{or} \qquad x = 0.26$$

The concentration of $\mathrm{NH_3}$ at equilibrium is 0.26 mol/L. The amount of $\mathrm{NH_3}$ used in the formation of 0.00100 mol/L of complex is 0.0040 mol/L, an amount that is insignificant compared with the amount remaining at equilibrium. Therefore, the amount of $\mathrm{NH_3}$ to be added is 0.26 mol/L.

18.4. A solution was prepared in which, prior to the formation of complexes, the Cd^{2+} concentration was 0.00025 M and that of I^- was 0.0100 M. K_1 is 190 and K_2 is 44 for forming complexes of Cd^{2+} with I^-. What are the percentages of cadmium tied up in Cd^{2+}, $[\mathrm{CdI}]^+$, and $\mathrm{CdI_2}$ at equilibrium?

Let $[\mathrm{Cd}^{2+}] = x$, $\{[\mathrm{CdI}]^+\} = y$, and $[\mathrm{CdI_2}] = z$. Assume that $[\mathrm{I}^-]$ remains 0.0100 within the precision of this calculation. (At most, only 0.0005 could be complexed.)

$$\begin{array}{ccccccc} \mathrm{Cd}^{2+} & + \mathrm{I}^- \rightleftharpoons & [\mathrm{CdI}]^+ & \qquad\qquad & [\mathrm{CdI}]^+ & + \mathrm{I}^- \rightleftharpoons & \mathrm{CdI_2} \\ x & 0.0100 & y & & y & 0.0100 & z \end{array}$$

$$K_1 = \frac{y}{0.0100x} = 190 \qquad y = 1.90x \qquad K_2 = \frac{z}{0.0100y} = 44 \qquad z = 0.44y$$

$$z = (0.44)(1.90x) = 0.84x$$

$$x + y + z = 0.00025 = x + 190x + 0.84x = 3.74x$$

$$x = 6.7 \times 10^{-5}\mathrm{M} \qquad y = 12.7 \times 10^{-5}\mathrm{M} \qquad z = 5.6 \times 10^{-5}\mathrm{M}$$

$$[\mathrm{Cd}^{2+}] = \frac{6.7 \times 10^{-5}\,\mathrm{M}}{2.5 \times 10^{-4}\,\mathrm{M}} \times 100\% = 27\% \qquad \{[\mathrm{CdI}]^+\} = \frac{1.27 \times 10^{-5}\,\mathrm{M}}{2.5 \times 10^{-4}\,\mathrm{M}} \times 100\% = 51\%$$

$$[\mathrm{CdI_2}] = \frac{5.6 \times 10^{-5}\,\mathrm{M}}{2.5 \times 10^{-4}\,\mathrm{M}} \times 100 = 22\%$$

Note the contrast between this problem and Problem 18.2. In the latter case, the concentration of the complexing agent was so high, and the value of K_2 sufficiently greater than K_1, that the complexation was driven almost completely to the fully complexed form.

SOLUBILITY PRODUCT AND PRECIPITATION

18.5. The solubility of $PbSO_4$ in water is 0.038 g/L. Calculate the solubility product of $PbSO_4$.

$$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$$

The concentrations of the ions must be expressed in moles per liter. To convert 0.038 g/L to moles of ions per liter, divide by the molar mass of $PbSO_4$, which is 303, using rounded-off masses.

$$\frac{0.038\ \text{g/L}}{303\ \text{g/mol}} = 1.23 \times 10^{-4}\ \text{mol/L}$$

Since 1.25×10^{-4} mol dissolved $PbSO_4$ yields 1.25×10^{-4} mol each Pb^{2+} and SO_4^{2-}, K_{sp} is calculated by

$$K_{sp} = [Pb^{2+}][SO_4^{2-}] = (1.25 \times 10^{-4})(1.25 \times 10^{-4}) = 1.6 \times 10^{-8}$$

This method may be applied to any fairly insoluble salt whose ions do not hydrolyze appreciably or form soluble complexes. Sulfides, carbonates, and phosphates and the salts of many of the transition metals, like iron, must be treated by taking into account hydrolysis and, in some cases, complexation. Some examples are given in the problems that follow.

18.6. The solubility of Ag_2CrO_4 in water is 0.022 g/L. Determine the solubility product.

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

To convert 0.022 g/L to mol/L of ions, divide by the molar mass of Ag_2CrO_4, 332.

$$0.022\ \text{g/L} = \frac{0.022\ \text{g/L}}{332\ \text{g/mol}} = 6.6 \times 10^{-5}\ \text{mol/L}$$

Since 1 mol of dissolved Ag_2CrO_4 yields 2 mol Ag^+ and 1 mol CrO_4^{2-},

$$[Ag^+] = 2(6.6 \times 10^{-5}) = 1.3 \times 10^{-4} \qquad [CrO_4^{2-}] = 6.6 \times 10^{-5}$$

and $$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (1.3 \times 10^{-4})^2(6.6 \times 10^{-5}) = 1.1 \times 10^{-12}$$

18.7. The solubility product of $Pb(IO_3)_2$ is 2.5×10^{-13}. What is the solubility of $Pb(IO_3)_2$ (*a*) in mol/L and (*b*) in g/L?

(*a*) Let the solubility of $Pb(IO_3)_2$ be x mol/L. Then, $[Pb^{2+}] = x$ and $[IO_3^-] = 2x$.

$$K_{sp} = [Pb^{2+}][IO_3^-]^2 \qquad \text{which is} \qquad x(2x)^2 = 2.5 \times 10^{-13}$$

Then, $$4x^3 = 2.5 \times 10^{-13},\ x^3 = 6.2 \times 10^{-14},\ \text{and}\ x = 4.0 \times 10^{-5}$$

(*b*) $$\text{Solubility} = (4.0 \times 10^{-5}\ \text{mol/L})(557\ \text{g/mol}) = 0.022\ \text{g/L}$$

18.8. The $[\mathrm{Ag}^+]$ of a solution is 4×10^{-3}. Calculate $[\mathrm{Cl}^-]$ that must be exceeded before AgCl can precipitate. The solubility product of AgCl at 25°C is 1.8×10^{-10}.

$$K_{sp} = [\mathrm{Ag}^+][\mathrm{Cl}^-] \qquad 1.8 \times 10^{-10} = (4 \times 10^{-3})[\mathrm{Cl}^-] \qquad [\mathrm{Cl}^-] = 5 \times 10^{-8}$$

The above tells us that a saturated solution of AgCl contains 5×10^{-8} mol/L chloride ion (recall that K_{sp} is stated at saturation). If the concentration of chloride ion were to be increased above 5×10^{-8}, precipitation of AgCl would occur.

This problem differs from the previous ones because the two ions forming the precipitate are furnished to the solution independently. This represents a typical analytical situation in which some soluble chloride is added (any soluble chloride compound will work, like NaCl), causing the precipitation of silver ion present in solution.

18.9. Calculate the molar solubility of CaF_2 in 0.015 M NaF solution. K_{sp} of CaF_2 is 3.9×10^{-11}.

Because of the large concentration of F^-, the common ion, the solubility will be quite low. Any F^- from the dissolved CaF_2 will be assumed insignificant compared to the concentration of F^- from NaF.

$$K_{sp} = [\mathrm{Ca}^{2+}][\mathrm{F}^-]^2 \qquad 3.9 \times 10^{-11} = [\mathrm{Ca}^{2+}](0.015)^2 \qquad [\mathrm{Ca}^{2+}] = \frac{3.9 \times 10^{11}}{(0.015)^2} = 1.7 \times 10^{-7}$$

The solubility of CaF_2 will be 1.7×10^{-7} mol/L. The $[\mathrm{F}^-]$ from CaF_2 will be $2(1.7 \times 10^{-7})$, which is 3.4×10^{-7} M F^-, which can be ignored as mentioned above, as insignificant compared to 0.015 M F^-.

18.10. Calculate the concentration of Ag^+, CrO_4^{2-}, NO_3^-, and K^+ after 30 mL of 0.0100 M $AgNO_3$ are mixed with 20 mL of 0.010 M K_2CrO_4 and equilibrium is reached. K_{sp} for Ag_2CrO_4 is 1.1×10^{-12}.

If precipitation did not occur, the following concentrations would be found, allowing for the dilution upon mixing (30 mL $AgNO_3(aq)$ + 20 mL $K_2CrO_4(aq)$ = 50 mL after mixing).

$$[\mathrm{CrO_4^{2-}}] = \left(\frac{20}{50}\right)(0.010) = 0.0040\,\mathrm{M} \qquad [\mathrm{K}^+] = 2[\mathrm{CrO_4^{2-}}] = 0.0080\,\mathrm{M}$$

$$[\mathrm{Ag}^+] = [\mathrm{NO_3^-}] = \left(\frac{30}{50}\right)(0.010) = 0.0060\,\mathrm{M}$$

Since K^+ and NO_3^- do not react, the values of $[\mathrm{K}^+]$ and $[\mathrm{NO_3^-}]$ are as calculated above regardless of what happens to Ag^+ and CrO_4^{2-}.

To determine whether a precipitate will form, calculate the *ion product*, Q, and compare to K_{sp}.

$$Q = [\mathrm{Ag}^+]^2[\mathrm{CrO_4^{2-}}] = (0.0060)^2(0.004) = 1.4 \times 10^{-7} \qquad K_{sp} = 1.1 \times 10^{-12}$$

Since $Q > K_{sp}$, a precipitate will form.

Only 0.0030 mol/L of $CrO_4^{2-}$is required to precipitate all the Ag^+. The excess CrO_4^{2-}, 0.0010 mol/L, ensures that very little Ag^+ will remain in solution. The $[\mathrm{CrO_4^{2-}}]$ equivalent to the remaining $[\mathrm{Ag}^+]$ will also be very small compared to the 0.0010 mol/L excess. So, after Ag_2CrO_4 precipitates:

$$K_{sp} = 1.1 \times 10^{-12} = [\mathrm{Ag}^+]^2[\mathrm{CrO_4^{2-}}] = [\mathrm{Ag}^+]^2(0.0010)$$

$$[\mathrm{Ag}^+]^2 = 1.1 \times 10^{-9} \qquad \text{solved, becomes} \qquad [\mathrm{Ag}^+] = 3.3 \times 10^{-5}$$

The above value is small enough to justify the assumption made. The final solution contains 3.3×10^{-5} M Ag^+ and 0.0010 M CrO_4^{2-}.

18.11. Calculate the solubility of AgCN in a buffer solution of pH 3.00. K_{sp} for AgCN is 6.0×10^{-17} and the K_a for HCN is 4.93×10^{-10}.

This solution contains the silver that dissolves and remains as Ag^+, but the cyanide that dissolves is converted mostly to HCN because of the fixed acidity of the buffer. Let us calculate the ratio of [HCN] to $[CN^-]$ at this pH.

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \qquad \text{becomes} \qquad \frac{[HCN]}{[CN^-]} = \frac{[H^+]}{K_a} = \frac{1.0 \times 10^{-3}}{4.93 \times 10^{-10}} = 2.0 \times 10^6$$

The two equilibria can be combined to give an overall K for the dissolution process:

$$\begin{array}{lrl} & AgCN(s) \rightleftharpoons Ag^+ + CN^- & K_{sp} \text{ is } 6.0 \times 10^{-17} \\ \text{Subtract:} & \underline{HCN \rightleftharpoons H^+ + CN^-} & K_a \text{ is } 4.93 \times 10^{-10} \\ & AgCN(s) + H^+ \rightleftharpoons Ag^+ + HCN & K = \dfrac{K_{sp}}{K_a} = \dfrac{6.0 \times 10^{-17}}{4.93 \times 10^{-10}} = 1.22 \times 10^{-7} \end{array}$$

Let the solubility of AgCN be x mol/L; then,

$$x = [Ag^+] \text{ at equilibrium} \qquad x = [CN^-] + [HCN]$$

Very little error is made by neglecting $[CN^-]$ in comparison to [HCN] (1 part in 2 million) and equating [HCN] to x.

$$K = 1.22 \times 10^{-7} = \frac{[Ag^+][HCN]}{[H^+]} = \frac{x^2}{1.00 \times 10^{-3}} \qquad \text{solving} \qquad x = 1.1 \times 10^{-5}$$

18.12. Calculate the ammonium ion concentration (from NH_4Cl) needed to prevent $Mg(OH)_2$ from precipitating in 1 L of solution which contains 0.0100 mol ammonia and 0.00100 mol of Mg^{2+}. The ionization constant of ammonia is 1.75×10^{-5}. The solubility product of $Mg(OH)_2$ is 7.1×10^{-12}.

First, find the maximum $[OH^-]$ that can be present in the solution without precipitation of $Mg(OH)_2$.

$$[Mg^{2+}][OH^-]^2 = 7.1 \times 10^{-12}$$

$$[OH^-] = \sqrt{\frac{7.1 \times 10^{-12}}{[Mg^{2+}]}} = \sqrt{\frac{7.1 \times 10^{-12}}{0.0010}} = \sqrt{7.1 \times 10^{-9}} = 8.4 \times 10^{-5}$$

Next, find the ammonium ion concentration (from NH_4Cl) needed to keep the hydroxide ion concentration at or below 8.4×10^{-5} M.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$1.75 \times 10^{-5} = \frac{[NH_4^+](8.4 \times 10^{-5})}{0.0100} \qquad \text{becomes} \qquad [NH_4^+] = 2.1 \times 10^{-3}\,\text{M}$$

Since 0.0100 M NH_3 is only slightly ionized, especially in the presence of excess NH_4^+, the ammonia concentration may be considered to be 0.0100 M.

18.13. Given: 2×10^{-4} mol each of Mn^{2+} and Cu^{2+} were contained in 1 L of a 0.003 M $HClO_4$ solution; then this solution was saturated with H_2S. Determine whether or not each of these ions, Mn^{2+} and Cu^{2+}, will precipitate as the sulfide. The solubility of H_2S, 0.10 mol/L, is assumed to be independent of the presence of other substances in the solution. K_{sp} of MnS is 3×10^{-14} and the K_{sp} of CuS is 8×10^{-37}. For H_2S, K_1 is 1.0×10^{-7} and K_2 is 1.2×10^{-13}.

$[H_2S] = 0.10$, since the solution is saturated with H_2S. Further, since the H_2S contributes negligible H^+ compared with $HClO_4$, $[H^+] = 0.003$. Calculate $[S^{-2}]$ from the combined ionization constants.

$$H_2S \rightleftharpoons 2H^+ + S^- \qquad K_1K_2 = \frac{[H^+]^2[S^-]}{[H_2S]}$$

$$K_1K_2 = (1.0 \times 10^{-7})(1.2 \times 10^{-13}) = 1.2 \times 10^{-20}$$

$$[S^{2-}] = (1.2 \times 10^{-20})\frac{[H_2S]}{[H^+]^2} = (1.2 \times 10^{-20})\frac{0.10}{(0.003)^2} = 1.3 \times 10^{-16}$$

From the ion product, Q, in each case, using the initial concentrations, and compared to K_{sp}:

For MnS: $Q = [Mn^{2+}][S^-] = (2 \times 10^{-4})(1.3 \times 10^{-16}) = 2.6 \times 10^{-20} < 3 \times 10^{-14} = K_{sp}$

For CuS: $Q = [Cu^{2+}][S^-] = (2 \times 10^{-4})(1.3 \times 10^{-16}) = 2.6 \times 10^{-20} > 8 \times 10^{-37} = K_{sp}$

Our conclusions are that MnS remains in solution and that CuS precipitates. This example illustrates how two metal ions can be separated by controlling the acidity of the solution while adding a reagent. There is no reason why this process could not be used as a commercial process, especially since the acid used is very inexpensive.

Actually, as the precipitation of CuS occurs, some additional H^+ will be added from the H_2S and the equilibrium concentration of S^{2-} will decrease. However, the decrease is not enough to change the outcome predicted above. This feature will be treated in greater detail in the following problem.

18.14. In Problem 18.13, how much Cu^{2+} remains in solution?

Most of the Cu^{2+} will precipitate, and an increment of $2(2 \times 10^{-4})$ mol/L of H^+ will be added to the solution from H_2S, bringing the total $[H^+]$ to 0.0034 M. Making this correction,

$$[S^{2-}] = (1.2 \times 10^{-20})\frac{0.10}{(0.0034)^2} = 1.0 \times 10^{-16}$$

$$[Cu^{2+}] = \frac{K_{sp}}{[S^{2-}]} = \frac{8 \times 10^{-37}}{1.0 \times 10^{-16}} = 8 \times 10^{-21}$$

This tells us that 8×10^{-21} mol Cu^{2+} remain in solution. On a percentage basis, the amount of Cu^{2+} remaining that is not tied up in the precipitate:

$$\frac{8 \times 10^{-21}}{2 \times 10^{-4}} \times 100\% = 4 \times 10^{-15}\%$$

18.15. If the solution in Problem 18.13 is made neutral by lowering the $[H^+]$ to 10^{-7} M, will MnS precipitate?

$$[S^{2-}] = (1.2 \times 10^{-20})\frac{0.10}{(10^{-7})^2} = 1.2 \times 10^{-7}$$

$$Q = [Mn^{2+}][S^{2-}] = (2 \times 10^{-4})(1.2 \times 10^{-7}) = 2.4 \times 10^{-11}$$

Since 2.4×10^{-11} is greater than the K_{sp} of MnS, which is 3×10^{-14}, MnS will precipitate.

Lowering the $[H^+]$ to 10^{-7} increases the ionization of H_2S to such an extent that sufficient S^{2-} is furnished for the solubility product of MnS to be exceeded.

18.16. How much NH_3 must be added to 0.0040 M Ag^+ solution to prevent the precipitation of AgCl when $[Cl^-]$ reaches 0.0010? K_{sp} for AgCl is 1.8×10^{-10} and K_d for $[Ag(NH_3)_2]^+$ is 6.0×10^{-8}.

Just as acids may be used to lower the concentration of anions in solution, so complexing agents may be used in some cases to lower the concentration of cations. In this problem, the addition of ammonia converts most of the silver to the complex ion, $[Ag(NH_3)_2]^+$. The upper limit for uncomplexed $[Ag^+]$ without formation of a precipitate can be calculated from the solubility product.

$$[Ag^+][Cl^-] = 1.8 \times 10^{-10} \qquad \text{or} \qquad [Ag^+] = \frac{1.8 \times 10^{-10}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{0.0010} = 1.8 \times 10^{-7}$$

Enough NH_3 must be added to keep the $[Ag^+]$ below 1.8×10^{-7}. The concentration of $[Ag(NH_3)_2]^+$ at this limit would then be $0.0040 - (1.8 \times 10^{-7})$, or practically 0.0040.

$$\frac{[Ag^+][NH_3]^2}{\{[Ag(NH_3)_2]^+\}} = K_d \qquad \text{or} \qquad [NH_3]^2 = \frac{K_d\{[Ag(NH_3)_2]^+\}}{[Ag^+]} = \frac{(6.0 \times 10^{-8})(0.0040)}{1.8 \times 10^{-7}} = 1.33 \times 10^{-3}$$

Then, $[NH_3]$ is 0.036 M. The amount of NH_3 that must be added is equal to the sum of the amount of free NH_3 remaining in the solution and the amount of NH_3 used up in forming 0.0040 mol/L of the complex ion, $[Ag(NH_3)_2]^+$. This sum is $0.036 + 2(0.004) = 0.044$ mol NH_3 to be added per liter solution.

18.17. What is the solubility of AgSCN in 0.0030 M NH_3? K_{sp} for AgSCN is 1.1×10^{-12} and the K_d for $[Ag(NH_3)_2]^+$ is 6.0×10^{-8}.

We may assume that practically all the dissolved silver will exist as the complex ion, $[Ag(NH_3)_2]^+$. If the solubility of AgSCN is x M, $x = [SCN^-] = [Ag(NH_3)_2]^+$. Then, the concentration of uncomplexed Ag^+ can be estimated from K_d, assuming for simplification that $[NH_3]$ is essentially unchanged.

$$\frac{[Ag^+][NH_3]^2}{\{[Ag(NH_3)_2]^+\}} = K_d \qquad \text{or} \qquad [Ag^+] = \frac{K_d\{[Ag(NH_3)_2]^+\}}{[NH_3]^2} = \frac{(6.0 \times 10^{-8})x}{(0.0030)^2} = 6.7 \times 10^{-3}x$$

This result agrees with our first assumption: The ratio of uncomplexed to complexed silver in solution is only 6.7×10^{-3}. The two equilibria can be combined, which results in an overall K for the dissolution process:

$$\begin{array}{lll} & AgSCN(s) \rightleftharpoons Ag^+ + SCN^- & K_{sp} \\ \text{Subtract:} & \underline{[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3} & K_d \\ & AgSCN + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + SCN & K = \dfrac{K_{sp}}{K_d} = \dfrac{1.1 \times 10^{-12}}{6.0 \times 10^{-8}} = 1.8 \times 10^{-5} \end{array}$$

$$K = 1.8 \times 10^{-5} = \frac{\{[Ag(NH_3)_2]^+\}[SCN^-]}{[NH_3]^2} = \frac{x^2}{(0.0030)^2} \qquad \text{solving} \qquad x = 1.3 \times 10^{-5}$$

Our second assumption is confirmed by the answer. If 1.3×10^{-5} mol of complex is formed per liter, the amount of NH_3 used up for complexation is $2(1.3 \times 10^{-5}) = 2.6 \times 10^{-5}$ mol/L. The concentration of the remaining free NH_3 in solution is practically unchanged from its initial value, 0.0030 M.

18.18. Calculate the simultaneous solubility of CaF_2 and SrF_2. The K_{sp} for CaF_2 is 3.9×10^{-11} and the K_{sp} for SrF_2 is 2.9×10^{-9}.

The two solubilities are not independent of each other because there is fluoride as a common ion. Let us assume that most of the fluoride in the saturated solution is contributed by the SrF_2, since its K_{sp} is so much larger than that of CaF_2. We can then proceed to solve for the solubility of SrF_2 as if the CaF_2 were not present.

If the solubility of SrF_2 is x M, $x = [Sr^{2+}]$ and $2x = [F^-]$. Then,

$$4x^3 = K_{sp} = 2.9 \times 10^{-9} \qquad \text{or} \qquad x = 9 \times 10^{-4}$$

The CaF_2 solubility will have to change due to the concentration of F^- set by the SrF_2 solubility.

$$[Ca^{2+}] = \frac{K_{sp}}{[F^-]^2} = \frac{3.9 \times 10^{-11}}{(2 \times 9 \times 10^{-14})^2} = 1.2 \times 10^{-5}$$

This information gives us the solubility of CaF_2, which is 1.2×10^{-5}.

Check of assumption: The amount of F^- contributed by the solubility of CaF_2 is twice the concentration of Ca^{2+}, or 2.4×10^{-5} M. This is quite small compared with the amount of F^- from SrF_2, $2(9 \times 10^{-4}) = 1.8 \times 10^{-3}$ M.

A more general solution requiring no assumptions is as follows: Let $x = [Ca^{2+}]$; $x[F^-]^2 = 3.9 \times 10^{-11}$; $[Sr^{2+}][F^-]^2 = 2.9 \times 10^{-9}$.

$$\text{Dividing} \qquad \frac{[Sr^{2+}][F^-]^2}{x[F^-]^2} = \frac{2.9 \times 10^{-9}}{3.9 \times 10^{-11}} = 74.4 \qquad \text{or} \qquad [Sr^{2+}] = 74.4x$$

[Note that the squared fluoride ions cancel.]

$$[F^-] = 2([Ca^{2+}] + [Sr^{2+}]) = 2(x + 74.4x) = 2(75.4x) = 151x$$

Then, substituting in the K_{sp} for CaF_2:

$$(x)(151x)^2 = 3.9 \times 10^{-11} \qquad x = 1.2 \times 10^{-5} \quad \text{(the solubility of CaF}_2\text{)}$$
$$74.4x = 8.9 \times 10^{-4} \quad \text{(the solubility of SrF}_2\text{)}$$

18.19. Calculate the simultaneous solubility of AgSCN and AgBr. The solubility products for these two salts are 1.1×10^{-12} and 5.0×10^{-13}.

Since the solubilities are not very different, the second approach of Problem 18.18 is *required*. Let $x = [Br^-]$; then take the ratio of the K_{sp}'s.

$$\frac{[Ag^+][SCN^-]}{[Ag^+][Br^-]} = \frac{1.1 \times 10^{-12}}{5.0 \times 10^{-13}} = \frac{[SCN^-]}{x} \qquad \text{or} \qquad [SCN^-] = 2.2x$$

[Note that the silver ions cancel.]

Then, substituting in the K_{sp} expression for AgBr,

$$[Ag^+][Br^-] = (3.2x)(x) = 5.0 \times 10^{-13} \qquad \text{solving} \qquad 3.2x^2 = 5.0 \times 10^{-13}$$
$$x = 4.0 \times 10^{-7} \quad \text{(solubility of AgBr)}$$
$$2.2x = 8.8 \times 10^{-7} \quad \text{(solubility of AgSCN)}$$

18.20. Calculate the solubility of MnS in pure water. K_{sp} is 3×10^{-14}. The K_1 and K_2 for H_2S are 1.0×10^{-7} and 1.2×10^{-13}, respectively.

This problem differs from the similar problems dealing with chromates, oxalates, sulfates, and iodates. The difference lies in the large amount of hydrolysis of the sulfide ion.

$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^- \qquad K_b = \frac{K_w}{K_2} = \frac{10^{-14}}{1.2 \times 10^{-13}} = 0.083$$

If x mol/L is the solubility of MnS, we cannot simply equate x to $[S^{2-}]$. Instead, $x = [S^{2-}] + [HS^-] + [H_2S]$. To simplify, we can take the approach that the first stage of hydrolysis is nearly complete and that the second stage proceeds to only a slight extent (little or no H_2S in solution). In other words: $x = [Mn^{2+}] = [HS^-] = [OH^-]$.

$$[S^{2-}] = \frac{[HS^-][OH^-]}{K_b} = \frac{x^2}{0.083}$$

At equilibrium, $$[Mn^{2+}][S^{2-}] = \frac{x(x)^2}{0.083} = K_{sp} = 3 \times 10^{-14} \qquad \text{or} \qquad x = 1.4 \times 10^{-5}$$

Check of assumptions:

(1) $$[S^{2-}] = \frac{x^2}{0.083} = \frac{(1.4 \times 10^{-5})^2}{0.083} = 2.4 \times 10^{-9}$$

$[S^{2-}]$ is negligible compared with $[HS^-]$.

(2) $$[H_2S] = \frac{[H^+][HS^-]}{K_1} = \frac{K_w[HS^-]}{K_1[OH^-]} = \frac{10^{-14}x}{10^{-7}x} = 10^{-7}$$

$[H_2S]$ is also small compared with $[HS^-]$.

The above approximations would not be valid for sulfides, like CuS, which are much more insoluble than MnS. First, the water dissociation would begin to play an important role in determining $[OH^-]$. Second, the second stage of hydrolysis, which produces $[H_2S]$, would not be negligible compared with the first. Even for MnS, an additional complication arises because of the complexation of Mn^{2+} with OH^-. The full treatment of sulfide solubilities is a complicated problem because of the multiple equilibria that must be considered.

If hydrolysis had not been considered, the answer would have been simply the square root of 3×10^{-14}, which is 1.7×10^{-7}, underestimating the solubility by a factor of 80! ($1.4 \times 10^{-5}/1.7 \times 10^{-7} = 80$). Then, hydrolysis significantly increases the solubility of the sulfides and cannot be ignored.

18.21. A solution was mixed using 500 mL of 0.0100 M $AgNO_3$ and 500 mL of a solution that was both 0.0100 M NaCl and 0.0100 M NaBr. K_{sp} for AgCl is 1.8×10^{-10} and the K_{sp} for AgBr is 5.0×10^{-13}. Calculate the equilibrium concentrations of the following: $[Ag^+]$, $[Cl^-]$, and $[Br^-]$.

If there were no precipitation, the diluting effect of mixing would make

$$[Ag^+] = [Cl^-] = [Br^-] = \frac{1}{2}(0.0100) = 0.0050$$

AgBr is the more insoluble salt and would precipitate before the others. To find whether AgCl also precipitates, we assume that it does not in the early calculations. Once we know this information, we can calculate Q for AgCl and compare it to K_{sp}, as we have done in previous problems. In the case of this solution, only Ag^+ and Br^- would be removed by precipitation and the concentrations of these two ions in solution would remain equal to each other.

$$[Ag^+][Cl^-] = [Ag^+]^2 = K_{sp} = 5.0 \times 10^{-13}$$

or

$$[Ag^+] = [Br^-] = 7.1 \times 10^{-7}$$

We can now examine the ion product for AgCl.

$$[Ag^+][Cl^-] = (7.1 \times 10^{-7})(5.0 \times 10^{-3}) = 3.6 \times 10^{-9}$$

Since this ion product is larger than the value of K_{sp} for AgCl, as least some AgCl must also precipitate. This proved our first assumption incorrect.

Since both halides precipitate, both solubility product requirements must be met at the same time.

$$[Ag^+][Cl^-] = 1.8 \times 10^{-10} \quad (1)$$

$$[Ag^+][Br^-] = 5.0 \times 10^{-13} \quad (2)$$

The third equation needed to define the three unknowns is an equation expressing the balancing of positive and negative charges in solution:

$$[Na^+] + [Ag^+] = [Cl^-] + [Br^-] + [NO_3^-]$$

$$0.0100 + [Ag^+] = [Cl^-] + [Br^-] + 0.0050$$

or

$$[Cl^-] + [Br^-] - [Ag^+] = 0.0050 \quad (3)$$

Dividing (*1*) by (*2*): $[Cl^-]/[Br^-] = 360$. We see that Br^- plays an insignificant role in the total anion concentration of the solution. Also, $[Ag^+]$ must be negligible in (*3*) because of the insolubility of the two silver salts. We can now assume in (*3*) that $[Cl^-] = 0.0050$.

From (*1*),
$$[Ag^+] = \frac{1.8 \times 10^{-10}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{0.0050} = 3.6 \times 10^{-8}$$

From (*2*),
$$[Br^-] = \frac{5.0 \times 10^{-13}}{[Ag^+]} = \frac{5.0 \times 10^{-13}}{3.6 \times 10^{-8}} = 1.4 \times 10^{-5}$$

Check of assumptions: Both $[Ag^+]$ and $[Br^-]$ are negligible compared with 0.0050 M.

Note that in general, in the presence of both precipitates, the ratio of the anion concentrations must be the same as the corresponding ratio of the K_{sp}'s (as can be confirmed by the above results). Also, observe that the addition of a few extra drops of $AgNO_3$ (not enough to decrease $[Cl^-]$ substantially) will produce more AgCl(*s*), but will not change the above answers.

18.22. How much Ag^+ would remain in solution after mixing equal volumes of 0.080 M $AgNO_3$ and 0.080 M HOCN? The K_{sp} for AgOCN is 2.3×10^{-7}. The K_a for HOCN is 3.5×10^{-4}.

The overall reaction is

$$Ag^+ + HOCN \rightleftharpoons AgOCN(s) + H^+ \qquad (1)$$

Assume this reaction goes nearly to completion (mostly to the right), then write the K for the reverse reaction by combining K_{sp} and K_a.

$$\begin{array}{lrcl}
 & AgOCN(s) \rightleftharpoons Ag^+ + OCN^- & & K_{sp} \\
\text{Subtract} & \underline{HOCN \rightleftharpoons H^+ + OCN^-} & & K_a \\
 & AgOCN(s) + H^+ \rightleftharpoons Ag^+ + HOCN & & K = \dfrac{K_{sp}}{K_a}
\end{array}$$

After accounting for the dilution when the solutions were mixed, the silver ion concentration was 0.040 M, which would yield 0.040 M H^+. There would be no appreciable excess of HOCN when equilibrium (assumed near to or at completion) was reached. Using these data, if $[Ag^+] = x$, then $[HOCN] = x$ and $[H^+] = 0.040 - x$.

$$K = \frac{[Ag^+][HOCN]}{[H^+]} = \frac{x^2}{0.040 - x} = \frac{2.3 \times 10^{-7}}{3.5 \times 10^{-4}} = 6.6 \times 10^{-4}$$

Solving the quadratic, $x = 4.8 \times 10^{-3}$ = remaining $[Ag^+]$.

In summary, although the same amounts of reagents were mixed, about one-eighth of the Ag^+ failed to precipitate $(4.8 \times 10^{-3})/(0.040)$. The H^+ generated in the precipitation reaction prevented the ionization of the HOCN with the result that insufficient OCN^- was available.

Supplementary Problems

COMPLEX IONS

18.23. If 0.0100 mol pure $[Cu(NH_3)]SO_4 \cdot H_2O$ is dissolved in a liter of pure water, (*a*) estimate the molar concentration of Cu^{2+} neglecting the intermediate stages of dissociation. (*b*) Estimate the Cu^{2+} molar concentration if 0.0100 mol NH_3 were added to the solution. (*c*) Which is a better estimate, (*a*) or (*b*), and provide an explanation for your answer. K_d for $[Cu(NH_3)_4]^{2+}$ is 4.35×10^{-13}.

Ans. (*a*) 4.43×10^{-4}; (*b*) 4.35×10^{-7}; (*c*) Estimate (*a*) may be high if a significant quantity of NH_3 is released in partial dissociation. Estimate (*b*) should be accurate because the added ammonia is, by far, much greater than that released by the complex.

18.24. A 0.0010 mol sample of solid NaCl was added to 1 L of 0.010 M $Hg(NO_3)_2$. Calculate the $[Cl^-]$ at equilibrium with the newly formed $HgCl^+$. K_1 for $HgCl^+$ formation is 5.5×10^6. Neglect the K_2 equilibrium.

Ans. 2×10^{-9}

18.25. What is the $[Cd^{2+}]$ in 1 L of solution prepared by dissolving 0.0010 mol $Cd(NO_3)_2$ and 1.5 mol NH_3? The K_d for the dissociation of $[Cd(NH_3)_4]^{2+}$ into Cd^{2+} and $4NH_3$ is 3.6×10^{-8}. Neglect the amount of cadmium in complexes containing fewer than 4 NH_3 groups.

Ans. 7×10^{-12}

18.26. Silver ion forms $[Ag(CN)_2]^-$ in the presence of excess CN^-. How much KCN in moles should be added to 1 L of a 0.0005 M Ag^+ solution in order to reduce $[Ag^+]$ to 1.0×10^{-19}? The K_d for the complete dissociation of $[Ag(CN)_2]^-$ is 3.3×10^{-21}.

Ans. 0.005 mol

18.27. An investigation of the complexation of SCN^- with Fe^{3+} led to values of 130, 16, and 10 for K_1, K_2, and K_3, respectively. What is the overall formation constant of $Fe(SCN)_3$ from its component ions and what is the dissociation constant of $Fe(SCN)_3$ into its simplest ions on the basis of these data?

Ans. $K_s = 2.1 \times 10^4$ and $K_d = 4.8 \times 10^{-5}$

18.28. Sr^{2+} forms a very unstable complex with NO_3^-. A dilute solution containing 0.00100 M $Sr(ClO_4)_2$ and 0.050 M KNO_3 was found to have 75% of its strontium in the uncomplexed Sr^{2+} form with the balance $[Sr(NO_3)]^+$. What is the K_1 for complexation?

Ans. 6.7

18.29. A solution made up to be 0.0100 M $Co(NO_3)_2$ and 0.0200 M N_2H_4 at a total ionic strength of 1 was found to have an equilibrium $[Co^{2+}]$ of 6.2×10^{-3}. Assuming that the only complex formed was $[Co(N_2H_4)]^{2+}$, what is the apparent K_1 for complex formation at this ionic strength?

Ans. 38

18.30. Suppose the solution in Problem 18.29 is diluted by a factor of 2, while maintaining its ionic strength at 1. Calculate the molar concentrations of (*a*) $[CoN_2H_4]^{2+}$, (*b*) Co^{2+}, and (*c*) N_2H_4.

Ans. (*a*) 0.0012; (*b*) 0.0038; (*c*) 0.0088

18.31. Equal volumes of 0.0010 M $Fe(ClO_4)_3$ and 0.10 M KSCN are mixed. Using the data in Problem 18.27, find the equilibrium percentages of the iron existing as Fe^{3+}, $[FeSCN]^{2+}$, $[Fe(SCN)_2]^+$, and $Fe(SCN)_3$.

Ans. 8%, 50%, 40%, and 2%

18.32. What is the concentration of free Cd^{2+} in 0.0050 M $CdCl_2$? K_1 for chloride complexation of Cd^{2+} is 100; K_2 need not be considered because it is very small in comparison to K_1.

Ans. 2.8×10^{-3} M

18.33. (*a*) How many moles of NaCl would have to be added to a liter of the solution in Problem 18.32 to reduce the free Cd^{2+} concentration to one-tenth the total cadmium? (*b*) At what molar concentration of pure $CdCl_2$ in water is the free Cd^{2+} only one-tenth of the total cadmium?

Ans. (*a*) 0.085 M; (*b*) 0.082 M

SOLUBILITY PRODUCT AND PRECIPITATION

18.34. Calculate the K_{sp} of the following compounds whose solubilities are given in mol/L (M): (*a*) $BaSO_4$, 1.05×10^{-5} M; (*b*) TlBr, 1.9×10^{-3} M; (*c*) $Mg(OH)_2$, 1.21×10^{-4} M; (*d*) $Ag_2C_2O_4$, 1.15×10^{-4} M; (*e*) $La(IO_3)_3$, 7.8×10^{-4} M

Ans. (*a*) 1.1×10^{-10}; (*b*) 3.6×10^{-6}; (*c*) 7.1×10^{-12}; (*d*) 6.1×10^{-12}; (*e*) 1.0×10^{-11}

18.35. Calculate the solubility products of the following salts whose solubilities are in g/L: (*a*) CaC_2O_4, 0.0055 g/L; (*b*) $BaCrO_4$, 0.0037 g/L; (*c*) CaF_2, 0.017 g/L.

Ans. (*a*) 1.8×10^{-9}; (*b*) 2.1×10^{-10}; (*c*) 4.1×10^{-11}

18.36. The solubility product of SrF_2 at 25°C is 2.9×10^{-9} (*a*) Determine the solubility of SrF_2 at 25°C, in mol/L and in mg/ML. (*b*) In mol/L, what are the $[Sr^{2+}]$ and $[F^-]$ in a saturated SrF_2 solution?

Ans. (*a*) 9×10^{-4} mol/L, 0.11 mg/L; (*b*) $[Sr^{2+}] = 9 \times 10^{-4}$, $[F^-] = 1.8 \times 10^{-3}$

18.37. What $[SO_4^{2-}]$ must be exceeded to produce a radium sulfate, $RaSO_4$, precipitate in 500 mL of a solution containing 0.00010 mol Ra^{2+}? K_{sp} of $RaSO_4$ is 4×10^{-11}.

Ans. 2×10^{-7}

18.38. A solution is 0.001 M Mg^{2+}. Will $Mg(OH)_2$ precipitate if the OH^- concentration of the solution is (*a*) 10^{-5} M, (*b*) 10^{-3} M? The K_{sp} of $Mg(OH)_2$ is 7.1×10^{-12}.

Ans. (*a*) no; (*b*) yes

18.39. Radioactive tracers provide a convenient way of measuring the small concentrations encountered in determining K_{sp} values. Exactly 20.0 mL of 0.0100 M $AgNO_3$ solution containing radioactive silver (activity of 29,610 counts/min per mL) was mixed with 100 mL of 0.0100 M KIO_3. The mixture is diluted to exactly 400 mL. After equilibrium was reached, a portion of solution was filtered to remove any solids and was found to have an activity of 47.4 counts/min per mL. Calculate K_{sp} of $AgIO_3$.

Ans. 3.2×10^{-8}

18.40. An old procedure for the determination of sulfur in gasoline involves the precipitation of $BaSO_4$ as the final chemical step and specifies that no more than 1 μg of sulfur be permitted to remain behind in solution. If the precipitation is made from 400 mL, what must the concentration of excess barium ion be? K_{sp} for $BaSO_4$ is 1.1×10^{-10}.

Ans. $[Ba^{2+}]$ must be at least 1.4×10^{-3} M

18.41. A solution contains 0.0100 mol/L each of Cd^{2+} and Mg^{2+}. (*a*) To what pH should it be raised to precipitate the maximum amount of one metal (identify which it is) as the hydroxide without precipitating the other? (*b*) What fraction of the precipitated metal will still remain in solution? (*c*) To avoid accidentally precipitating any of the more soluble metal, a careful chemist stops the addition of base when the pH is 0.50 units less than that calculated in part (*a*). Now, what fraction of the less soluble metal remains in solution? The K_{sp} values are 7.1×10^{-12} for $Mg(OH)_2$ and 4.5×10^{-15} for $Cd(OH)_2$.

Ans. (*a*) 9.43 to precipitate $Cd(OH)_2$; (*b*) 6.2×10^{-4}; (*c*) 6.2×10^{-3}

18.42. When ammonia is used to precipitate a metal hydroxide, the solution becomes buffered by ammonium formed as follows:

$$Fe^{2+} + 2NH_3 + 2H_2O \rightarrow Fe(OH)_2(s) + 2NH_4^+$$

To a liter of 0.0100 M $FeSO_4$ 0.0400 moles of concentrated NH_3 were added (no significant volume change). For $Fe(OH)_2$, $K_{sp} = 2 \times 10^{-15}$, and for NH_3, $K_b = 1.75 \times 10^{-5}$. Calculate (*a*) the final $[Fe^{2+}]$, and (*b*) the final pH.

Ans. (*a*) 6×10^{-6}; (*b*) pH = 9.24

18.43. Repeat Problem 18.42 for Mg^{2+}, rather than Fe^{2+}. You will find it much more complicated because K_{sp} for $Mg(OH)_2$ is 7.1×10^{-12}. (*Hint*: The higher-order algebraic equation can be solved readily by trial and error.)

Ans. (*a*) $[Mg^{2+}] = 0.0041$; (*b*) pH = 9.62

18.44. After seeing the results of Problem 18.43, a chemist decided to precipitate his $Mg(OH)_2$ by simply adding 0.0400 moles per liter of NaOH to his 0.0100 M Mg^{2+} solution. (Besides, the calculation becomes very easy!) Calculate (*a*) the final $[Mg^{2+}]$, and [*b*] the final pH. (*c*) If the solution also contained 0.0200 M Ca^{2+}, would $Ca(OH)_2$ also precipitate? The K_{sp} for $Ca(OH)_2$ is 6.5×10^{-6}.

Ans. (*a*) 1.8×10^{-8}; (*b*) 12.30; (*c*) yes

18.45. Returning to Problem 18.43, the magnesium could have been completely precipitated simply by using a sufficiently large amount of ammonia. Recalculate (*a*) and (*b*) for the case of 0.400 moles of NH_3 rather than 0.0400 moles, and also answer Problem 18.44(*c*) for this case.

Ans. (*a*) $[Mg^{2+}] = 6.4 \times 10^{-5}$; (*b*) pH = 10.52; (*c*) no, ion product $< K_{sp}$

18.46. After solid $SrCO_3$ was brought to equilibrium with a pH 8.60 buffer, the solution was found to have $[Sr^{2+}] = 1.6 \times 10^{-4}$. What is the K_{sp} for $SrCO_3$? The K_2 for H_2CO_3, carbonic acid, is 5.61×10^{-11}.

Ans. 5.6×10^{-10}

18.47. Calculate the solubility at 25°C of $CaCO_3$ in a closed vessel containing a solution of pH 8.60. K_{sp} for $CaCO_3$ is 7.55×10^{-9}. K_2 for carbonic acid is 5.61×10^{-11}.

Ans. 5.9×10^{-4} M

18.48. How much AgBr could dissolve in 1 L of 0.40 M NH_3? K_{sp} for AgBr is 5.0×10^{-13} and K_d for $[Ag(NH_3)_2]^+$ is 6.0×10^{-8}.

Ans. 1.2×10^{-3} mol

18.49. Solution A was made by mixing equal volumes of 0.0010 M Cd^{2+} and 0.0072 M OH^- solutions as neutral salt and strong base, respectively. Solution B was made by mixing equal volumes of 0.0010 M Cd^{2+} and a standard KI solution. What was the concentration of the standard KI solution if the final $[Cd^{2+}]$ in solutions A and B was the same? K_{sp} for $Cd(OH)_2$ is 4.5×10^{-15} and K_s for the formation of $[CdI_4]^{2-}$ from its simple ions is 4×10^5. Neglect any cadmium in all iodide complexes other than $[CdI_4]^{2-}$.

Ans. 2.3 M

18.50. Ag_2SO_4 and $SrSO_4$ are both shaken with pure water. K_{sp} values for these two salts are 1.5×10^{-5} and 3.2×10^{-7}, respectively. Evaluate $[Ag^+]$ and $[Sr^{2+}]$ in the resulting saturated solution.

Ans. 3.1×10^{-2}, 2.1×10^{-5}

18.51. Calculate $[F^-]$ in a solution saturated with respect to both MgF_2 and SrF_2 (made by dissolving both MgF_2 and SrF_2 in H_2O until an excess of both solids remains). K_{sp} values for the two salts are 6.6×10^{-9} and 2.9×10^{-9}, respectively.

Ans. 2.7×10^{-3}

18.52. Equal volumes of 0.0200 M $AgNO_3$ and 0.0200 M HCN were mixed. Calculate $[Ag^+]$ at equilibrium. K_{sp} for AgCN is 6.0×10^{-17} and K_a for HCN is 4.93×10^{-10}.

Ans. 3.5×10^{-5}

18.53. Equal volumes of 0.0100 M $Sr(NO_3)_2$ and 0.0100 M $NaHSO_4$ were mixed. Calculate $[Sr^{2+}]$ and $[H^+]$ at equilibrium. K_{sp} for $SrSO_4$ is 3.2×10^{-7} and K_a for HSO_4^- (the same as K_2 for H_2SO_4) is 1.2×10^{-2}. Take into account the amount of H^+ needed to balance the charge of the SO_4^{2-} remaining in the solution.

Ans. 6.7×10^{-4} and 4.8×10^{-3}

18.54. Excess solid $Ag_2C_2O_4$ is shaken with (*a*) 0.00100 M HNO_3 and separately with (*b*) 0.00030 M HNO_3. What is the equilibrium value of $[Ag^+]$ in the resulting solutions (*a*) and (*b*)? The K_{sp} for $Ag_2C_2O_4$ is 6×10^{-12} and K_2 for $H_2C_2O_4$ is 6.4×10^{-5}. (K_1 is so large that the concentration of free oxalic acid is insignificant.)

Ans. (*a*) 5×10^{-4}; (*b*) 3×10^{-4}

18.55. How much solid $Na_2S_2O_3$ should be added to 1 L of water so that 0.00050 mol $Cd(OH)_2$ could just barely dissolve? K_{sp} for $Cd(OH)_2$ is 4.5×10^{-15}. K_1 and K_2 for $S_2O_3^{2-}$ complexation with Cd^{2+} are 8.3×10^3 and 2.5×10^2, respectively. (*Hint*: Determine whether CdS_2O_3 or $[Cd(S_2O_3)_2]^{2-}$ is the predominant species in solution.)

Ans. 0.23 mol

18.56. Precipitation titrations with $AgNO_3$ can be carried out using electrometric measurement of $[Ag^+]$ (to be discussed in the next chapter). Consider the feasibility of titrating a solution containing 0.0010 M NaCl and 0.0010 M NaI with standard 0.100 M $AgNO_3$. Calculate the $[Ag^+]$ (*a*) halfway to the first end point; (*b*) at the first end point; (*c*) halfway to the second end point; (*d*) at the second end point; (*e*) after the addition of an excess of titrant equivalent to the original NaCl. The K_{sp} for AgCl is 1.8×10^{-10}; the K_{sp} for AgI is 8.5×10^{-17}. (To simplify, assume no volume changes due to addition of titrant.)

Ans. (*a*) 1.7×10^{-13}; (*b*) 9.2×10^{-9}; (*c*) 3.6×10^{-7}; (*d*) 1.3×10^{-5}; (*e*) 1.0×10^{-3}

For Problem 18.57 through Problem 18.62, use the following physical constants for H_2S:

$$\text{Solubility} = 0.10\,\text{mol/L} \qquad K_1 = 1.0 \times 10^{-7} \qquad K_2 = 1.2 \times 10^{-13}$$

18.57. What is the maximum possible $[Ag^+]$ in a saturated H_2S solution from which precipitation has not occurred? K_{sp} for Ag_2S is 6.7×10^{-50}.

Ans. 7.5×10^{-19}

18.58. Determine the $[S^{2-}]$ in a saturated H_2S solution to which enough HCl has been added to produce a hydrogen ion concentration of 2×10^{-4} M.

Ans. 3×10^{-14}

18.59. Will FeS precipitate in a saturated H_2S solution if the solution contains 0.01 mol/L Fe^{2+} and (*a*) 0.2 mol/L of H^+? (*b*) 0.001 mol/L H^+? K_{sp} of FeS is 8×10^{-19}.

Ans. (*a*) no; (*b*) yes

18.60. Given that 0.0010 mol each of Cd^{2+} and Fe^{2+} are contained in 1 L of 0.020 M HCl and that this solution is saturated with H_2S (K_{sp} of CdS is 1.4×10^{-29} and FeS is 8×10^{-19}). (*a*) Determine which (if any) of the cations precipitates as the sulfide. (*b*) How much Cd^{2+} remains in solution at equilibrium?

Ans. (*a*) only CdS precipitates; (*b*) 4.7×10^{-12} mol

18.61. In an attempted determination of the solubility product of Tl_2S, the solubility of this compound in pure CO_2-free water was determined as 3.6×10^{-5} mol/L. What is the K_{sp} for Tl_2S? Assume that the dissolved sulfide hydrolyzes practically completely to HS^-, and that there is no further hydrolysis to H_2S .

Ans. 8×10^{-21}

18.62. Calculate the solubility of FeS in pure water. $K_{sp} = 8 \times 10^{-19}$. (*Hint*: The second stage of hydrolysis, producing H_2S, cannot be neglected.)

Ans. 4×10^{-7} M

CHAPTER 19

Electrochemistry

In this chapter, we deal with two aspects of the connection between chemistry and electricity. The first is *electrolysis*, the splitting (lysis) of compounds when electricity passes through the solutions involved. The second topic is *galvanic cell action*, which is the generation of *electricity* (a flow of electrons) during chemical reaction.

ELECTRICAL UNITS

The *coulomb* (C) is the SI unit of electrical charge. From the point of view of fundamental particles, the *elementary* unit (Chapter 8) is the charge of one proton (or an electron, which is equal in size, opposite in charge). No chemical particle is known whose charge is not a multiple of this elementary charge, which is 1.602×10^{-19} C.

Electrical current is the rate of flow of a charge. The SI unit is the *ampere* (A), which is the flow rate of one coulomb per second (1 A = 1 C/s).

The *electrical potential difference* between two points in a circuit causes the transfer of charge from one point to the other. The *volt* (V) is the SI unit of electrical potential. When a charge of 1 C moves through a potential of 1 V, it gains 1 J of energy. Summarized:

$$\begin{aligned}\text{Energy (J)} &= (\text{charge in coulombs}) \times (\text{potential difference in volts}) \\ &= (\text{current in amperes}) \times (\text{time in seconds}) \times (\text{potential difference in volts}) \qquad (19\text{-}1)\end{aligned}$$

The *watt* (W) is the SI unit of *power* (electrical and others). One watt is developed when 1 J of work is performed in 1 s. From (*19-1*),

$$\text{Power (W)} = (\text{current in amperes}) \times (\text{potential difference in volts}) \qquad (19\text{-}2)$$

In electrochemistry, we are normally concerned with direct current (DC) for reasons mentioned later. However, the above discussion of units applies equally well to alternating current (AC), the type of power normally used in the home and the laboratory.

FARADAY'S LAWS OF ELECTROLYSIS

1. The mass of any substance liberated or deposited at an electrode is proportional to the electrical charge (i.e., the number of coulombs) that has passed through the electrolyte.
2. The masses of different substances liberated or deposited by the same amount of electricity (i.e., the same number of coulombs) are proportional to the equivalent masses (Chapter 12) of the substances.

These laws (determined by Michael Faraday over a half century before the discovery of the electron) can now be shown to be simple consequences of the electrical nature of matter. In any electrolysis, an oxidation must occur at the anode to supply the electrons that leave this electrode. Also, a reduction must occur at the cathode removing electrons coming into the system from an outside source (battery or other DC source). By the principle of continuity of current, electrons must be discharged at the cathode at exactly the same rate at which they are supplied to the anode. By definition of the equivalent mass for oxidation-reduction reactions, the number of *equivalents* of electrode reaction must be proportional to the amount of charge transported into or out of the electrolytic cell. Further, the number of equivalents is equal to the number of *moles of electrons* transported in the circuit. The *Faraday constant* (F) is equal to the charge of one mole of electrons, as shown in this equation:

$$\mathsf{F} = N_a \times e = (6.022 \times 10^{23} e^-/\text{mol})(1.602 \times 10^{-19}\ \text{C}/e^-) = 96{,}500\,\text{C/mol}$$

The symbol N_a is Avogadro's number of electrons and e is the elementary charge, 1.602×10^{-19} C/e^-. As has been utilized in previous chapters, $n(e^-)$ may be used for moles of electronic charge, the number of equivalents.

The equivalent mass needed for electrolytic calculations can be found by inspecting the balanced half-reaction for the electrode process. For instance, the reduction of Cu^{2+} is

$$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \qquad \text{at the cathode}$$

The equivalent mass of copper is the amount of copper involved with *one* mole of electrons; there are two moles of electrons required for each mole of copper. Therefore, the equivalent mass of copper is $\frac{1}{2}$ the molar mass. Suppose the reaction for the reduction of copper were to be

$$\text{Cu}^{+} + e^- \rightarrow \text{Cu} \qquad \text{at the cathode}$$

then the equivalent mass of copper would be one mole. Note that one mole of copper is reduced by one mole of electrons in this case.

Suppose we had these reactions:

$$(a)\ \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \qquad (b)\ \text{Fe}^{3+} + 3e^- \rightarrow \text{Fe}$$

In the case of (*a*), an equivalent mass would be one mole iron ($1e^-$), but an equivalent mass for (*b*) would be $\frac{1}{3}$ mole Fe ($3e^-$).

VOLTAIC CELLS

Many oxidation-reduction reactions may be carried out in such a way as to generate electricity. These cells are known as *voltaic* (older term: *galvanic*) cells. In principle, any spontaneous, oxidation-reduction reaction (aqueous) can be set up to generate electricity by the following requirements:

1. The oxidizing and reducing agents are not in physical contact with each other, but are continued in separate compartments (*half-cells*). Each half-cell contains a solution and a conductor (electrode), which is usually a metal.

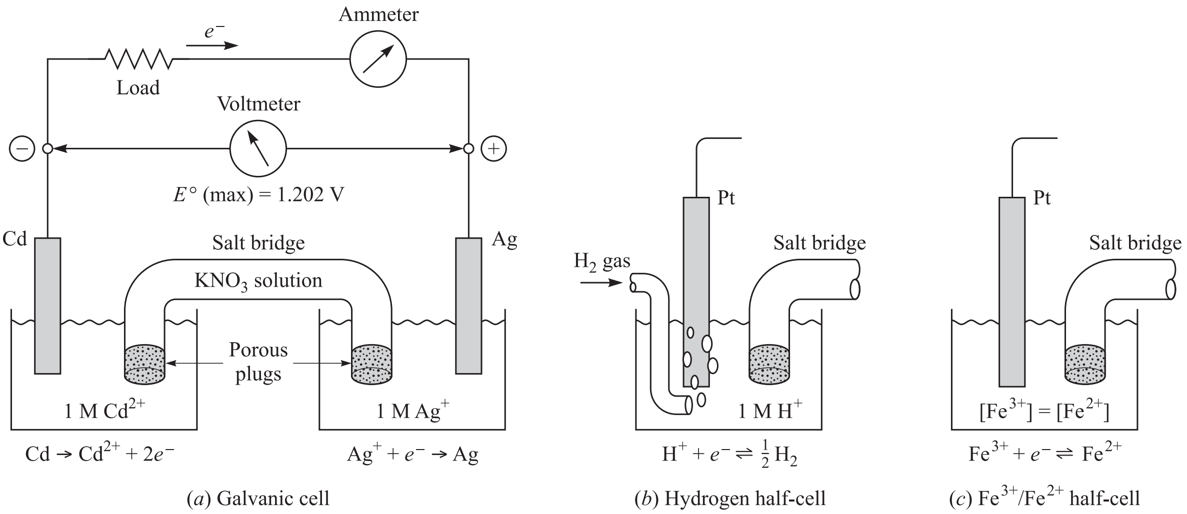
2. The reducing or oxidizing agent in a half-cell may be either the electrode itself, a solid substance deposited on the electrode, a gas which bubbles around the electrode, or a solute in solution which bathes the electrode. Just as in electrolysis, the electrode at which reduction occurs is the *cathode* and that at which oxidation occurs is the *anode*. (*Hint*: *Oxidation-anode* and *reduction-cathode* are alphabetical.)

3. The solutions of the two half-cells are connected in some way that allows ions to move between them. Among the possible arrangements are (*a*) careful layering of the less dense solution over the more dense solution; (*b*) separation of the two solutions by a porous substance, such as unglazed porcelain or a fibrous substance soaked in an electrolyte; or (*c*) insertion of a connecting electrolyte solution (a *salt bridge*) between the two solutions.

The potential developed across the two electrodes causes an electrical current to flow and the half-cell reactions to proceed so long as there is a complete circuit and reactants. The flow of electricity must travel essentially in a circle; the e^- flow starts somewhere, flows out, and returns to the flow's origin.

Figure 19-1(*a*) shows a galvanic cell in which each half-cell consists of a metal in contact with a solution of the ions of the same metal. The direction of the reaction, direction of the current, and the voltage have been arrived at by the methods described in the following sections. There are different structures for half-cells depending on the states of matter of reactants and products. Figure 19-1(*b*) shows a setup for a hydrogen (gas) half-cell in which the reduced form (H_2 gas) is adsorbed onto the surface of platinum. The platinum electrode is inert and serves as a conductor of the electrons involved. Figure 19-1(*c*) is a half-cell in which the electrode is platinum (inert, but a conductor of electrons), but both the oxidized and reduced forms are in solution.

This chapter deals primarily with reactions in aqueous media, but the principles can be extended to fuel cells and other batteries like the high-temperature batteries with exotic nonaqueous electrolytes.



(*a*) Galvanic cell (*b*) Hydrogen half-cell (*c*) Fe^{3+}/Fe^{2+} half-cell

Fig. 19-1

STANDARD HALF-CELL POTENTIALS

The reaction occurring in each half-cell may be represented by an ion-electron partial equation of the type described in Chapter 11. The whole-cell operation involves a flow of electrons in an external circuit. The electrons generated in the oxidation half-reaction (oxidation) enter the anode, travel through the external circuit to the cathode, and are taken up by the half-reaction (reduction) that occurs at the cathode. Since the overall charge of a complete set of reactions must be neutral, the number of electrons given off at the anode (oxidation reaction) and those taken up at the cathode (reduction reaction) must be exactly the same number. This is also required of the combining (adding together) of the two half-reactions involved to produce the summation reaction as in Chapter 11. As with the balanced reactions in previous chapters, there will be no electrons written into the summation reaction.

In the half-cell containing the cathode, the oxidation product accumulates while the half-cell is operating. The reducing agent is also located in this half-cell (it is the substance being oxidized). The reducing agent and its oxidation product are known as a *couple* and are in the same half-cell. Similarly, the other half-cell contains a couple consisting of the oxidizing agent and its reduction product. A particular couple, consisting of both product and reactant of an oxidation-reduction half-reaction, may be the reducing part of the galvanic cell and sometimes the oxidizing part—the role depends on what the other couple is. The (Fe^{3+}/Fe^{2+}) couple, for example, takes on an oxidizing role when paired against the strongly reducing (Zn^{2+}/Zn) couple. On the other hand, ($Fe^{3+}|Fe^{2+}$)

takes a reducing role when paired against the strongly oxidizing ($Ce^{4+}|Ce^{3+}$) couple. *The notation used toward the end of this paragraph*, ($Fe^{3+}|Fe^{2+}$) *as an example, has the oxidized form* (Fe^{3+}) *on the left, a vertical line separating the components of the half-cell, and the reduced form*, (Fe^{2+}), *on the right.*

Each couple has the ability to consume electrons. This ability can be assigned by numerical value, called the *electrode potential*. The electrode potential is the potential of a half-cell compared to the hydrogen cell (hydrogen standard cell), which is taken to produce 0.000 volts. When two couples are combined into a whole cell, the couple with the higher electrode potential provides the oxidizing agent, absorbs electrons from the external circuit at its electrode, and is positive. The other couple provides the reducing agent, delivers electrons from its electrode to the external circuit, and is negative. The driving force for the flow of current is the *algebraic difference* between the two potentials. This difference is equal to the voltage output of the cell under standard conditions.

Table 19-1 Standard Reduction Potentials at 25°C

Reaction	E°/V
$F_2 + 2e^- \rightarrow 2F^-$	2.87
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	1.96
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.92
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.763
$Ce^{4+} + e^- \rightarrow Ce^{3+}$ (in 1 M $HClO_4$)	1.70
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.358
$Tl^{3+} + 2e^- \rightarrow Tl^+$	1.25
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.23
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229
$Br_2 + 2e^- \rightarrow 2Br^-$	1.065
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	1.002
$Pd^{2+} + 2e^- \rightarrow Pd$	0.915
$Ag^+ + e^- \rightarrow Ag$	0.7991
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.771
$O_2 + 2H^+ + 2e^- \rightarrow 2H_2O_2$	0.695
$I_2(s) + 2e^- \rightarrow 2I^-$	0.535
$Cu^+ + e^- \rightarrow Cu$	0.520
$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$	0.361
$[Co(dip)_3]^{3+} + e^- \rightarrow [Co(dip)_3]^{2+}$	0.34
$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Ge^{2+} + 2e^- \rightarrow Ge$	0.247
$[PdI_4]^{2-} + 2e^- \rightarrow Pd + 4I^-$	0.18
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.15
$[Ag(S_2O_3)_2]^{3-} + e^- \rightarrow Ag + 2S_2O_3^{2-}$	0.017
$2H^+ + 2e^- \rightarrow H_2$	0.0000
$Ge^{4+} + 2e^- \rightarrow Ge^{2+}$	0.00
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.126
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.257
$Tl^+ + e^- \rightarrow Tl$	−0.336
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.403
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.7626
$Na^+ + e^- \rightarrow Na$	−2.713
$Li^+ + e^- \rightarrow Li$	−3.040

The numerical value of an electrode potential depends on the nature of the particular chemicals, the temperature, and on the concentrations of the various members of the couple. For the purposes of reference, half-cell potentials are taken at the standard states of all chemicals. *Standard state* is defined as 1 atm pressure of each gas (the difference between 1 bar and 1 atm is insignificant for the purposes of this chapter), the pure substance of each liquid or solid, and 1 molar concentrations for every nongaseous solute appearing in the balanced half-cell reaction. Reference potentials determined with these parameters are called *standard electrode potentials* and, since they are represented as reduction reactions (Table 19-1), they are more often than not referred to as *standard reduction potentials* (E°). E° is also used to represent the standard potential, calculated from the standard reduction potentials, for the whole cell. Some values in Table 19-1 may not be in complete agreement with some sources, but are used for the calculations in this book.

A couple with a large positive E°, like ($F_2|F^-$), is strongly oxidizing, captures electrons from the electrode, and is experimentally *positive* with respect to the hydrogen electrode. Conversely, a couple with a large negative E°, like ($Li^+|Li$), is strongly reducing and therefore undergoes oxidation, transferring electrons to the electrode. Such a standard half-cell is *negative* when compared to a standard hydrogen electrode since the external circuit receives electrons from the half-cell's electrode.

COMBINATIONS OF COUPLES

There is a way of combining two half-cell reactions, in which the electrons do not cancel. This cannot correspond to a whole cell, since its electrons always cancel. The situation to which we refer is a hypothetical one used to calculate an unknown half-cell potential on the basis of two known half-cell potentials. In such a case, the electron number cannot be left out and is algebraically added. As discussed in the next section, if n is the number of electrons in a half-reaction, nE° is proportional to the free energy associated with it. As in Chapter 16, when we add two reactions, we may also add their free energies to get the free energy of the overall (net) reaction. The rule for this case is as follows:

If two reduction half-reactions are added or subtracted to give a third reduction half-reaction, the two nE° products are added or subtracted correspondingly to give the nE° value for the resulting half-reaction.

EXAMPLE 1 Calculate E° for the ($Fe^{3+}|Fe$) couple using values from Table 19-1.

		E°	n	nE°
	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44 V	2	−0.88 V
	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77 V	1	0.77 V
Sum:	$Fe^{3+} + 3e^- \rightarrow Fe$		3	−0.11 V

Since nE^0 for the resulting half-reaction is −0.11 V, and n is 3, E° must be $-0.11/3 = -50.04$ V.

This rule makes it possible to reduce the length of compiled tables, since many half-reactions can be computed, even if they are not tabulated.

FREE ENERGY, NONSTANDARD POTENTIALS, AND THE DIRECTION OF OXIDATION-REDUCTION REACTIONS

The discussion following (*16-4*) indicated that the *decrease* in free energy of a system can be equated to the maximum amount of work the system can perform at constant temperature and pressure in forms other than expansive or contractive work. At this point, we can make use of that principle by noting from (*19-1*) that the electrical work performed by a galvanic cell is equal to the voltage times the electrical charge transferred at either electrode. For the passage of n moles of electrons, the charge transferred is $n\mathsf{F}$. This tells us that the electrical work in joules equals $n\mathsf{F}E$. The *maximum* amount of work performed by a galvanic cell is the value of $n\mathsf{F}E$ under conditions where the electrode processes are reversible. Reversibility may be approximated for many electrodes if the cell potential is measured at very low current; such measurements are the basis of the values using the construction of tables, like Table 19-1. Since the electrical work is the only form of work other than expansive or contractive work performed in the typical galvanic cell, the free-energy principle may be stated as

$$\Delta G = -n\mathsf{F}E \tag{19-3}$$

The dependence of a cell potential on the concentrations of the reactants and products may be derived from the known dependence of *G* upon concentration, (*16-6*).

$$E = \frac{\Delta G}{n\mathsf{F}} = \frac{\Delta G^{\mathrm{o}} + RT\ \ln\ Q}{n\mathsf{F}} \tag{19-4}$$

As in Chapter 16, (*19-4*) uses $R = 8.3145\,\mathrm{J/K}$ and ΔG is in joules. When all reactants and products are in the standard states, $Q = 1$ (Chapter 16) and $E = E^{\mathrm{o}}$. Substitution into (*19-4*) provides the *Nernst equation*:

$$E = E^{\mathrm{o}} - \frac{RT}{n\mathsf{F}}\ln\ Q \tag{19-5}$$

When the constants are combined and the natural logarithm converted to a common logarithm, the expression for the potential (in volts) at 25°C becomes

$$E = E^{\mathrm{o}} - \frac{0.0592}{n}\log\ Q \tag{19-6}$$

In (*19-6*), *n* has been made dimensionless. For a half-reaction, *n* is the number of electrons in the half-equation; for the whole-cell reaction, *n* is the number of electrons in *one* of the multiplied half-equations before canceling the electrons. The Nernst equation is closely related to the laws of chemical equilibrium. Le Chatelier's principle applies to the potential of a cell in the same sense as it applies to the yield of an equilibrium process. Since *Q* is a fraction that has product concentrations in the numerator (top) and reactant concentrations in the denominator (bottom), an increased concentration of the product reduces the potential and an increased concentration of reactant raises the potential.

The same type of equation may be used to describe the concentration dependence of the potential of a single half-cell (i.e., the electrode potential). In this case, *Q* contains terms in the numerator containing the products of the balanced half-cell reaction written as a reduction. The terms in the denominator contain the reactants. Neither the numerator nor the denominator contain electron(s). For example:

$$E(\mathrm{Fe^{3+}}|\mathrm{Fe^{2+}}) = E^{\mathrm{o}}(\mathrm{Fe^{3+}}|\mathrm{Fe^{2+}}) - 0.0592\log\frac{[\mathrm{Fe^{2+}}]}{[\mathrm{Fe^{3+}}]}$$

$$E(\mathrm{MnO_4^-}|\mathrm{Mn^{2+}}) = E^{\circ}(\mathrm{MnO_4^-}|\mathrm{Mn^{2+}}) - \frac{0.0592}{5}0.0592\log\frac{[\mathrm{Mn^{2+}}]}{[\mathrm{MnO_4^-}][\mathrm{H^+}]^8}$$

Spontaneous oxidation-reduction reactions

If the potential of a whole cell is positive, the free-energy change is negative, according to (*19-3*). Then, the corresponding oxidation-reduction reaction is spontaneous as written. The galvanic cell would operate spontaneously with electrons provided to the external circuit at the half-cell where oxidation takes place. If the potential is negative, the free-energy is positive, and the corresponding reaction does not take place spontaneously. These statements about the direction of spontaneous reaction are valid whether the reaction is set up as a galvanic cell or as an ordinary process where the reactants and products are all mixed in the same vessel. This is true because the free-energy change for a reaction depends on the concentrations, but not on the way in which the reaction is carried out. In particular, if both reduced and oxidized members of the two couples are mixed (all at standard states), any reducing agent can reduce an oxidizing agent occurring higher in the table of standard electrode potentials. The same rule of relative position may be applied for general values of concentrations, with E for each half-cell, as computed from the Nernst equation, replacing E^o. Usually, the qualitative prediction based on E^o values is not changed, even for moderate deviations from standard states, if the two E^o values are separated by at least several tenths of a volt.

It should be noted that predictions under this rule indicate what reactions *might* occur, but says nothing about the rate at which they *do* occur.

Electrode reactions in electrolysis

An oxidation-reduction reaction that is not spontaneous, for which the calculated cell potential is negative, may be induced by electrolysis. This reaction can be due to an external electrical potential to force electrons into the couple undergoing reduction and to extract electrons from the couple undergoing oxidation. The *minimum* external potential required for electrolysis is the value of the calculated cell potential for the reaction.

Under nearly reversible conditions, the following rule applies:

> **Of all possible reductions that might occur during electrolysis at a cathode, the one for which the electrode potential is algebraically greatest is the most likely.**

Of course, the reverse is also true: the most probable oxidation at the anode is that for which the electrode potential is algebraically the least. In applying the rule, we must keep in mind that (*a*) a solute molecule or ion may undergo oxidation or reduction; (*b*) the anode electrode may itself undergo oxidation; (*c*) the solvent may undergo oxidation or reduction.

EXAMPLE 2 Let us illustrate possibility (*c*) for water at 25°C.

Reduction of molecular hydrogen is found in Table 19-1:

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^o = 0.000\,\mathrm{V}$$

Assume that H_2 gas is allowed to accumulate to a partial pressure of 1 atm. In neutral solutions, where $[H^+] = 10^{-7}$ and the H_2 pressure retains its unit value. the calculation is

$$E = E^o - \frac{0.0592}{2}\log\frac{P(H_2)}{[H^+]^2} = 0.000 - 0.0296\log\frac{1}{(10^{-7})^2}$$

$$E = 0.000 - 0.0296 \times 14 = -0.414\,\mathrm{V}$$

Water is much more difficult to reduce, but hydrogen is easier to oxidize in neutral solutions than in acids.

For the oxidation of water to molecular oxygen, the most appropriate entry in Table 19-1 is

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^o = 1.229\,\mathrm{V}$$

The standard states to which this E^o value refers are 1 atm for oxygen gas and 1 mol/L for H^+. We can calculate E for the above half-cell for neutral solutions, in which $[H^+] = 10^{-7}$, by using the Nernst equation. Assuming the oxygen remains at its standard state, $P(O_2) = 1$ atm,

$$E = E^o - \frac{0.0592}{4}\log\frac{1}{[H^+]^4 P(O_2)} = 1.229 - 0.0148\log\frac{1}{(10^{-7})^4}$$

$$E = 1.229 - 0.0148 \times 28 = 0.815\,\mathrm{V}$$

Then, it is harder for oxygen to be reduced, but easier for water to be oxidized, in neutral than in acid solutions.

Solved Problems

ELECTRICAL UNITS

19.1. A lamp draws a current of 2.0 A. Find the charge in coulombs used by the lamp in 30 s.

$$\text{Charge in coulombs} = (\text{current in amperes}) \times (\text{time in seconds}) = (20.0\,\mathrm{A})(30\,\mathrm{s}) = 60\,\mathrm{C}$$

19.2. What is the time required to pass 36,000 C through an electroplating bath using a current of 5 A?

$$\text{Time in seconds} = \frac{\text{charge in coulombs}}{\text{current in amperes (C/s)}} = \frac{36{,}000\,\text{C}}{5\,\text{C/s}} = 7200\,\text{s} \qquad \text{or} \qquad 2\,\text{h}$$

19.3. A generator delivers 15 A at 120 V. (*a*) Calculate the power in kW supplied by the generator. (*b*) How much electrical energy, in kilowatt-hours, is supplied by the generator in 2 hours? (*c*) What is the cost of this energy at 6¢ per kilowatt-hour?

(*a*) $$\text{Power} = (15\,\text{A})(120\,\text{V}) = 1800\,\text{W} = 1.8\,\text{kW}$$

(*b*) $$\text{Energy} = (1.8\,\text{kW})(2\,\text{h}) = 3.6\,\text{kW}\cdot\text{h}$$

(*c*) $$\text{Cost} = (3.6\,\text{kW}\cdot\text{h})(6¢/\text{kW}\cdot\text{h}) = 22¢$$

19.4. A resistance heater was wound around a 50-g metallic cylinder. A current of 0.65 A was passed through the heater for 24 s while the measured voltage drop across the heater was 5.4 V. The temperature of the cylinder was 22.5°C before the heating period and 29.8°C afterward. On this basis, what is the specific heat of the cylinder metal in J/*g* · *K*?

By (*19–1*) $$\text{Energy input} = (0.65\,\text{A})(5.4\,\text{V})(24\,\text{s}) = 84\,\text{J}$$
But, also, $$\text{Energy input} = (\text{mass}) \times (\text{specific heat}) \times (\text{temperature rise})$$
Therefore, $$84\,\text{J} = (50\,\text{g})(\text{specific heat})[(29.8 - 22.5)\,\text{K}]$$

The last equation above is solved and the specific heat = 0.23 J/g · K.

19.5. How many electrons per second pass through a cross section of copper wire carrying 10^{-16} A?

Since 1 A = 1 C/s $$\text{Rate} = \frac{1 \times 10^{-16}\,\text{C/s}}{1.6 \times 10^{-19}\,\text{C}/e^-} = 600e^-/\text{s}$$

FARADAY'S LAWS OF ELECTROLYSIS

19.6. Exactly 0.2 mol of electrons are passed through three electrolytic cells in series. One contains silver ion, the next zinc ion, and the last iron(III) ion. Assume that the only cathode reaction in each cell is the reduction of the ion to metal. How many grams of each metal will be deposited?

One mole of electrons deposits 1 eq of an element. Equivalent masses of Ag^+, Zn^{2+}, and Fe^{3+} are

$$\frac{107.9\,\text{g Ag}}{1\,\text{mol}\,e^-} = 107.9\ \text{g Ag/mol}\,e^- \qquad \frac{65.39\,\text{g Zn}}{2\,\text{mol}\,e^-} = 32.70\,\text{g Zn/mol}\ e^- \qquad \frac{55.85\,\text{g Fe}}{3\,\text{mol}\,e^-} = 18.62\,\text{g Fe/mol}\,e^-$$

Then, applying the information from the problem and that found directly above:

$$\text{Ag deposited} = (0.2\,\text{mol}\,e^-)(107.9\,\text{g/mol}\,e^-) = 21.58\,\text{g Ag}$$
$$\text{Zn deposited} = (0.2\,\text{mol}\,e^-)(32.70\,\text{g/mol}\,e^-) = 6.54\,\text{g Zn}$$
$$\text{Fe deposited} = (0.2\,\text{mol}\,e^-)(18.62\,\text{g/mol}\,e^-) = 3.72\,\text{g Fe}$$

19.7. A current of 5.00 A flowing for 30 min deposits 3.048 g Zn at the cathode. Calculate the equivalent mass of zinc from this information.

$$\text{Number of coulombs used} = (5.00\,\text{A})[(30 \times 60)\,\text{s}] = 9.00 \times 10^3\,\text{C}$$
$$n(e^-)\ \text{used} = \frac{9.00 \times 10^3\text{C}}{9.65 \times 10^4\,\text{C/mol}\,e^-} = 0.0933\,\text{mol}\,e^-$$
$$\text{Equivalent mass} = \text{mass deposited by 1 mol}\ e^- = \frac{3.048\,\text{g}}{0.0933\,\text{mol}\,e^-} = 32.7\,\text{g/eq}$$

19.8. A certain current liberates 0.504 g of hydrogen in 2 hours. How many grams of oxygen and copper (from Cu^{2+} solution) can be liberated by the same current during the same time?

Masses of different substances liberated by the same number of coulombs are proportional to their equivalent masses. The equivalent mass of hydrogen is 1.008 g; of oxygen, 8.00 g; of copper, 31.8 g.

$$\text{Number of eq of hydrogen in 0.504 g} = \frac{0.504\ \text{g}}{1.008\ \text{g/eq}} = 0.500\ \text{eq}$$

Then, 0.500 eq of any element can be liberated under the same conditions.

$$\text{Mass of oxygen liberated} = 0.500\ \text{eq} \times 8.00\ \text{g/eq} = 4.00\ \text{g oxygen}$$
$$\text{Mass of copper liberated} = 0.500\ \text{eq} \times 31.8\ \text{g/eq} = 15.9\ \text{g}$$

The equivalent mass of any substance in an electrolysis is determined from the balanced half-reaction. For the liberation of oxygen from water, the anode reaction is

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

The molar mass of O_2 is 32.00. The equivalent mass is the molar mass divided by the number of electrons which must flow to produce one molecule, or $32.00/4 = 8.00$.

19.9. The same quantity of electricity that liberated 2.158 g Ag was passed through a solution of a gold salt and 1.314 g Au were deposited. The equivalent mass of silver is 107.9 g. Calculate the equivalent mass of gold and provide the oxidation state of the gold in this salt.

$$\text{Number of eq Ag in 2.158 g} = \frac{2.158\ \text{g Ag}}{107.9\ \text{g Ag/eq}} = 0.02000\ \text{eq Ag}$$

Since 1.314 g Au must represent 0.02000 eq, then

$$\text{Equivalent mass Au} = \frac{1.314\ \text{g}}{0.02000\ \text{eq}} = 65.70\ \text{g/eq}$$

The oxidation state is the number of electrons needed to form one gold atom by reduction.

$$\text{Oxidation state} = \frac{\text{molar mass of Au}}{\text{equivalent mass of Au}} = \frac{197.0}{65.7} = 3$$

And, since this is a *reduction*, the oxidation number of the gold involved is positive, Au^{3+}.

19.10. How long would it take to deposit 100 g Al from an electrolytic cell containing Al_2O_3 at a current of 125 A?

The equivalent mass of Al from Al^{3+} and further calculations are

$$\text{Equivalent mass of Al} = \frac{1}{3}\ \text{molar mass} = \frac{1}{3}(27.0) = 9.0\ \text{g Al/mol}\ e^-$$
$$n(e^-) = \frac{100\ \text{g Al}}{9.0\ \text{g Al/mol}\ e^-} = 11.1\ \text{mol}\ e^-$$
$$\text{Time} = \frac{\text{charge}}{\text{current}} = \frac{(11.1\ \text{mol}\ e^-)(9.65 \times 10^4\ \text{C/mol}\ e^-)}{125\ \text{A}} = 8.65 \times 10^3\ \text{s} \quad \text{or} \quad 2.4\ \text{h}$$

19.11. A current of 15.0 A is used to plate nickel on a surface from a $NiSO_4$ bath. Both Ni and H_2 are formed at the cathode. The current efficiency with respect to the formation of Ni is 60%. (*a*) How many grams of Ni are plated on the cathode per hour? (*b*) What is the thickness of the plating if the cathode consists of a sheet of metal 4.0 cm square, which is coated on both facts? (Density of Ni is 8.9 g/cm^3) (*c*) What volume of H_2 (S.T.P.) is formed per hour?

(*a*)

$$\text{Total number of coulombs used} = (15.0\,\text{A})(3600\,\text{s}) = 5.40 \times 10^4\,\text{C}$$

$$n(e^-)\text{ used} = \frac{5.40 \times 10^4\,\text{C}}{9.65 \times 10^4\,\text{C/mol}\,e^-} = 0.560\,\text{mol}\,e^-$$

$$\text{Number eq of Ni deposited} = (0.60)(0.560\,\text{mol}\,e^-)(1\,\text{eq Ni/mol}\,e^-) = 0.336\,\text{eq Ni}$$

$$\text{Equivalent mass of Ni} = \frac{1}{2}(\text{molar mass}) = \frac{1}{2}(58.69) = 29.3\,\text{g/eq}$$

$$\text{Mass of Ni deposited} = (0.336\,\text{eq})(29.3\,\text{g/eq}) = 9.8\,\text{g Ni}$$

(*b*) The calculations are based on the determination of the area of both sides of the metal sheet and the determination of the total volume of the plated Ni.

$$\text{Area of two faces} = 2[(4.0\,\text{cm})(4.0\,\text{cm})] = 32\,\text{cm}^3$$

$$\text{Volume of 9.8 g Ni} = \frac{\text{mass}}{\text{density}} = \frac{9.8\,\text{g}}{8.9\,\text{g/cm}^3} = 1.10\,\text{cm}^3$$

$$\text{Thickness of Ni} = \frac{\text{volume}}{\text{area}} = \frac{1.10\,\text{cm}^3}{32\,\text{cm}^2} = 0.034\,\text{cm}$$

(*c*) This part of the problem is similar to previously worked problems. For a bit of variety, we show the use of the faraday, F, a somewhat-out-of date unit which is one mole of electrons.

$$\text{Number eq H}_2\text{ liberated} = (0.40)(0.560\,\mathsf{F})(1\,\text{eq H}_2/\mathsf{F}) = 0.224\,\text{eq H}_2$$

$$\text{Volume of 1 eq}\left(\frac{1}{2}\,\text{mol}\right)\text{H}_2 = \frac{1}{2}(22.4\,\text{L}) = 11.2\,\text{L H}_2\ (\text{S.T.P.})$$

$$\text{Volume of H}_2\text{ liberated} = (0.224\,\text{eq})(11.2\,\text{L/eq}) = 2.51\,\text{L H}_2$$

19.12. How many coulombs must be supplied to a cell for the electrolytic production of 245 g $NaClO_4$ from $NaClO_3$? Because of side reactions, the anode efficiency is only 60% for the reaction.

First, it is necessary to know the equivalent mass of $NaClO_4$ for this reaction. The balanced anode reaction is as follows:

$$ClO_3^- H_2O \rightarrow ClO_4^- + 2H^+ + 2e^-$$

$$\text{Equivalent mass of NaClO}_4 = \frac{\text{molar mass}}{\text{electrons transferred}} = \frac{122.5}{2} = 61.2\,\text{g NaClO}_4$$

$$\text{Equivalents of NaClO}_4 = \frac{\text{molar mass}}{\text{electrons transferred}} = \frac{245\,\text{g}}{61.2\,\text{g/eq}} = 4.00\,\text{eq NaClO}_4$$

$$n(e^-)\text{ required} = \frac{4.00\,\text{eq}}{0.60\,\text{eq product/mol}\,e^-} = 6.7\,\text{mol}\,e^-$$

$$\text{Coulombs required} = (6.7\,\text{mol}\,e^-)(9.6 \times 10^4\,\text{C/mol}\,e^-) = 6.4 \times 10^5\,\text{C}$$

VOLTAIC (GALVANIC) CELLS AND ELECTRODE PROCESSES

19.13. What is the standard potential of a cell that uses the ($Zn^{2+}|Zn$) and ($Ag^+|Ag$) couples? Which couple is negative? Write the equation for the cell reaction occurring at standard states.

The standard potentials for ($Zn^{2+}|Zn$) and ($Ag^+|Ag$) are −0.763 V and 0.799 V from Table 19-1. The standard potential of the cell is the difference between these two numbers, $0.779\,\text{V} - (-0.763) = 1.542\,\text{V}$. The silver potential is higher, and this means that the silver ion is the oxidizing agent. The zinc couple provides the reducing agent and is the negative electrode. The equation for the cell is

$$Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$$

19.14. Can Fe^{3+} oxidize Br^- to Br_2 under the circumstances in which Table 19-1 is constructed?

From Table 19-1, which provides the values at 25°C, 1 atm, and standard states, the $(Fe^{3+}|Fe^{2+})$ couple has a lower standard reduction potential, 0.771 V, than the $(Br_2|Br^-)$ couple, 1.065 V. Therefore Fe^{2+} can reduce Br_2, but Br^- cannot reduce Fe^{3+}. This also means that Fe^{3+} cannot oxidize Br^-.

19.15. What is the standard electrode potential for $(MnO_4^-|MnO_2)$ in acid solution? ($[H^+] = 1.00\,M$)

The reduction half-reaction for the couple is

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + H_2O$$

The reaction can be written as the difference of two half-reactions whose reduction potentials are listed in Table 19-1. The $nE°$ values can be calculated as standard reduction potentials so long as one is reversed to an oxidation. The reversal of the reaction results in the opposite sign for the potential.

		n	E^{o}	nE^{o}
	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	5	1.51 V	7.55
(Reaction reversed to oxidation)	$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-$	2	−1.23 V	−2.46 V
Difference:	$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	3		5.09 V

$$E^{\mathrm{o}} \text{ for the desire reaction} = \frac{5.09}{3} = 1.70\,\mathrm{V}$$

19.16. Predict the stabilities at 25°C of aqueous solutions of the uncomplexed intermediate oxidation states of (*a*) thallium and (*b*) copper.

(*a*) The question is whether the intermediate state, Tl^+, spontaneously decomposes into the lower and higher states, Tl and Tl^{3+}. We can take the reaction to be

$$3Tl^+ \rightarrow 2Tl + Tl^{3+}$$

This reaction could be written in the ion-electron method as

		E^{o} (red) for the couple (Table 19-1)	
	$2 \times (TL^+ + e^- \rightarrow TL)$	−0.336 V	(*1*)
(Reversed)	$TL^+ \rightarrow TL^{3+} + 2e^-$	−1.25 V	(*2*)

In (*1*), the $(Tl^+|Tl)$ couple functions as the oxidizing agent; in (*2*), the $(Tl^{3+}|Tl^+)$ couples functions as the reducing agent. The reaction would occur at standard concentrations if E^{o} for the reducing couple were to be less than E^{o} for the oxidizing couple. Since the reduction potential of 1.25 V is greater than −0.336 V, the reaction cannot occur as written. We can now conclude that Tl^+ does not spontaneously decompose to Tl and Tl^{3+}. Actually, the reverse reaction is the spontaneous reaction: $2Tl + Tl^{3+} \rightarrow 3Tl^+$.

(*b*) As in (*a*), we can take the following reaction to incorporate both possibilities:

$$2Cu^+ \rightarrow Cu + Cu^{2+}$$

The ion-electron partial reactions are as follows:

	E^{o} (red) for the couple (Table 19-1)
$Cu^+ + e^- \rightarrow Cu$	0.520 V
$Cu^+ \rightarrow Cu^{2+} + e^-$	0.160 V (*calculated*)

This process could occur if E^{o} for the supposed reducing couple, $(Cu^{2+}|Cu^+)$, were to be less than E^{o} for the oxidizing couple, $(Cu^+|Cu)$. If we use the method of Problem 19.15, we calculate 0.16 V, which is less than 0.52 V. Therefore, Cu^+ is unstable in solution. Compounds of Cu^+ can exist only as extremely insoluble substances or as such stable complexes that only a very small concentration of free Cu^+ can exist in solution.

19.17. (*a*) What is the potential of the cell containing the ($Zn^{2+}|Zn$) and ($Cu^{2+}|Cu$) couples, if the Zn^{2+} and Cu^{2+} concentrations are 0.1 M and 10^{-9} M, respectively at 25°C? (*b*) What is ΔG for the reduction of 1 mol of Cu^{2+} by Zn at the indicated concentrations of the ions, and what is ΔG° for the reaction, both at 25°C?

(*a*) The cell reaction is $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$, with an *n*-value of 2.

$$E = E^{\circ} - \frac{0.0592 \log Q}{n}$$

E°, the standard cell potential, is equal to the difference between the standard electrode potentials.

$$0.34 - (-0.76) = 1.10\,\text{V}$$

Q, the concentration function, does not include terms for solid metals, because the metals are in their standard states.

$$E = 1.10 - \frac{0.0592}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]} = 1.10 - 0.0296 \log \frac{10^{-1}}{10^{-9}}$$

$$E = 1.10 - (0.0296)(8) = 0.86\,\text{V}$$

(*b*) From (*19-3*)

$$\Delta G = -n\mathsf{F}E = -(2\,\text{mol}\ e^-)(9.65 \times 10^4\ \text{C/mol}\ e^-)(0.86\,\text{V}) = -166 \times 10^3\ \text{C}\cdot\text{V} = -166\,\text{kJ}$$

$$\Delta G^\circ = -n\mathsf{F}E = -(2 \times 9.65 \times 10^4 \times 1.10)\,\text{J} = -212\,\text{kJ}$$

19.18. By how much is the oxidizing power of the ($MnO_4^-|Mn^{2+}$) couple decreased if the H^+ concentration is decreased from 1 M to 10^{-4} M at 25°C?

The half-cell reaction for this reduction is

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

with an *n*-value of 5 because Mn goes from Mn^{7+} in MnO_4^- to Mn^{2+}. Assume that *only* the H^+ concentration deviates from 1 mol/L.

$$E = E^\circ - \frac{0.0592}{n} \log Q$$

Then,

$$E - E^{\circ} = -\frac{0.0592}{5} \log \frac{[Mn^{+}]}{[MnO_4^-][H^+]^8} = -0.0118 \log \frac{1}{(1)(10^{-4})^8}$$

$$E - E^\circ = -(0.0118)(32) = -0.38\,\text{V}$$

The couple has moved down the table 0.38 V from its standard value. This is a position of less oxidizing power.

19.19. In the continued electrolysis of each of the following solutions at pH 7.0 and 25°C, predict the main product at each electrode if there are no (irreversible) electrode polarization effects: (*a*) 1 M $NiSO_4$ with palladium electrodes; (*b*) 1 M $NiBr_2$ with inert electrodes; (*c*) 1 M Na_2SO_4 with Cu electrodes.

(*a*) *Cathode reaction*. The following two possible reduction processes may be considered:

	E°
(*1*) $Ni^{2+} + 2e^- \rightarrow Ni$	−0.25 V
(*2*) $2H^+ + 2e^- \rightarrow H_2$	0.00 V

By the rule that the most probable cathode process is that for which the corresponding electrode potential is algebraically greatest, the hydrogen couple is favored as a standard cell. Allowing for the effect of the pH 7.0

buffer, however, E for (2) is lowered to -0.41 V, as calculated in Example 2. The reduction of nickel is the favored process at this pH.

Anode reaction. Three possible oxidation processes may be considered, the reverses of the following reduction half-reactions:

$$\begin{array}{lll} & & E^{\circ} \\ (3)\ O_2 + 4H^+ + 4e^- & \rightarrow 2H_2O & 1.23\,\text{V} \\ (4)\ Pd^{2+} + 2e^- & \rightarrow Pd & 0.915\,\text{V} \\ (5)\ S_2O_8^{2-} + 2e^- & \rightarrow 2SO_4^{2-} & 1.96\,\text{V} \end{array}$$

The standard potentials are reasonable values to take into consideration with (*4*) and (*5*). Although the initial concentration of Pd^{2+} and $S_2O_8^{2-}$ are zero, they would increase during prolonged electrolysis if these species were the principal products. In the case of (*3*), however, the buffering of the solution prevents the buildup of $[H^+]$, and it would be more appropriate to take the E-value calculated for pH 7.0 in Example 2, 0.82 V. It is apparent that of the three, (*3*) has the smallest E-value and the reverse of (3) would occur most readily among the possible anode reactions.

In conclusion, the electrode processes to be expected are:

$$\begin{array}{lll} \text{Anode:} & 2H_2O & \rightarrow O_2 + 4H^+ + 4e^- \\ \text{Cathode:} & Ni^{2+} + 2e^- & \rightarrow Ni \\ \text{Overall:} & 2H_2O + 2Ni^{2+} & \rightarrow O_2 + 4H^+ + 2Ni \end{array}$$

(*b*) *Cathode reaction.* As in (*a*), Ni reduction would occur.

Anode reaction. The expression "inert electrode" is often used to indicate that we may neglect reaction of the electrode itself. This can be due to the high value of its electrode potential or because of polarization effects related to the preparation of the electrode surface. The remaining possible anode reactions are the reverses of the following:

$$\begin{array}{lll} & & E^{\circ} \\ (6)\ Br_2 + 2e^- & \rightarrow 2Br^- & 1.065\,\text{V} \\ (3)\ O_2 + 4H^+ + 4e^- & \rightarrow 2H_2O & 1.23\,\text{V} \end{array}$$

When the E-value for (*3*) is calculated as 0.82 V for pH 7.0, as in (*a*), oxygen evolution takes precedence.

(*c*) *Cathode reaction.* The new couple to be considered is the sodium couple, which is

$$\begin{array}{ll} & E^{\circ} \\ (7)\ Na^+ + e^- \rightarrow Na & -2.71\,\text{V} \end{array}$$

This E-value is much lower algebraically than that of (*2*), the evolution of H_2 at pH 7.0. -0.41 V. Therefore, hydrogen evolution will occur at the cathode.

Anode reaction. In addition to (*3*) and (*5*), the reaction of the Cu anode must be considered, the reverse of which is

$$\begin{array}{ll} & E^{\circ} \\ (8)\ Cu^{2+} + 2e^- \rightarrow Cu & 0.34\,\text{V} \end{array}$$

Process (*8*) has the lowest E-value, and copper going into solution, the reverse of (*8*), would take precedence over oxygen evolution.

In this example, the sodium sulfate solution was not at all involved in the reaction, but served as an electrical conductor. Eventually, as Cu^{2+} builds up and copper migrates to the cathode, reaction (*8*) will replace reaction (*2*) as the cathode reaction.

19.20. Knowing that K_{sp} for AgCl is 1.8×10^{-10}, calculate E for a silver-silver chloride electrode immersed in 1 M KCl at 25°C.

The electrode process is a special case of the $(\mathrm{Ag^+}|\mathrm{Ag})$ couple, except that silver in the $+1$ oxidation state collects as solid AgCl on the electrode itself. Even solid AgCl, however, has some $\mathrm{Ag^+}$ in equilibrium with it in solution. This $[\mathrm{Ag^+}]$ can be calculated from the K_{sp} equation as follows:

$$[\mathrm{Ag^+}] = \frac{K_{sp}}{[\mathrm{Cl^-}]} = \frac{1.8\times10^{-10}}{1} = 1.8\times10^{-10}$$

This value for $[\mathrm{Ag^+}]$ can be inserted into the Nernst equation for the $(\mathrm{Ag^+}|\mathrm{Ag})$ half-reaction.

$$\mathrm{Ag^+} + e^- \rightarrow \mathrm{Ag} \qquad E^{\mathrm{o}} = 0.799\,\mathrm{V}$$

$$E = E^{\mathrm{o}} - \frac{0.0592}{n}\log Q = -\frac{0.0592}{1}\log\frac{1}{[\mathrm{Ag^+}]}$$

$$E = 0.779 - 0.0592\log\frac{1}{1.8\times10^{-10}} = 0.799 - 0.577 = 0.222\,\mathrm{V}$$

19.21. From data in Table 19-1, calculate the overall stability constant, K_s, of $[\mathrm{Ag(S_2O_3)_2}]^{3-}$ at 25°C.

There are two entries in the table for couples connecting the zero and $+1$ states of silver.

$$\begin{array}{llr} & & E^{\mathrm{o}} \\ (1)\ \mathrm{Ag^+} + e^- & \rightarrow \mathrm{Ag} & 0.799\,\mathrm{V} \\ (2)\ [\mathrm{Ag(S_2O_3)_2}]^{3-} + e^- & \rightarrow \mathrm{Ag} + 2\mathrm{S_2O_3^{2-}} & 0.915\,\mathrm{V} \end{array}$$

Process (*1*) refers to the couple in which $\mathrm{Ag^+}$ is at standard concentrations; the $\mathrm{Ag^+}$ concentration to which E^{o} refers is that value which satisfies the complex ion equilibrium when the other species are at standard concentration. The formation reaction for this complex is:

$$\mathrm{Ag^+} + 2\mathrm{S_2O_3^{2-}} \rightleftharpoons [\mathrm{Ag(S_2O_3)_2}]^{3-}$$

$$K_s = \frac{\{[\mathrm{Ag(S_2O_3)_2}]^{3-}\}}{[\mathrm{Ag^+}][\mathrm{S_2O_3^{2-}}]^2} \qquad \text{rearranged to} \qquad [\mathrm{Ag^+}] = \frac{\{[\mathrm{Ag(S_2O_3)_2}]^{3-}\}}{K_s[\mathrm{S_2O_3^{2-}}]^2} = \frac{1}{K_s}$$

In other words, the standard conditions for couple (*2*) may be thought of as a nonstandard condition, $[\mathrm{Ag^+}] = 1/K_s$, for couple (*1*). The Nernst equation for (*1*) gives us

$$E = E^{\mathrm{o}} - \frac{0.0592}{1}\log\frac{1}{[\mathrm{Ag^+}]} \qquad \text{or} \qquad 0.017 = 0.799 - 0.0592\log K_s$$

from which

$$\log K_s = \frac{0.799 - 0.017}{0.0592} = 13.21 \qquad \text{solved} \qquad K_s = 1.6\times10^{13}$$

19.22. (*a*) At equal concentrations of $\mathrm{Fe^{2+}}$ and $\mathrm{Fe^{3+}}$, what must $[\mathrm{Ag^+}]$ be so that the voltage of the galvanic cell made from the $(\mathrm{Ag^+}|\mathrm{Ag})$ and $(\mathrm{Fe^{3+}}|\mathrm{Fe^{2+}})$ electrodes equals zero? (*b*) Determine the equilibrium constant at 25°C for the reaction under standard conditions. The reaction for this cell is:

$$\mathrm{Fe^{2+}} + \mathrm{Ag^+}\mathrm{Fe^{3+}} + \mathrm{Ag}$$

(*a*) For the reaction as written,

$$E^{\mathrm{o}} = E^{\mathrm{o}}(\mathrm{Ag^+}|\mathrm{Ag}) - E^{\mathrm{o}}(\mathrm{Fe^{3+}}|\mathrm{Fe^{2+}}) = 0.799 - 0.771 = 0.028\,\mathrm{V}$$

Then, from the Nernst equation (only $1e^-$ is involved),

$$E = E^{\mathrm{o}} - \frac{0.0592}{1}\log\frac{[\mathrm{Fe^{3+}}]}{[\mathrm{Fe^{2+}}][\mathrm{Ag^+}]}$$

$$0 = 0.028 - 0.0592\log\frac{1}{[\mathrm{Ag^+}]} = 0.028 + 0.0592\log[\mathrm{Ag^+}]$$

$$\log[\mathrm{Ag^+}] = -\frac{0.028}{0.0592} = -0.47$$

Taking the antilog of both sides of the equation, we find that the $[\mathrm{Ag^+}]$ would be 0.34 M.

(*b*) To find the equilibrium constant, we must combine the relationship between K and ΔG°, (*16-8*), with the relationship between ΔG° and E° obtained from (*19-3*), $\Delta G^{\circ} = -n\mathsf{F}E^{\circ}$.

$$\log K = -\frac{\Delta G^{\circ}}{2.303RT} = \frac{n\mathsf{F}E^{\circ}}{2.303RT} = \frac{nE^{\circ}}{0.0592}$$

Note that the same combination of constants (of value 0.0592 at 25°C) occurs here as in the Nernst equation.

$$\log K = \frac{0.028}{0.0592} = 0.47 \qquad \text{then} \qquad K = \frac{[\mathrm{Fe}^{3+}]}{[\mathrm{Fe}^{2+}][\mathrm{Ag}^{+}]} = 3.0$$

Part (*a*) above could have been solved alternatively by using the equilibrium constant, noting that $[\mathrm{Fe}^{2+}] = [\mathrm{Fe}^{3+}]$ and solving for $[\mathrm{Ag}^{+}]$:

$$[\mathrm{Ag}^{+}] = \frac{[\mathrm{Fe}^{3+}]}{[\mathrm{Fe}^{2+}] \times 3.0} = \frac{1}{3.0} = 0.33$$

The two methods must be equivalent because the voltage of a galvanic cell becomes zero when the two couples are at equilibrium with each other.

19.23. An excess of liquid mercury was added to an acidified 1.00×10^{-3} M Fe^{3+} solution. It was found that only 5.4% of the iron remained as Fe^{3+} at equilibrium at 25°C. Calculate $E^{\circ}(\mathrm{Hg}_2^{2+}|\mathrm{Hg})$, assuming

$$2\mathrm{Hg} + 2\mathrm{Fe}^{3+} \rightleftharpoons \mathrm{Hg}_2^{2+} + 2\mathrm{Fe}^{2+}$$

The first step is to calculate the equilibrium constant for the reaction. At equilibrium,

$$[\mathrm{Fe}^{3+}] = (0.054)(1 \times 10^{-3}) = 5.4 \times 10^{-5}$$
$$[\mathrm{Fe}^{2+}] = (1 - 0.054)(1 \times 10^{-3}) = 9.46 \times 10^{-4}$$
$$[\mathrm{Hg}_2^{2+}] = \frac{1}{2}[\mathrm{Fe}^{2+}] = 4.73 \times 10^{-4}$$

Liquid mercury is in excess and is in its standard state (included in the K expression).

$$K = \frac{[\mathrm{Hg}_2^{2+}][\mathrm{Fe}^{2+}]^2}{[\mathrm{Fe}^{3+}]^2} = \frac{(4.73 \times 10^{-4})(9.46 \times 10^{-4})^2}{(5.4 \times 10^{-5})^2} = 0.145$$

The standard potential of the cell may be calculated from the relationship found in Problem 19.22(*b*).

$$E^{\circ} = \frac{0.0592}{n}\log K = \frac{(0.0592)(-0.839)}{2} = -0.025\,\mathrm{V}$$

For the reaction as written,

$$E^{\circ} = E^{\circ}(\mathrm{Fe}^{3+}|\mathrm{Fe}^{2+}) - E^{\circ}(\mathrm{Hg}_2^{2+}|\mathrm{Hg})$$

or $$E^{\circ} = E^{\circ}(\mathrm{Hg}_2^{2+}|\mathrm{Hg}) = E^{\circ}(\mathrm{Fe}^{3+}|\mathrm{Fe}^{2+}) - E^{\circ} = 0.771 - (-0.025) = 0.796\,\mathrm{V}$$

Supplementary Problems

ELECTRICAL UNITS

19.24. How many coulombs per hour pass through an electroplating bath using a current of 5 A?

Ans. 1.8×10^4 C/h

19.25. Calculate the cost at \$0.05 per kilowatt-hour of operating an electric motor using 15 A at 110 V for 8 hours.

Ans. \$0.66

19.26. A tank containing 0.2 m^3 of water was used as a constant-temperature bath. How long would it take to heat the bath from 20°C to 25°C with a 250-W immersion heater? Assume no heat loss.

Ans. 4.6 h

19.27. The specific heat of a liquid was measured by placing 100 g of the liquid in a calorimeter. The liquid was heated by an electrical immersion coil. The heat capacity of the calorimeter and coil was previously determined as 31.4 J/K. With the 100-g sample in place, a current of 0.500 A was passed through the coil for 3 min. The voltage across the terminals of the coil was measured to be 1.50 V. The temperature of the sample rose 0.800°C. Find the specific heat of the liquid.

Ans. 1.37 kJ/kg · K

19.28. The heat of solution of NH_4NO_3 in water was determined by measuring the amount of electrical work needed to compensate for the cooling which would otherwise occur when the salt dissolves. After the NH_4NO_3 was added to water, electrical energy was provided by passage of a current through a resistance coil until the temperature of the solution reached the value it had before the addition of the salt. In a typical experiment, 4.4 g NH_4NO_3 were added to 200 g H_2O. A current of 0.75 A was provided through the heater coil and the voltage was 6.0 V. The current was applied for 5.2 minutes. Calculate ΔH for the solution of 1 mol NH_4NO_3 in enough water to give the same concentration as was attained in the above experiment.

Ans. 25.5 kJ

FARADAY'S LAWS OF ELECTROLYSIS

Note: Unless indicated otherwise, the efficiency is 100% for all electrodes.

19.29. What current is required to pass 1 mol of electrons per hour through an electroplating cell? How many grams of aluminum will be liberated by 1 mol of electrons? How many moles of Cd/mol e^-?

Ans. 26.8 A; 8.99 g Al; 56.2 g Cd

19.30. What mass of aluminum is deposited by 40 A in 30 minutes?

Ans. 6.7 g Al

19.31. How many amperes are required to deposit 5.00 g Au/h from a solution of a Au^{3+} salt?

Ans. 2.04 A

19.32. How many hours will it take to produce 100 lb of electrolytic chorine from NaCl in a cell that carries 1000 A? The anode efficiency for the chlorine half-reaction is 85%.

Ans. 40.4 h

19.33. A quantity of electricity passes through two separate electrolytic cells; one contains a solution of $AgNO_3$ and the other contains a solution of $SnCl_2$. If 2.00 g Ag are deposited in one cell, how many grams Sn are deposited in the other cell?

Ans. 1.10 g Sn

19.34. An electrolytic cell contains a solution of $CuSO_4$ and an anode of impure copper. How many kilograms of copper will be refined (deposited on the cathode) by 150 A over 12.0 h? The copper deposited on the cathode comes from the solution; however, that copper deposited is replaced from the anode. This is a technique of separating the copper from the impurities in the anode (refining).

Ans. 2.13 kg Cu

19.35. A fuel cell designed for a spaceship is powered by the overall reaction:

$$2H_2 + O_2 \rightarrow 2H_2O$$

The cell delivers a steady current of 10.0 A and is fed H_2 gas from a 3.5 ft^3 tank at 2000 psi and 31°C. How long will the cell run? (psi = lb/in^2 from Problem 1.9)

Ans. 1.04×10^7 seconds (121 days)

19.36. Hydrogen peroxide, H_2O_2, can be prepared by the successive reactions below:

$$2NH_4HSO_4 \rightarrow H_2 + (NH_4)_2S_2O_8$$
$$(NH_4)_2S_2O_8 + 2H_2O \rightarrow 2NH_4HSO_4 + H_2O_2$$

The first reaction is an electrolytic reaction; the second is a steam distillation. What current would have to be used in the first reaction to produce enough $(NH_4)_2S_2O_8$ to yield 100 g of pure H_2O_2 per hour from the second reaction? Assume 50% anode current efficiency.

Ans. 315 A

19.37. A lead-acid battery, as used in cars, uses the following reaction at the anode:

$$\text{Pb}(s) + \text{HSO}_4^-(aq) \rightarrow \text{PbSO}_4(s) + \text{H}^+(aq) + 2e^-$$

Suppose that this is a 75 ampere-hours battery, meaning that the battery will put out 1 amp for 75 hours (or 75 amps for 1 hour).What is the mass of lead that would be used up during a complete discharge of the battery?

Ans. 290 g Pb

19.38. The reaction presented in this problem is that of the anode and the cathode added together. Suppose we are still interested in a 75 ampere-hour battery, what mass of lead and lead(IV) oxide must be used in the construction of the battery?

$$\text{Pb}(s) + \text{PbO}_2(s) + 2\text{H}^+(aq) + 2\text{HSO}_4^-(aq) \rightarrow 2\text{PbSO}_2(s) + 2\text{H}_2\text{O}(l)$$

Ans. 290 g Pb and 335 g PbO_2

19.39. An important measure of the efficiency of a battery is the *energy density*, the amount of energy delivered divided by the mass of reactants consumed. For comparison purposes, calculate the energy density of (*a*) the 2.00 V (approximate) lead storage battery that discharges by the following reaction:

$$\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$$

(*b*) and calculate the energy density of a 1.30 V (approximate) NiCad battery, which discharges by

$$\text{Cd} + 2\text{NiOOH} + 2\text{H}_2\text{O} \rightarrow \text{Cd(OH)}_2 + 2\text{Ni(OH)}_2$$

Note that these calculations do not take into account such practical factors as the cost of the chemicals required, fraction of reactants not utilized, or nonreactive structural materials. These factors and others add to the cost of the batteries.

Ans. (*a*) 601 kJ/kg; (*b*) 756 kJ/kg

19.40. Engineers interested in developing low-weight batteries have turned to the Group IA elements Li and Na, both of which, in addition to their low equivalent mass, have a very negative reduction potential. (Because the electrolytes are not aqueous, the battery voltages cannot be calculated accurately from tabulations such as Table 19-1. The voltages given below are very rough estimates.) Calculate the energy densities of (*a*) the approximately 3.00 V lithium-titanium(IV) sulfide battery, and (*b*) the approximately 2.60 V sodium-sulfur battery. The discharge reactions are

$$(a)\ \text{Li} + \text{TiS}_2 \rightarrow (\text{Li}^+)(\text{TiS}_2^-) \quad (b)\ 2\text{Na} + \text{S}_2 \rightarrow (\text{Na}^+)_2(\text{S}_2^{2-})$$

Ans. (*a*) 2.43×10^3 kJ/kg; (*b*) 4.56×10^3 kJ/kg

19.41. Predict the principal product at each electrode in the continued electrolysis at 25°C of each of the following: (*a*) 1 M $Fe_2(SO_4)_3$ with inert electrodes in 0.10 M H_2SO_4; (*b*) 1 M LiCl with silver electrodes; (*c*) 1 M $FeSO_4$ with inert electrodes at pH 7.0; (*d*) molten NaF with inert electrodes.

Ans. (*a*) Fe^{2+} and O_2; (*b*) H_2 and AgCl; (*c*) H_2 and Fe^{3+}; (*d*) Na and F_2

19.42. A voltaic cell was operated under almost ideally reversible conditions at a current of 10^{-16} A. (*a*) At this current, how long would it take to deliver 1 mol e^-? (*b*) How many electrons would be delivered by the cell to a pulsed measuring circuit in 10 ms?

Ans. (*a*) 3×10^{13} years; (*b*) $6e^-$

19.43. The quantity of antimony in a solution can be determined by converting it to the +3 oxidation state and titrating with standard iodine in bicarbonate solution:

$$H_2SbO_3^- + 3HCO_3^- + I \rightarrow HSbO_4^{2-} + 2I^- + CO_2 + 2H_2O$$

In a variation of this method, particularly useful when dealing with very small samples, excess iodide ion is added to the solution and the requisite iodine is generated by electrolysis:

$$2I \rightarrow I_2 + 1e^-$$

Determine the mass of antimony in a solution which required a steady current of 23.2 milliamperes for 182 s to reach the end point in the above "coulometric" titration.

Ans. 2.66 mg Sb

VOLTAIC (GALVANIC) CELLS AND OXIDATION-REDUCTION

All problems refer to 25°C.

19.44. (*a*) What is the standard potential of a cell made up of ($Cd^{2+}|Cd$) and ($Cu^{2+}|Cu$) couples? (*b*) Which couple is positive?

Ans. (*a*) 0.74 V; (*b*) ($Cu^{2+}|Cu$)

19.45. What is the standard potential of a cell containing the ($Sn^{2+}|Sn$) and ($Br_2|Br^-$) couples?

Ans. 1.20 V

19.46. Why are Co^{3+} salts unstable in water?

Ans. Co^{3+} can oxidize H_2O, the principal products being Co^{2+} and O_2.

19.47. If H_2O_2 is mixed with Fe^{2+}, which reaction is more likely: the oxidation of Fe^{2+} to Fe^{3+} or the reduction of Fe^{2+} to Fe? In answering, write the reaction for each possibility and calculate the standard potential of the equivalent electrochemical cell.

Ans. More likely: $H_2O_2 + 2H^+ + 2Fe^{2+} \rightarrow 2H_2O + 2Fe^{3+}$; $E^o = 0.99$ V

Less likely: $H_2O_2 + Fe^{2+} \rightarrow Fe + O_2 + 2H^+$. The reverse of this reaction occurs with a standard potential of 1.14 V.

19.48. What substance can be used to oxidize fluorides to fluorine?

Ans. Fluorides may be oxidized during electrolysis, but not chemically by any substance listed in Table 19-1.

19.49. Are Fe^{2+} solutions stable in air? Why can such solutions be preserved by the presence of iron nails?

Ans. They are not stable because the O_2 oxidizes Fe^{2+} to Fe^{3+}, but the Fe in the nails reduces Fe^{3+} to Fe^{2+}.

19.50. What is the standard potential of the ($Tl^{3+}|Tl$) electrode?

Ans. 0.72 V

19.51. Which of the following intermediate oxidation states is stable with respect to the possible oxidation reactions of the elements in oxygen-free noncomplexing media: germanium(II), tin(II)?

Ans. tin(II)

19.52. Would H_2O_2 behave as oxidant or reductant with respect to each of the following couples at standard concentrations: (*a*) $(I_2|I^-)$; (*b*) $(S_2O_8^{2-}|SO_4^{2-})$; (*c*) $(Fe^{3+}|Fe^{2+})$?

Ans. (*a*) oxidant; (*b*) reductant; (*c*) both; in fact, very small amounts of iron salts in either +2 or +3 oxidation states catalyze the self-oxidation-reduction of H_2O_2.

19.53. What is the potential of a cell containing two hydrogen electrodes, the negative one in contact with 10^{-8} M H^+ and the positive one in contact with 0.025 M H^+?

Ans. 0.379 V

19.54. The cell in the preceding problem is, in a sense, a pH meter. Suppose one half-cell contained 1.00 M H^+, the standard state. Describe the relationship (at 25°C) between the pH of the other half-cell and the observed voltage (connecting the positive terminal of the meter to the standard half-cell).

Ans. V = 0.0592 pH units

19.55. A voltmeter can replace the traditional indicator in titrations by making the titration vessel a half-cell (with an appropriate electrode) and connecting it to a reference half-cell via a salt bridge. To follow the titration in Problem 18-57, a silver/silver chloride electrode is inserted into the halide solution, and the reference half-cell is a silver/silver chloride electrode immersed in 1.00 M KCl. The reference electrode goes to the positive terminal of the voltmeter. Calculate the voltage reading at each of the five points in the titration specified in Problem 18.56.

Ans. (*a*) 0.179 V; (*b*) −0.101 V; (*c*) −0.195 V; (*d*) −0.288 V; (*e*) −0.399 V

19.56. The burning of methanol could be the basis of a convenient fuel cell. The anode reaction is

$$CH_3OH(l) + 6OH^- \rightarrow CO_2(g) + 5H_2O(l) + 6e^-$$

The cathode reaction is the same as in the successful hydrogen-oxygen fuel cell:

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-$$

Calculate the voltage of this fuel cell (for the standard states). (*Hint*: Use data from Table 16-1.)

Ans. $E^o = 1.213$ V

19.57. (*a*) Calculate the potential of the $(Ag^+|Ag)$ couple with respect to $(Cu^{2+}|Cu)$ if the concentration of Ag^+ and Cu^{2+} are 4.2×10^{-6} and 3.2×10^{-3} M, respectively. (*b*) What is the value of ΔG for the reduction of 1 mol Cu^{2+} by Ag at the indicated ion concentration?

Ans. (*a*) 0.23 V; (*b*) −44 kJ

19.58. Copper can reduce zinc ions if the resultant copper ions can be kept at a sufficiently low concentration by the formation of an insoluble salt. What is the maximum concentration of Cu^{2+} in solution if this reaction is to occur (assume 1 M Zn^{2+})?

Ans. 7×10^{-38} M Cu^{2+}

19.59. Evaluate the equilibrium constant for the following reaction at 298 K:

$$[Fe(CN)_6]^{4-} + [Co(dip)_3]^{3+} \rightleftharpoons [Fe(CN)_6]^{3-} + [Co(dip)_3]^{2+}$$

Ans. 0.5

19.60. When a rod of metallic lead was added to a 0.0100 M solution of $[Co(en)_3]^{3+}$, it was found that 68% of the cobalt complex was reduced to $[Co(en)_3]^{2+}$ by the lead. Find the value of *K* at 298 K for

$$Pb + 2[Co(en)_3]^{3+} \rightleftharpoons Pb^{2+} + 2[Co(en)_3]^{2+}$$

Ans. 0.0154

19.61. A $(Tl^+|Tl)$ couple was prepared by saturating 0.1 M KBr with TlBr and allowing the Tl^+ from the relative insoluble bromide to come to equilibrium. This couple was observed to have a potential of −0.443 V with respect to a $(Pb^{2+}|Pb)$ couple in which the Pb^{2+} was 0.1 molar. What is the solubility product of TlBr?

Ans. 3.7×10^{-6}

19.62. K_d for the complete dissociation of $[Ag(NH_3)_2]^+$ into Ag^+ and NH_3 is 6.0×10^{-8}. Calculate E^o for the following half-reaction (refer to Table 19-1):

$$[Ag(NH_3)_2]^+ + e^- \rightarrow Ag + 2NH_3$$

Ans. 0.372 V

19.63. Calculate K_d for the formation of $[PdI_4]^{2-}$ from Pd^{2+} and I^-.

Ans. 1×10^{25}

19.64. Reference tables give the following entry:

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \qquad E^o = 0.88\,V$$

Combining this information with relevant entries in Table 19-1, find K_1 for the acid dissociation of H_2O_2.

Ans. 1×10^{-12}

CHAPTER 20

Rates of Reactions

Have you noticed that during discussions of chemical equilibria, reaction direction, spontaneity, and other topics there is no mention of how fast a reaction proceeds? Even the chapter on thermodynamics does not investigate the rate of reaction. As a matter of fact, many texts specifically state that *rate* of reaction is not tied to thermodynamic considerations. The branch of chemistry that treats the rates of reactions is *chemical kinetics*. There are two main objectives in this chapter. The first objective is to provide a systematic approach for dealing with data relating to the dependence of the rates of reactions on controllable variables. The second objective is to show the relationship between reaction rate and the reaction's molecular mechanism.

RATE CONSTANTS AND THE ORDER OF REACTIONS

Homogeneous reactions are those reactions that occur within a single phase (physical state), especially a liquid or gaseous phase. *Heterogeneous reactions* are those reactions that take place at least in part at the interface between two phases, such as solid and liquid or liquid and gas, etc. The discussion and problems in this chapter will address homogeneous reactions unless otherwise stated. Please note that *rate* means that there is a time element involved which is usually expressed in seconds (s), minutes (min), or hours (h).

According to the *law of mass action*, the rate of chemical reaction at a constant temperature (amount of reaction per unit of time) depends only on the concentrations of the substances that influence the rate. The substances that influence the rate of reaction are usually one or more of the reactants, but can occasionally be a product. Another influence on the rate of reaction can be a catalyst that does not appear in the balanced overall chemical equation.

The dependence of the rate of reaction on the concentrations can often be expressed as a direct proportionality in which the concentrations may appear to the zero, first, or second power. The power to which the concentration of a substance appears in the rate expression (formula) is the *order of the reaction* with respect to that substance. Table 20-1 provides examples of rate expressions.

The order is not a result of the nature of the chemical equation; it is dependent on data collected from experiments. Those data are then used to determine a mathematical equation that fits, the *rate equation*. The *overall order* of a reaction is the sum of the orders with respect to various substances (the sum of the exponents). Further, the order of a reaction is stated with respect to a named substance in the reaction (see listing above).

The proportionality factor, k, called the *rate constant* or *specific rate*, is constant at a fixed temperature. The rate constant varies with temperature. There are dimensions to k, and the units should be expressed when the k-values are tabulated. The rate itself is defined as the change in concentration of a reactant or product per unit of time. If A is a reactant and C a product, the rate might be expressed as

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} \qquad \text{or as} \qquad \text{Rate} = \frac{\Delta[\text{C}]}{\Delta t}$$

Table 20-1

Example	Rate*	Order Statement	Overall Order
(*1*)	$k_1[\mathrm{A}]$	First-order in A	1
(*2*)	$k_2[\mathrm{A}][\mathrm{B}]$	First-order in A and first-order in B	2
(*3*)	$k_3[\mathrm{A}]^2$	Second-order in A	2
(*4*)	$k_4[\mathrm{A}]^2[\mathrm{B}]$	Second-order in A and first-order in B	3
(*5*)	k_5	Zero-order	0

*As in previous chapters, the square brackets, [X], indicate molarity (mol/L).

where $\Delta[\mathrm{X}]$ is the *change* in concentration (in math, Δ usually means a change) of X and Δt is the time interval over which the change is measured (or the experiment observed). If the rate changes rapidly, Δt will be small. The law of mass action applies only at very small values of Δt, in which case the notation is that of calculus:

$$-\frac{d[\mathrm{A}]}{dt} \quad \text{or} \quad \frac{d[\mathrm{C}]}{dt}$$

This notation, then, would replace the form of ratio expression above. The minus sign is used to express the rate in terms of a reactant concentration (decreases during reaction) and a plus sign for a product concentration (increases during reaction), so that the rate is always a positive quantity.

EXAMPLE 1 For some reactions, there is no doubt in defining the rate, For example, in

$$\mathrm{CH_3OH + HCOOH \rightarrow HCOOCH_3 + H_2O}$$

the rate could be expressed as

$$-\frac{\Delta[\mathrm{CH_3OH}]}{\Delta t} \quad \text{or} \quad -\frac{\Delta[\mathrm{HCOOH}]}{\Delta t} \quad \text{or} \quad \frac{\Delta[\mathrm{HCOOCH_3}]}{\Delta t}$$

since these three ratios are all equal when concentrations are in molarity and there are no competing or side reactions. In the following reaction, however,

$$\mathrm{N_2 + 3H_2 \rightarrow 2NH_3}$$

the coefficients for the different substances are not the same. The concentration of H_2 decreases three times as fast as that of N_2 and NH_3 is formed twice as fast as N_2 is used up. Any one of the three ratios below could be used to specify the rate, but the choice should be specified because the numerical value of k depends on the choice. Note that the order does not depend on the choice, just the size of k.

$$-\frac{\Delta[\mathrm{N_2}]}{\Delta t} \qquad -\frac{\Delta[\mathrm{H_2}]}{\Delta t} \qquad \frac{\Delta[\mathrm{NH_3}]}{\Delta t}$$

First-order reactions

In the particular case of a first-order reaction, where the rate is proportional to the concentration of the reactant [A], as in Table 20-1(*1*), the methods of integral calculus yield

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-kt} \qquad (20\text{-}1)$$

The symbol e refers to the number on which natural logarithms are based, 2.71828. $[\mathrm{A}]_0$ is the concentration of [A] at the beginning of the experiment (initial concentration at $t = 0$). The logarithmic form (base 10) can be derived from the above.

$$2.303 \log \frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -kt \qquad (20\text{-}2)$$

The amount of time, $t_{1/2}$, for the first-order reaction to go 50 percent toward completion is given by (*20-2*) as

$$t_{1/2} = -\frac{2.303 \log \frac{1}{2}}{k} = \frac{0.693}{k} \qquad (20\text{-}3)$$

The *half-life*, $t_{1/2}$, is independent of the initial concentration of A. This independence of $[\mathrm{A}]_0$ is characteristic only of first-order reactions. Also, note that $t_{1/2}$ and k are independent of the units in which A is expressed (although molarity is the most common unit, as indicated by [A]).

Other rate laws

Fractional orders also occur (for example, $\left(\frac{1}{2}\right)$-order and $\left(\frac{2}{3}\right)$-order, in which the rate is proportional to $[\mathrm{A}]^{1/2}$ or $[\mathrm{A}]^{3/2}$, respectively). Some reaction rates cannot be expressed in the proportional form shown in Table 20-1 at all. An example of a complex rate expression is the following:

$$(6) \quad \text{Rate} = \frac{k_1[\mathrm{A}]^2}{1 + k_2[\mathrm{A}]}$$

The rate of a heterogeneous reaction may be proportional to the interfacial area of contact between the phases, as well as to the concentrations of reactants within a particular phase, as in the case of many reactions catalyzed at surfaces.

ENERGY OF ACTIVATION

The temperature dependence of a reaction rate may be represented by the *Arrhenius equation*:

$$k = Ae^{-E_a/RT} \qquad (20\text{-}4)$$

The *pre-exponential factor*, A, is also called the *frequency factor*, and E_a is the *energy of activation*. The units of E_a (and of RT) are J/mol or cal/mol. Both A and E_a may be considered to be constant for at least a narrow temperature range. From (*20-4*), the rate constants at two different temperatures are related by

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (20\text{-}5)$$

MECHANISM OF REACTIONS

It has been said that a chemical equation accurately portrays the nature of the starting and final materials in a chemical reaction, but that the arrow conveniently covers our ignorance of what happens in between. Troubling questions can be raised: How many successive steps are there in the overall process? What are the spatial and energetic requirements for the interactions in each step? What is the rate of each step? A positive point is that rate measurements usually describe the overall reaction, but the measurement of rates under different conditions can often fill in the information needed for the understanding of reaction mechanisms.

Molecularity

The concept of molecularity specifies the number of molecules interacting in an individual reaction step. A *unimolecular* reaction is a step in which a single molecule spontaneously undergoes a reaction. A *bimolecular* reaction refers to the reaction of two molecules. In a *termolecular* reaction, three molecules interact in a single step. There are no known single-step reactions of higher molecularity than termolecular.

A *unimolecular* reaction is first-order in the species that undergoes the spontaneous rearrangement or decomposition. This is true because there is a natural probability that a molecule will undergo the reaction in a specific time interval. Also, the overall rate per unit volume is the product of this probability per unit time and the total number of molecules per unit volume (which in turn is proportional to concentration).

A *bimolecular* reaction rate is proportional to the frequency of collisions between the two molecules of the reacting species. It is known from kinetic theory that the frequency of collisions between two like molecules, A, is proportional to $[A]^2$, and the frequency of collisions between an A and a B molecule is proportional to the product of the concentrations, [A][B]. If the species whose molecules collide are starting materials in limited concentrations, the reaction is second-order. This reaction follows the rate equation of either type (*3*) or (*2*), Table 20-1.

A *termolecular* reaction rate is proportional to the frequency of the collision of three bodies. These reactions are proportional to $[A]^3$, $[A]^2[B]$, or [A][B][C], depending on whether the molecules taking part in the reaction are of one, two, or three species. If these species are the starting materials, the reaction is third-order; however, termolecular reactions are rare because of the low probability that three species will come together.

Although the order of a single step can be predicted from the molecularity, the molecularity of a step, or steps, cannot be predicted from the order of the overall reaction. There are a number of complications which make it impossible to automatically determine the order of the reaction. In other words, stating that a unimolecular reaction is first-order, that a bimolecular reaction is second-order, or a termolecular reaction is third-order *cannot be made with ensured accuracy*. In many cases, the reaction is a sequence of steps, and the overall rate is governed by the slowest step(s). Experimental conditions might interchange the relative speeds of different steps, making the order appear to change. Another complication arises because the slowest (rate-limiting) step may involve the reaction of an unstable intermediate species, and it is necessary to express the concentration of this species in terms of the reactants before the overall order of the reaction can be determined. The solved problems provide examples of some of these complexities.

Energetics

Most molecular collisions do not result in reaction. Even if the appropriate number of molecules came together, only those possessing enough energy can undergo the violent distortions of bond lengths and angles necessary for the rearrangements that lead to chemical reaction. Often times, the amount of energy necessary is a great deal more than the average energy of the molecules. The *energy of activation*, E_a, is a measure of the energy necessary to get the molecules to react. The exponential term in the Arrhenius equation, (*20-4*), is of the order of magnitude of the fraction of molecules possessing the necessary amount of energy beyond the average.

The *activated state* has been defined as that distorted combination of reacting molecules having the minimum amount of excess energy (beyond the average energy of the molecules) so that the combination, or *complex*, could as easily rearrange to form the products as revert to the reactants. The energy of the activated state may be thought of as the potential energy of a mountain pass which a climber must cross in order to go from one side of the mountain to the other. For a set of reversible reactions, the same activation energy must be crossed for the reactions in the two directions. Then, for reactions carried out at constant pressure:

$$\Delta H = (1\ \text{mol})[E_a(\text{forward}) - E_a(\text{reverse})] \qquad (20\text{-}6)$$

The factor, (1 mol), has been inserted in (*20-6*) so that the enthalpy change (ΔH) will, as usual, have the units of energy. The relationship between the energy of the reactants, the energy of activation required, and the energy of the products is graphically presented in Fig. 20-1. When two or more fast-moving molecules collide, their kinetic energy is converted into the high energy of the complex. When the complex breaks up, the fragments (products

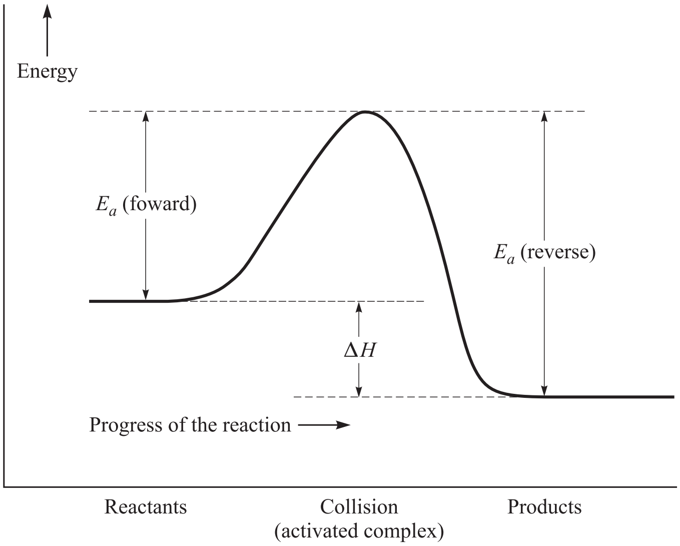


Fig. 20-1 Energy relationships in a reaction (forward reaction is exothermic)

or reactants, depending on the direction of the reaction) fly apart, their kinetic energy coming from that energy stored in the complex.

Solved Problems

RATE CONSTANTS AND ORDER OF REACTION

20.1. In a catalytic experiment involving the Haber process, $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of reaction was measured as

$$\frac{\Delta[NH_3]}{\Delta t} = 2.0 \times 10^{-4}\,\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$$

If there were no side reaction, what was the rate of reaction expressed in terms of (*a*) N_2, (*b*) H_2?

(*a*) From the coefficients in the balanced equation, $\Delta n(N_2) = -\frac{1}{2}\Delta n(NH_3)$. Therefore

$$-\frac{\Delta[N_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = 1.0 \times 10^{-4}\,\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$$

(*b*) Similarly,

$$-\frac{\Delta[H_2]}{\Delta t} = \frac{3}{2}\frac{\Delta[NH_3]}{\Delta t} = 3.0 \times 10^{-4}\,\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$$

20.2. Using concentrations expressed in molarity and time in seconds, what are the units of the rate constant, k, for (*a*) a zero-order reaction; (*b*) a first-order reaction; (*c*) a second-order reaction; (*d*) a third-order reaction; (*e*) a half-order reaction?

In each case, we write out the full equation and find the units of k that will satisfy the equation.

(*a*) $$-\frac{\Delta[A]}{\Delta t} = k \qquad \text{Units of } k = \text{units of } \frac{[A]}{t} = \frac{\text{mol/L}}{\text{s}} = \text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$$

Note that the units of $\Delta[A]$, the change in concentration, are the same as the units of [A] itself; similarly for Δt.

(*b*)

$$-\frac{\Delta[\mathrm{A}]}{\Delta t} = k[\mathrm{A}] \qquad \text{or} \qquad k = -\frac{1}{[\mathrm{A}]}\frac{\Delta[\mathrm{A}]}{\Delta t}$$

$$\text{Units of } k = \frac{1}{\text{mol/L}} \times \frac{\text{mol/L}}{\text{s}} = \text{s}^{-1}$$

First-order reactions are the only reactions for which k has the same numerical value, regardless of the units used for expressing the concentrations of reactants or products.

(*c*)

$$-\frac{\Delta[\mathrm{A}]}{\Delta t} = k[\mathrm{A}]^2 \qquad \text{or} \qquad k = -\frac{1}{[\mathrm{A}]^2}\frac{\Delta[\mathrm{A}]}{\Delta t}$$

and

$$-\frac{\Delta[\mathrm{A}]}{\Delta t} = k[\mathrm{A}][\mathrm{B}] \qquad \text{or} \qquad k = -\frac{1}{[\mathrm{A}][\mathrm{B}]}\frac{\Delta[\mathrm{A}]}{\Delta t}$$

then,

$$\text{Units of } k = \frac{1}{(\text{mol/L})^2} \times \frac{\text{mol/L}}{\text{s}} = \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

Note that the units of k depend on the *total* order of the reaction, not the way the total order is composed of the orders with respect to different reactants.

(*d*)

$$-\frac{\Delta[\mathrm{A}]}{\Delta t} = k[\mathrm{A}]^3 \qquad \text{or} \qquad k = -\frac{1}{[\mathrm{A}]^3}\frac{\Delta[\mathrm{A}]}{\Delta t}$$

$$\text{Units of } k = \frac{1}{(\text{mol/L})^3} \times \frac{\text{mol/L}}{\text{s}} = \text{L}^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-1}$$

(*e*)

$$-\frac{\Delta[\mathrm{A}]}{\Delta t} = k[\mathrm{A}]^{1/2} \qquad \text{or} \qquad k = -\frac{1}{[\mathrm{A}]^{1/2}}\frac{\Delta[\mathrm{A}]}{\Delta t}$$

$$\text{Units of } k = \frac{1}{(\text{mol/L})^{1/2}} \times \frac{\text{mol/L}}{\text{s}} = \text{mol}^{1/2} \cdot \text{L}^{-1/2} \cdot \text{s}^{-1}$$

20.3. Ozone is one of the indicators of polluted air. Suppose the steady-state ozone concentration is 2.0×10^{-8} mol/L, and the hourly production of O_3 by all sources is estimated to be 7.2×10^{-13} mol/L. Assume the only mechanism for the destruction of O_3 is the second-order reaction $2O_3 \rightarrow 3O_2$. Calculate the rate constant for the destruction reaction defined by the rate law for $-\Delta[O_3]/\Delta t$ to maintain the steady-state concentration.

At the steady state, the rate of destruction of O_3 must equal the rate of its generation, which is 7.2×10^{-13} $\text{mol} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$. From the second-order rate law,

$$-\frac{\Delta[\mathrm{O_3}]}{\Delta t} = k[\mathrm{O_3}]^2$$

$$k = -\frac{1}{[\mathrm{O_3}]^2}\frac{\Delta[\mathrm{O_3}]}{\Delta t} = \frac{1}{(2.0 \times 10^{-8}\ \text{mol/L})^2}\,\frac{7.2 \times 10^{-13}\ \text{mol} \cdot \text{L}^{-1} \cdot \text{h}^{-1}}{3.6 \times 10^3\ \text{s} \cdot \text{h}^{-1}} = 0.5\ \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

20.4. A viral preparation was inactivated in a chemical bath. The inactivation process was found to be first-order in virus concentration, and at the beginning of the experiment 2.0% of the virus was found to be inactivated per minute. Evaluate k for the inactivation process in units (1/s).

From the first-order law,

$$-\frac{\Delta[\mathrm{A}]}{\Delta t} = k[\mathrm{A}] \qquad \text{or} \qquad k = -\frac{\Delta[\mathrm{A}]}{[\mathrm{A}]}\frac{1}{\Delta t}$$

It is seen that only the *fractional* change in concentration, $-[\mathrm{A}]/[\mathrm{A}]$, is needed; namely, 0.020 when $\Delta t = 1$ min $= 60$ s. This form of the equation may be used for the *initial* rate when the value of [A] is not changing appreciably. This condition is met when only 2% is inactivated in the first minute.

$$k = \frac{0.020}{60\ \text{s}} = 3.3 \times 10^{-4}\ \text{s}^{-1}$$

20.5. For the process described in Problem 20.4, how much time would be required for the virus to become (*a*) 50% inactivated, (*b*) 75% inactivated?

The method used in Problem 20.4 cannot be used here because [A] changes appreciably over the course of the reaction. Equation (*20-1*), (*20-2*), or (*20-3*) is appropriate here.

(*a*) The time for 50% reaction is the half-life, and (*20-3*) gives

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3.3 \times 10^{-4}\,\mathrm{s}^{-1}} = 2.1 \times 10^3\,\mathrm{s} \qquad \text{or} \qquad 35\,\mathrm{min}$$

(*b*) Equation (*20-2*) may be used. If 75% of the virus is inactivated, the fraction remaining, $[\mathrm{A}]/[\mathrm{A}]_0$, is 0.25.

$$t = -\frac{2.303 \log \dfrac{[\mathrm{A}]}{[\mathrm{A}]_0}}{k} = -\frac{2.303 \log 0.25}{3.3 \times 10^{-4}\,\mathrm{s}^{-1}} = 4.2 \times 10^3\,\mathrm{s} \qquad \text{or} \qquad 70\,\mathrm{min}$$

An alternate solution is to apply the half-life concept twice. Since it takes 35 min for half of the virus to become inactivated, regardless of the initial concentration, the time for the virus to be reduced from 50% to 25% full strength will be another half-life. The total time for reduction to $\left(\frac{1}{4}\right)$ strength is two half-lives (70 minutes).

Similarly, the total time required to reduce the initial activity to $\left(\frac{1}{8}\right)$ is three half-lives; to $\left(\frac{1}{16}\right)$, four half-lives; and so on. This method can be used *only* for first-order reactions.

20.6. The fermentation of sugar in an enzymatic solution is under investigation. The beginning concentration is 0.12 M. The concentration of the sugar is reduced to 0.06 M in 10 hours and 0.03 M in 20 hours. What is the order of the reaction and what is the rate constant in 1/h and 1/s?

This problem is similar to Problem 20.5. Since doubling the time reduces the amount of sugar by half, it must be a first-order reaction. Alternatively, the reduction of the sugar concentration from 0.06 M to 0.03 M may be thought of as a new experiment with an initial concentration of 0.06 M. Since the same half-life (10 hours) was observed in both experiments, the reaction must be first-order because only in a first-order reaction is the half-life independent of the initial concentration. The rate constant may be evaluated from the half-life using equation (*20-3*).

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10\,\mathrm{h}} = 6.9 \times 10^{-2}\,\mathrm{h}^{-1}$$

$$k = \frac{6.9 \times 10^{-2}\,\mathrm{h}^{-1}}{3.6 \times 10^3\,\mathrm{s \cdot h}^{-1}} = 1.9 \times 10^{-5}\,\mathrm{s}^{-1}$$

20.7. A reaction between substances A and B is by the reaction, A + B → C. Observations on the rate of this reaction are obtained in three separate experiments as follows:

Exp.	Initial Conc. $[\mathrm{A}]_0$/M	Initial Conc. $[\mathrm{B}]_0$/M	Duration of Experiment Δt/h	Final Conc. $[\mathrm{A}]_f$/M
(*1*)	0.1000	1.0	0.50	0.0975
(*2*)	0.1000	2.0	0.50	0.0900
(*3*)	0.0500	1.0	2.00	0.0450

What is the order with respect to each reactant, and what is the value of the rate constant?

Let us set up the information for the initial rate of the reaction for each experiment, noting that $\Delta[\mathrm{A}] = [\mathrm{A}]_f - [\mathrm{A}]_0$ in each case is small enough in size to allow the rate to be expressed in terms of changes over the entire time of the experiment.

In comparing experiments (*1*) and (*2*), we notice that [A] is the same in both, but [B] is twice as great in (*2*). Since the rate in (*2*) is 4 times that in (*1*), the reaction must be second-order in B.

Exp.	Initial Conc. $[A]_0$/M	Initial Conc. $[B]_0$/M	$\Delta[A]$/M	Δt/h	Initial Rates $-\dfrac{\Delta[A]}{\Delta t}$/M·h^{-1}
(*1*)	0.1000	1.0	−0.0025	0.50	0.0050
(*2*)	0.1000	2.0	−0.0100	0.50	0.0200
(*3*)	0.0500	1.0	−0.0050	2.00	0.0025

When comparing experiments (*1*) and (*3*), we see that [B] is the same in both, but [A] is twice as great in (*1*). Since the rate in (*1*) is twice that in (*3*), the reaction must be first-order in A.

The rate equation may be written accordingly as

$$-\frac{\Delta[A]}{\Delta t} = k[A][B]^2$$

and k may be evaluated from any of the experiments. We take (*1*) as an example, using average values of [A] and [B]. ([B] does not change appreciably during the experiment since it is in such large excess.)

$$k = \frac{-\dfrac{\Delta[A]}{\Delta t}}{[A][B]^2} = \frac{0.0050\,\text{M}\cdot\text{h}^{-1}}{(0.099\,\text{M})(1.0\,\text{M})^2} = 0.051\,\text{L}^2\cdot\text{mol}^{-2}\cdot\text{s}^{-1}$$

or $5.1 \times 10^{-2}\,\text{L}^2\cdot\text{mol}^{-2}\cdot\text{s}^{-1}$. We suggest that you confirm that the same result will be obtained by using data from either of the other two experiments.

20.8. Acetic anhydride and ethyl alcohol react to form an ester (an organic salt) by the following:

$$\underset{\text{A}}{(CH_3CO)_2O} + \underset{\text{B}}{C_2H_5OH} \rightarrow CH_3COOC_2H_5 + CH_3COOH$$

When the reaction is carried out in dilute hexane solution, the rate may be represented by k[A][B]. When ethyl alcohol (B) is the solvent, the rate may be represented by k[A]. (The values of k are not the same in the two cases.) Explain the difference in the apparent order of the reaction.

When a solvent is also a reactant, its concentration is so large compared with the extent of reaction that it does not change. Since this is the case, the dependence of the rate on the concentration of ethyl alcohol cannot be determined unless ethyl alcohol becomes a solute in some other solvent. If another substance is the solvent, then the concentration of the alcohol can be varied, allowing the calculation. For the reaction in ethyl alcohol (ethanol), $k_{\text{exp}} = k[B]$ with [B] essentially constant. Such reactions are called *pseudo-first-order reactions*.

20.9. At elevated temperatures, gaseous chloroethane decomposes into ethene and HCl according to

$$CH_3CH_2Cl \rightarrow CH_2CH_2 + HCl$$

A constant-volume, constant-temperature experiment was run and the following data were collected:

Time	0	1	3	5	10	20	30	50	>100
[Ethene]/ (mol/L)	0	8.3×10^{-4}	2.3×10^{-3}	3.6×10^{-3}	6.1×10^{-3}	9.0×10^{-3}	1.05×10^{-2}	1.16×10^{-2}	1.19×10^{-2}

Test the data to determine whether or not the reaction is first-order. If the reaction is first-order, determine the rate constant.

Since the reaction is essentially complete after 100 hours, the initial concentration of chloroethane, $[A]_0$, was 1.19×10^{-2} M and subsequent concentrations, [A], can be obtained by subtracting the ethane concentrations from this. Then, we substitute into the ratio, $[A]/[A]_0$, and take the log. These steps are provided in the table below. (The 50-hour point, which corresponds to the least accurate value of the ratio, is omitted.)

A graph of $\log([A]/[A]_0)$ vs. t is shown in Fig. 20-2. Since the points fall in nearly a straight line, the reaction is first-order. The slope of the graph, calculated on the figure, is $-0.0321\ \text{h}^{-1}$, which, according to equation (*20-2*), is equal to $-k/2.303$. This gives us $k = 7.2 \times 10^{-2}\,\text{h}\,(2.0 \times 10^{-5}\ \text{s}^{-1})$. Our numerical work can be roughly checked by inspecting $t_{1/2} = 0.693/k = 9.6\,\text{h}$, and in the original table of data, in 10 h the reaction is slightly more than half completed.

Time, t	0	1	3	5	10	20	30
$[A] \times 10^2$	1.19	1.11	0.96	0.83	0.58	0.29	0.14
$[A]/[A]_0$	1.00	0.933	0.807	0.0697	0.487	0.244	0.118
$\log([A]/[A]_0)$	0	−0.030	−0.093	−0.156	−0.312	−0.613	−0.929

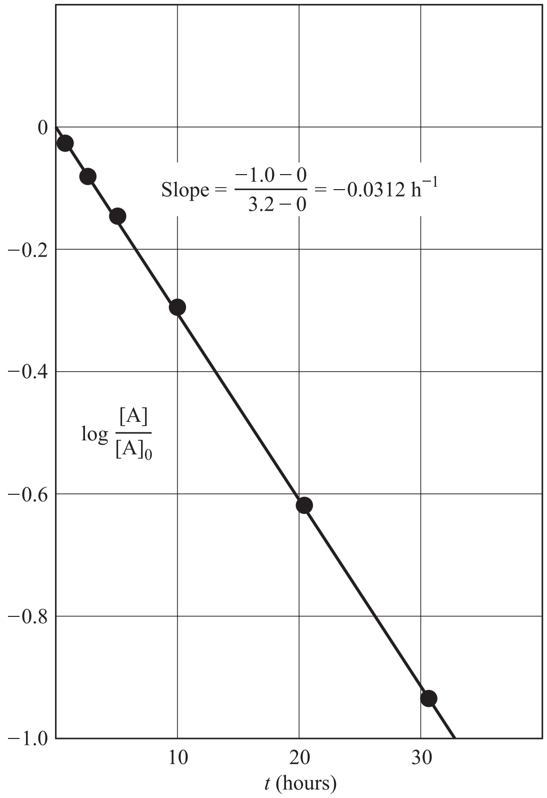


Fig. 20-2 First-order test for data of Problem 20-9

20.10. The complexation of Fe^{2+} with the chelating agent dipyridyl (abbreviated *dip*) has been studied kinetically in both the forward and the reverse directions. For the complexation reaction

$$Fe^{2+} + 3\ \text{dip} \rightarrow [Fe(\text{dip})_3]^{2+}$$

the rate of formation of the complex at 25°C is given by

$$\text{Rate} = (1.45 \times 10^{13}\ \text{L}^3 \cdot \text{mol}^{-3} \cdot \text{s}^{-1})[Fe^{2+}][\text{dip}]^3$$

and, for the reverse of the above reaction, the rate of disappearance of the complex is

$$(1.22 \times 10^{-4}\,\text{s}^{-1})\{[\text{Fe(dip)}_3]^{2+}\}$$

What is K_s, the stability constant, for the complex?

Not all reactions can be studied conveniently in both directions. When it is possible, we know that the rate of formation of the complex must equal the rate of decomposition at equilibrium. This is particularly true since the concentrations of the various species stay constant (do not change).

$$\text{Rate of the forward reaction} = \text{rate of the reverse reaction}$$

$$(1.45 \times 10^{13}\,\text{L}^3 \cdot \text{mol}^{-3} \cdot \text{s}^{-1})[\text{Fe}^{2+}][\text{dip}]^3 = (1.22 \times 10^{-4}\,\text{s}^{-1})\{[\text{Fe(dip)}_3]^{2+}\}$$

Solving,
$$K_s = \frac{\{[\text{Fe(dip)}_3]^{2+}\}}{[\text{Fe}^{2+}][\text{dip}]^3} = \frac{1.45 \times 10^{13}}{1.22 \times 10^{-4}} = 1.19 \times 10^{17}$$

(In the equilibrium constant equation, as opposed to rate equations, K does not have dimensions, being the concentration relative to the standard state of 1 M.)

ENERGY OF ACTIVATION AND MECHANISM OF REACTIONS

20.11. The decomposition of N_2O into N_2 and O in the presence of gaseous argon follows second-order kinetics as indicated below. What is the energy of activation of this reaction?

$$k = (5.0 \times 10^{11}\,\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})e^{-29{,}000\,K/T}$$

Comparing the equation for k in this case with (*20.4*), we note that the exponent of e is $-E_a/RT$.

$$\frac{E_a}{RT} = \frac{29{,}000\,\text{K}}{T}$$
$$E_a = (29{,}000\ \text{K})R = (29{,}000\,\text{K})(8.3145\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 241\,\text{kJ} \cdot \text{mol}^{-1}$$

20.12. The first-order rate constant for the hydrolysis of CH_3Cl (methyl chloride) in H_2O has a value of $3.32 \times 10^{-10}\,\text{s}^{-1}$ at 25°C and $3.13 \times 10^{-9}\,\text{s}^{-1}$ at 40°C. What is the value of the energy of activation?

Solve equation (*20-5*) for E_a.

$$E_a = 2.303R\left(\frac{T_1T_2}{T_2 - T_1}\right)\left(\log\frac{k_2}{k_1}\right)$$

$$E_a = (2.303)(8.3145\,\text{J} \cdot \text{mol}^{-1})\left(\frac{298 \times 313}{313 - 298}\,\text{K}\right)\left(\log\frac{3.13 \times 10^{-9}}{3.32 \times 10^{-10}}\right)$$

$$E_a = (119\,\text{kJ} \cdot \text{mol}^{-1})(\log 9.4) = 116\,\text{kJ} \cdot \text{mol}^{-1}$$

20.13. A second-order reduction whose rate constant at 800°C was found to be $5.0 \times 10^{-3}\,\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ has an activation energy of $45\,\text{kJ} \cdot \text{mol}^{-1}$. What is the value of the rate constant at 875°C?

Equation (*20-5*) is solved for k_2, the rate constant at the higher temperature.

$$\log\frac{k_2}{k_1} = \frac{E_a(T_2 - T_1)}{2.303RT_1T_2}$$

$$\log\frac{k_2}{k_1} = \frac{(4.5 \times 10^4\,\text{J} \cdot \text{mol}^{-1})[(1148 - 1073)\,\text{K}]}{(2.303)(8.3145\,\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(1073\,\text{K})(1148\,\text{K})} = 0.143 \qquad \text{then,} \qquad \frac{k_2}{k_1} = 1.39$$

$$k_2 = (1.39)(5.0 \times 10^{-3}\,\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}) = 7.0 \times 10^{-3}\,\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

20.14. The *trans* → *cis* isomerization of 1,2-dichloroethylene proceeds if supplied with the energy of activation of $55.3\,\text{kcal}\cdot\text{mol}^{-1}$. ΔH associated with the reaction is 1.0 kcal. What do you predict is the value of E_a for the reverse isomerization, *cis* → *trans*?

From equation (*20-6*),

$$E_a(\text{reverse}) = E_a(\text{forward}) - \frac{\Delta H}{1\ \text{mol}} = 55.3 - 1.0 = 54.3\,\text{kcal}\cdot\text{mol}^{-1}$$

20.15. A gaseous molecule, A, can undergo a unimolecular decomposition into C, if it is supplied with a critical amount of energy. An energized molecule of A, designated as A*, can be formed by a collision between two ordinary A molecules. Competing with the unimolecular decomposition of A* into C is the bimolecular deactivation of A*by collision with an ordinary A molecule.

(*a*) Write a balanced equation and the rate law for each of the above steps.

(*b*) Making the assumptions that A* disappears by all processes at the same rate at which it is formed, and that [A*] is much less than [A], what would be the rate law for the formation of C in terms of [A] and constants of individual steps only?

(*c*) What limiting order in A would the formation of C show at low pressures of A, and what limiting order at high pressures?

(*a*)

$$\begin{array}{lll} (1)\ \text{Activation:} & \text{A} + \text{A} \rightarrow \text{A}^* + \text{A} & \dfrac{\Delta[A^*]}{\Delta t} = k_1[\text{A}]^2 \\ (2)\ \text{Deactivation:} & \text{A}^* + \text{A} \rightarrow \text{A} + \text{A} & -\dfrac{\Delta[\text{A}^*]}{\Delta t} = k_2[\text{A}^*][\text{A}] \\ (3)\ \text{Reaction:} & \text{A}^* \rightarrow \text{C} & -\dfrac{\Delta[\text{A}^*]}{\Delta t} = k_3[\text{A}^*] \end{array}$$

(*b*) Notice that A* appears in each of the three separate steps. The net change in [A*] can be evaluated by taking the summation of the three steps.

$$\left(\frac{\Delta[\text{A}^*]}{\Delta t}\right)_{\text{net}} = k_1[\text{A}]^2 - k_2[\text{A}^*][\text{A}] - k_3[\text{A}^*]$$

We can make a *steady-state assumption* by assuming that the net rate of change of [A*] is zero. Then, the right side of the equation has the value of zero.

$$k_1[\text{A}]^2 - k_2[\text{A}^*][\text{A}] - k_3[\text{A}^*] = 0 \qquad \text{or} \qquad [\text{A}^*] = \frac{k_1[\text{A}]^2}{k_3 + k_2[\text{A}]}$$

Inserting this value into the rate law for step (*3*), and recognizing that $-\Delta[\text{A}^*] = \Delta[\text{C}]$ for this step,

$$(4) \quad \frac{\Delta[\text{C}]}{\Delta t} = \frac{k_3 k_1[\text{A}]^2}{k_3 + k_2[\text{A}]}$$

Then, the formation of C follows a complex kinetic formulation and is definitely not represented by a simple order.

(*c*) At very low pressure (meaning small [A]), the second term in the denominator on the right side of (*4*) becomes insignificant when compared with the first term. After making the deletion of the term,

$$\text{Low-pressure limit:} \frac{\Delta[\text{C}]}{\Delta t} = \frac{k_3 k_1[\text{A}]^2}{k_3} = k_1[\text{A}]^2$$

At very high pressures, the first term of the denominator becomes negligible in comparison with the second term. After making the deletion of the term,

$$\text{High-pressure limit:}\frac{\Delta[\mathrm{C}]}{\Delta t}=\frac{k_3k_1[\mathrm{A}]^2}{k_2[\mathrm{A}]}=\frac{k_3k_1}{k_2}[\mathrm{A}]$$

Now, it appears as though the reaction is first-order with k_3k_1/k_2 as the apparent rate constant.

This problem illustrates the concept of the rate-limiting step. The example commonly used to teach the concept is that of getting water from a source to a fire. A bucket brigade is formed for passing water from one person to the next, and so on, until it finally reaches the fire. The overall rate of transfer of water cannot be greater than the rate of the slowest person in the brigade. In the above reactions, the activation step (*1*) becomes the slowest step when [A] is low and the reaction step (*3*) becomes the slowest step when [A] is high. Step (*1*), depending on the square of [A], is more sensitive to pressure than step (*3*).

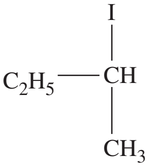
20.16. For the hydrolysis of methyl formate, $HCOOCH_3$, in acid solutions, the reaction and rate are

$$\mathrm{HCOOCH_3 + H_2O \rightarrow HCOOH + CH_3OH} \qquad \mathrm{Rate} = k[\mathrm{HCOOCH_3}][\mathrm{H^+}]$$

$[H^+]$ is not in the equation for the reaction; propose an explanation of why $[H^+]$ appears in the rate law?

$[H^+]$ is a catalyst for the reaction. It is actually a reactant in an early intermediate stage of the reaction and is then released back into the solution at a later stage.

20.17. The conversion of the D-optical isomer of gaseous



$$\mathrm{C_2H_5{-}CH(I)(CH_3)}$$

into the L-isomer in the presence of iodine vapor follows the law rate $= kP(\mathrm{A})P(\mathrm{I_2})^{1/2}$, where A represents the D-isomer. (Partial pressures are a reasonable form of expression of concentrations of gases in rate laws.) Suggest a mechanism that could account for the fractional order.

I_2 can undergo a slight dissociation into I atoms in a quickly established equilibrium.

$$\mathrm{I_2 \rightleftharpoons 2I} \qquad K_P=\frac{P(\mathrm{I})^2}{P(\mathrm{I_2})}$$

The partial pressure of iodine atoms can be evaluated in terms of this equilibrium as

$$P(\mathrm{I})=K_P^{1/2}\times P(\mathrm{I_2})^{1/2}$$

If an intermediate stage of the reaction involves the addition of an iodine atom to A followed by a loss of the iodine atom that was initially a part of the A molecule, and if the addition of I to A is bimolecular (rate constant k_2) and the step is slow, it determines the overall rate.

$$\text{Observed rate} = \text{rate of I addition}$$

$$\text{Observed rate} = k_2P(\mathrm{A})P(\mathrm{I}) = k_2P(\mathrm{A})\times K_P^{1/2}\times P(\mathrm{I_2})^{1/2}=(k_2K_P^{1/2})P(\mathrm{A})P(\mathrm{I_2})^{1/2}$$

The numerical value of the term in parentheses, $(k_2K_P^{1/2})$, is the numerical value of the apparent rate constant (experimental) for the overall $\left(\frac{3}{2}\right)$-order reaction.

The above mechanism is plausible and is consistent with the observations. We cannot be sure from the kinetic data alone that there is not some other mechanism which is also consistent with the observations. Other types of experimentation are needed to confirm a mechanism based on rate data. However, a proposed mechanism that yields a rate law other than the observed rate law can definitely be eliminated from consideration.

Supplementary Problems

RATE CONSTANTS AND THE ORDER OF REACTION

20.18. For the reaction

$$3BrO^- \rightarrow BrO_3^- + 2Br^-$$

in alkaline aqueous solution, the value of the second-order (in BrO^-) rate constant at 80°C in the rate law for $-\Delta[BrO^-]/\Delta t$ was found to be $0.056\,L \cdot mol^{-1} \cdot s^{-1}$. What is the rate constant when the rate law is written for (*a*) $\Delta[BrO_3^-]/\Delta t$, and for (*b*) $\Delta[Br^-]/\Delta t$?

Ans. (*a*) $0.0187\,L \cdot mol^{-1} \cdot s^{-1}$; (*b*) $0.037\,L \cdot mol^{-1} \cdot s^{-1}$

20.19. The hydrolysis of methyl acetate in alkaline solution is

$$CH_3COOCH_3 + OH^- \rightarrow CH_3COO^- + CH_3OH$$

The reaction followed the rate $= k[CH_3COOCH_3][OH^-]$, with $k = 0.137\,L \cdot mol^{-1} \cdot s^{-1}$ at 25°C. A reaction mixture was prepared to have initial concentrations of methyl acetate and hydroxide ion of 0.050 M each. How long would it take for 5.0% of the methyl acetate to be hydrolyzed at 25°C?

Ans. 7.7 s

20.20. A first-order reaction in aqueous solution was too fast to be detected by a procedure that could have followed a reaction having a half-life of at least 2.0 ns. What is the minimum value of k for this reaction?

Ans. $3.5 \times 10^8\,s^{-1}$

20.21. Gaseous cyclobutene isomerizes to butadiene in a first-order process which has a k-value at 153°C of $3.3 \times 10^{-4}\,s^{-1}$. How many minutes would it take for the isomerization to proceed 40% to completion at this temperature?

Ans. 26 min

20.22. The approach to the following equilibrium was observed kinetically from both directions:

$$[PtCl_4]^{2-} + H_2O \rightleftharpoons [Pt(H_2O)Cl_3]^- + Cl^-$$

At 25°C, it was found that at 0.3 ionic strength:

$$-\frac{\Delta\{[PtCl_4]^{2-}\}}{\Delta t} = (3.9 \times 10^{-5}\,s^{-1})\{[PtCl_4]^{2-}\} - (2.1 \times 10^{-3}\,L \cdot mol^{-1} \cdot s^{-1})\{[Pt(HO_2)Cl_3]^-\}[Cl^-]$$

What is the value of K_4' for the complexation of the fourth Cl^- by Pt(II) (the apparent equilibrium constant for the reverse of the reaction as written above) at 0.3 ionic strength?

Ans. 54

20.23. The following reaction was studied at 25°C in benzene solution containing 0.1 M pyridine:

$$\underset{A}{CH_3OH} + \underset{B}{(C_6H_5)_3CCl} \rightarrow \underset{C}{(C_6H_5)_3COCH_3} + HCl$$

The following sets of data were obtained in three separate experiments:

Exp.	Initial Conc. $[A]_0/M$	Initial Conc. $[B]_0/M$	Initial Conc. $[C]_0/M$	Δt/min	Final Conc. $[C]_f/M$
(*1*)	0.1000	0.0500	0.0000	2.5	0.0033
(*2*)	0.1000	0.1000	0.0000	15.0	0.0390
(*3*)	0.2000	0.1000	0.0000	7.5	0.0792

What rate law is consistent with the above data and what is the best average value for the rate constant expressed in seconds and molar concentration units?

Ans. Rate $= k[\mathrm{A}]^2[\mathrm{B}]$, $k = 4.6 \times 10^{-3}\ \mathrm{L^2 \cdot mol^{-2} \cdot s^{-1}}$

20.24. The decomposition of substance A at a steady temperature was followed closely, and the data were recorded below. Is the reaction first-order or second-order in A? Suggestions: First plot $\log([\mathrm{A}]/[\mathrm{A}]_0)$ against t for several points. Then calculate the ratio of $(\Delta[\mathrm{A}]/\Delta t)/[\mathrm{A}]^2$ and compare the results over several short intervals.

t/min	0	20	40	60	80	100	120	140	160	180	200	220	240
[A]/(mol/L)	0.462	0.449	0.437	0.426	0.416	0.406	0.396	0.387	0.378	0.370	0.362	0.354	0.347

Ans. Second-order reaction

ENERGY OF ACTIVATION AND MECHANISM OF REACTIONS

20.25. The rate constant for the first-order decomposition of ethylene oxide into CH_4 and CO may be described by the equation

$$\log k(\text{in s}^{-1}) = 14.34 - \frac{1.25 \times 10^4\ \mathrm{K}}{T}$$

(*a*) What is the energy of activation for this reaction? (*b*) What is the value of k at 670 K?

Ans. (*a*) $239\ \mathrm{kJ \times mol^{-1}}$; (*b*) $5 \times 10^{-5}\ \mathrm{s^{-1}}$

20.26. The first-order gaseous decomposition of N_2O_4 into NO_2 has a k-value of $4.5 \times 10^3\ \mathrm{s^{-1}}$ at 1°C and an energy of activation of $58\ \mathrm{kJ \times mol^{-1}}$. At what temperature would k be $1.00 \times 10^4\ \mathrm{s^{-}}$?

Ans. 10°C

20.27. Biochemists often define Q_{10} for a reaction as the ratio of the rate constant at 37°C to the rate constant at 27°C. What must be the energy of activation for a reaction that has a Q_{10} of 2.5?

Ans. $71\ \mathrm{kJ \cdot mol^{-1}}$

20.28. In gaseous reactions important for the understanding of the upper atmosphere, H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and E_a is $77\ \mathrm{kJ \cdot mol^{-1}}$. Estimate E_a for the bimolecular recombination of two OH radicals to form H_2O and O.

Ans. $5\ \mathrm{kJ \cdot mol^{-1}}$

20.29. H_2 and I_2 react bimolecularly in the gas phase to form HI. HI then decomposes bimolecularly into H_2 and I_2. The energies of activation for these two reactions were observed to be $163\ \mathrm{kJ \cdot mol^{-1}}$ and $184\ \mathrm{kJ \cdot mol^{-1}}$, respectively, at the same temperature of 100°C. What do you predict from these data for ΔH of the gaseous reaction $H_2 + I_2 \rightleftharpoons 2HI$ at 100°C?

Ans. -21 kJ

20.30. Predict the form of the rate law for the reaction $2A + B \rightarrow$ products, if the first step is the reversible dimerization of A ($2A \rightleftharpoons A_2$), followed by reaction of A_2 with B in a bimolecular step. Assume that the equilibrium concentration of A_2 is very small compared with [A].

Ans. Rate $= k[\mathrm{A}]^2[\mathrm{B}]$

20.31. The following reaction was observed in aqueous solution:

$$2\mathrm{Cu}^{2+} + 6\mathrm{CN}^- \rightarrow 2[\mathrm{Cu(CN)_2}]^- + (\mathrm{CN})_2$$

and the rate was found to be of the form $k[\mathrm{Cu}^{2+}]^2[\mathrm{CN}^-]^6$. If the first step is the rapid development of the complexation equilibrium to form the relatively unstable $[\mathrm{Cu(CN)_3}]^-$, what rate-limiting step could account for the observed kinetic data? (The ion, $[\mathrm{Cu(CN)_3}]^-$, is unstable with respect to reversal of the complexation step.)

Ans. Bimolecular decomposition: $2[\mathrm{Cu(CN)_3}]^- \rightarrow 2[\mathrm{Cu(CN)_2}]^- + (\mathrm{CN})_2$

20.32. The hydrolysis of $(i\text{-}C_3H_7O)_2POF$ was studied at different acidities. The apparent first-order rate constant, k, at a particular temperature was found to depend on pH but not on the nature or concentration of the buffer used to regulate the pH. The value of k was fairly constant from pH 4 to pH 7, but rose from this constant value with decreasing pH below 4 or with increasing pH above 7. What is the nature of the cause of this behavior?

Ans. The reaction is catalyzed by either H^+ or OH^-.

20.33. It has been found that the rates of reaction of a ketone in mildly basic solution are identical for the following three reactions: (*a*) reaction with Br_2 leading to the substitution of an H on the ketone by a Br; (*b*) conversion of the D-isomer of the ketone into a mixture of D- and L-isomers of equal concentration; and (*c*) isotopic exchange of a hydrogen atom on the carbon next to the C=O group of the ketone by a deuterium atom in the solvent. The rate of each of these reactions is equal to $k[\text{ketone}][OH^-]$ and is independent of $[Br_2]$. What can be concluded about the mechanism from these observations?

Ans. The rate-determining step for all three reactions must be the preliminary reaction of the ketone with OH^-, probably leading to the conjugate base of the ketone. The conjugate base subsequently reacts very rapidly with (*a*) Br_2; (*b*) some acid in the medium; or (*c*) the solvent with deuterium.

20.34. Many free radical reactions (polymerization and others) can be initiated by a light-sensitive substance, P. The molecules of P dissociate into two free radicals on the absorption of a photon. The following reactions are either *propagation*, in which one radical, R•, is produced for each radical consumed, or *termination*, in which two radicals combine to form products that are not radicals. The bulk of the chemical change is due to the propagation step. A small steady-state concentration of free radicals prevails throughout. Explain how such a mechanism accounts for the dependence of the rate on the square root of the light intensity, I.

Ans. Since propagation does not change the free radical concentration, the rate of initiation must equal the rate of termination. If the rate of initiation is first-order in P and proportional to the light intensity, $k_i[P]I$, and the rate of termination is a bimolecular reaction with a rate, $k_t[R\bullet]^{1/2}$, then at the steady state,

$$[R\bullet] = [(k_i/k_t)[P]I]^{1/2}$$

If the propagation step is first-order in [R•], i.e., proportional to [R•], then the observed rate is as shown above, proportional to $I^{1/2}$.

20.35. The addition of a catalyst to a certain reaction provides an alternative pathway in which the energy of activation is less than that of the uncatalyzed reaction by 14.7 kJ/mol. By what factor is the rate constant increased by the catalyst at a temperature of 420 K? By what factor is the rate constant of the reverse reaction increased? (Assume that the frequency factor is not affected by the catalyst.)

Ans. 67, the same as for the reverse reaction

CHAPTER 21

Nuclear Processes

In the chemistry that we have worked with so far, the atoms of reactants rearrange to form product molecules different from those reactants. In such reactions, the outer electrons of the atoms may be transferred completely or in part from one atom to another. The nuclei of the atoms are unchanged.

There are other reactions in which the nuclei themselves are broken down and the products do not contain the same elements as the reactants. The chemistry of such nuclear reactions is called *nuclear chemistry*. Spontaneous disintegration of individual nuclei is usually accompanied by high-energy emissions and/or high-speed particles. These products and, sometimes, the reactions that produce them are referred to as *radioactivity*. Additionally, there are other nuclear changes resulting from the interactions of a neutron or high-energy photon with a nucleus, or from the impact of a high-velocity particle. The results of such nuclear bombardment are highly dependent on the energy involved.

FUNDAMENTAL PARTICLES

Although there are particles not used here, the basic particles listed in Table 21-1 can be used to define and illustrate the concepts presented. Note that the proton and neutron are referred to as *nucleons*. The masses in Table 21-1 are presented in atomic mass units (u, Chapter 2) and their charges are expressed in multiples of the elementary charge (1.6022×10^{-19} C, Chapter 19). Note that the neutron has slightly more mass than the proton. Also, the mass of the electron is considered to be 1/1836 that of a proton or, if you prefer, the mass of 1 proton is 1836 times that of an electron.

BINDING ENERGIES

The mass of an atom is generally not equal to the sum of the masses of its component protons, neutrons, and electrons. If we could imagine a reaction in which free protons, neutrons, and electrons combine to form an atom, we would find that the mass of the atom is slightly less than the total mass of the component particles (an exception is ^{1}H as there is only 1 nuclear part, the proton). Further, a tremendous amount of energy is released during the reaction which produces the atom. The loss in mass is exactly equivalent to the released energy, according to Einstein's famous equation,

$$E = mc^2 \qquad \text{Energy} = (\text{change in mass}) \times (\text{velocity of light})^2$$

The calculated gain of energy equivalent to the loss of mass is called the *binding energy* of the atom (or nucleus, if it is being considered independently of the electrons in the shells). When the binding energy calculations are

Table 21-1

Particle	Symbol	Mass	Charge
Proton (a *nucleon*)	p, p^+	1.0072765 u $(1.673 \times 10^{-24}$ g)	+1
Neutron (a *nucleon*)	n, n^0	1.0086649 u $(1.675 \times 10^{-24}$ g)	0
Electron	e^-, β^-	0.0005486 u $(9.109 \times 10^{-28}$ g)	−1
Positron	e^+, β^+	0.0005486 u $(9.109 \times 10^{-28}$ g)	+1

done with m in kilograms and c in meters per second, the value of E is in joules. A more convenient unit of energy for nuclear reactions is the MeV (Chapter 8). By the Einstein equation,

$$\text{Energy} = \frac{(\text{change in mass in u})(1.6605 \times 10^{-27}\ \text{kg/u})(2.998 \times 10^{8}\ \text{m/s})^2}{1.6022 \times 10^{-13}\ \text{J/MeV}}$$

$$\text{Energy} = (931.5\ \text{MeV}) \times (\text{change in mass in u})$$

NUCLEAR EQUATIONS

Nuclear equations, like chemical equations, are a method of keeping track of the involved particles and energy. The rules for balancing nuclear equations are different from those we have been using for balancing ordinary chemical equations. They are as follows:

1. Each particle is assigned a superscript equal to its mass number (number of nucleons), A, and a subscript equal to its atomic number or nuclear charge, Z.
2. A free proton is the nucleus of the hydrogen atoms, and is assigned the notation ${}^1_1\text{H}$.
3. A free neutron is assigned zero atomic number because it has no charge. The mass number of a neutron is 1. The full notation for a neutron is ${}^1_0n$.
4. An electron (e^- or β^-) is assigned the mass number zero and the atomic number −1. We will use ${}^{\ 0}_{-1}e$ for the full notation, if the electron is part of an atom. We will use ${}^{\ 0}_{-1}\beta$ or β^- if the electron is emitted (a beta particle).
5. A positron (e^+ or β^+) is assigned the mass number zero and the atomic number +1. The full notation for a positron we will be using is ${}^{\ 0}_{+1}\beta$ or β^+, since the positron is only to be covered as an emitted particle in this chapter (conforming to 4 above).
6. An *alpha particle* (α-particle) is a helium nucleus. The full notation for an α-particle is ${}^4_2\text{He}$ (or ${}^4_2\alpha$).
7. A *gamma ray* (γ) is a very high-energy photon (Chapter 8). It has zero as the mass number and zero charge. The full notation for a gamma ray is ${}^0_0\gamma$.
8. In a balanced equation, the sum of the subscripts (atomic numbers), written or implied, must be the same on the two sides of the equation. The sum of the superscripts (mass numbers), written or implied, must also be the same on the two sides of the equation. For example, the equation for the first step in the radioactive decay of ${}^{226}\text{Ra}$ is:

$${}^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^4_2\text{He}$$

Notice that the charge associated with the helium nucleus without electrons (+2) can be ignored because electrons are eventually picked up from the environment to complete the atom.

Many nuclear processes may be indicated by a shorthand notation in which a light bombarding particle and a light product particle are represented by symbols in parentheses. These are located between the initial target nucleus and the final product nucleus. The symbols used are n, p, d, α, β^+, β^-, and γ, representing the neutron, proton, deuteron (${}^2_1\text{H}$), alpha, electron, positron, and gamma rays, respectively. The atomic numbers are commonly left out in this notation because the symbol for any element implies its atomic number. Examples of the longhand and shorthand notations are as follows:

$${}^{14}_{7}\text{N} + {}^{1}_{1}\text{H} \rightarrow {}^{11}_{6}\text{C} + {}^{4}_{2}\text{He} \qquad {}^{14}\text{N}(p, \alpha){}^{11}\text{C}$$

$${}^{27}_{13}\text{Al} + {}^{1}_{0}n \rightarrow {}^{27}_{12}\text{Mg} + {}^{1}_{1}\text{H} \qquad {}^{27}\text{Al}(n, p){}^{27}\text{Mg}$$

$${}^{55}_{25}\text{Mn} + {}^{2}_{1}\text{H} \rightarrow {}^{55}_{26}\text{Fe} + 2{}^{1}_{0}n \qquad {}^{55}\text{Mn}(d, 2n){}^{55}\text{Fe}$$

Just as an ordinary chemical equation is a shortened version of the complete thermochemical equation which expresses both energy and mass balance, each nuclear equation has a term (written or implied) expressing energy balance. The symbol Q is usually used to designate the net energy released when all reactant and product particles of matter are at zero velocity. Q is the energy equivalent of the mass decrease (discussed above) accompanying the reaction. Q is usually expressed in MeV.

RADIOCHEMISTRY

Special properties of radioactive *nuclides* (isotopes of an element, Chapter 2) make them useful tracers for following complex processes. *Radiochemistry* is the branch of chemistry which involves the applications of radioactivity to chemical problems, as well as the chemical processing of radioactive substances.

A radioactive nuclide (*radioisotope*) is spontaneously converted to another nuclide by one of the processes below; each definition is followed by an example. As discussed above, all are accompanied with a loss of mass and a release of energy.

1. *Alpha decay*: An α-particle (${}^4_2\alpha$ or ${}^4_2\text{He}$) is emitted and the daughter nucleus has an atomic number, Z, two units less. The mass number, A, is four units less than the parent nucleus.

$${}^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\alpha$$

2. *Beta decay*: A beta particle (${}^{0}_{-1}\beta$), an electron, is emitted and the daughter has a Z-value one unit greater than the parent's with no change in A.

$${}^{31}_{14}\text{Si} \rightarrow {}^{31}_{15}\text{P} + {}^{0}_{-1}\beta$$

3. *Positron emission*: A positron (${}^{0}_{+1}\beta$) is emitted and the daughter has a Z-value one unit less than the parent's with no change in A.

$${}^{40}_{21}\text{Sc} \rightarrow {}^{40}_{20}\text{Ca} + {}^{0}_{+1}\beta$$

4. *Electron capture*: A proton captures an electron (beta particle). The result is a change into a neutron. The capture is in the first shell of the proton, the K orbit, and may be called *K-electron capture*. (*Note:* This is essentially the reverse of beta decay.)

$${}^{7}_{4}\text{Be} + {}^{0}_{-1}\beta \rightarrow {}^{7}_{3}\text{Li}$$

A radioactive nucleus decays by a first-order process, so that (*20-1*), (*20-2*), and (*20-3*) apply. The stability of the nucleus with respect to spontaneous decay may be indicated by its first-order rate constant, k, or by the half-life, $t_{1/2}$.

Radioactivity is measured by observing the high-energy particles produced directly or indirectly as a result of the disintegration process. A convenient unit of radioactivity is the *curie*, Ci, defined by

$$1\text{Ci} = 3.700 \times 10^{10} \text{ disintegrations per second}$$

The activity of a sample, expressed in curies, depends both on the number of atoms of the radioisotope (determined from the mass of the sample) and on the half-life (disintegration rate constant). See Problem 21.14. The subunits are *millicurie* (mCi), *microcurie* (μCi), and others.

Solved Problems

21.1. Provide the number of protons, neutrons, and electrons in each of the following atoms: (*a*) ^{3}He; (*b*) ^{12}C; (*c*) ^{206}Pb.

(*a*) From the periodic table (chart), we see that the atomic number of helium is 2; there must be 2 protons. The mass number is 3, according to the question; there must be 1 neutron. The number of electrons is the same as protons in an atom, which is 2. ($2p$, $1n$, and $2e^-$)

(*b*) Carbon's atomic number is 6 and that is the number of protons. The mass number of 12 and the atomic number of 6 give us the number of neutrons, $12 - 6 = 6$ neutrons. The number of electrons equals the number of protons. ($6p$, $6n$, and $6e^-$)

(*c*) Lead has the atomic number 82, meaning there are 82 protons and 82 electrons in the atom. The mass number is 206, which tells us there are 124 neutrons. ($82p$, $124n$, and $82e^-$)

21.2. Complete the following nuclear equations:

$$(a)\ {}^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \rightarrow {}^{17}_{8}\text{O} + ? \qquad (b)\ {}^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \rightarrow {}^{12}_{6}\text{C} + ?$$

$$(c)\ {}^{9}_{4}\text{Be}\,(p, \alpha)? \qquad (d)\ {}^{30}_{15}\text{P} \rightarrow {}^{30}_{14}\text{S} + ?$$

$$(e)\ {}^{3}_{1}\text{H} \rightarrow {}^{3}_{2}\text{He} + ? \qquad (f)\ {}^{43}_{20}\text{Ca}(\alpha, ?)\,{}^{46}_{21}\text{Sc}$$

(*a*) The sum of the subscripts on the left is $7 + 2 = 9$. The subscript of the first product on the right is 8. Then the second product on the right must have a subscript of 1 to achieve a balance.

The sum of the superscripts on the left is $14 + 4 = 18$. The superscript of the first product on the right is 17. The second product must have a superscript of 1.

The particle missing on the right has nuclear charge of 1 and a mass number of 1. The particle must be ${}^{1}_{1}$H.

(*b*) The nuclear charge of the second product particle is $(4 + 2) - 6 = 0$. The mass number of the particle is $(9+4) - 12 = 1$. The notation for the particle, which must be a neutron, is ${}^{0}_{1}n$.

(*c*) The reactants have a combined nuclear charge of 5 and mass number of 10. In addition to the α-particle, a product will be formed with the charge of $5 - 2 = 3$, and mass number $10 - 4 = 6$. This is lithium, the element with atomic number 3. The notation is ${}^{6}_{3}$Li.

(*d*) The nuclear charge of the second particle is $15 - 14 = 1$. The mass number is $30 - 30 = 0$. The particle must be a positron, ${}^{\ 0}_{+1}\beta$.

(*e*) The nuclear charge of the second particle is $1 - 2 = -1$, while the mass number is $3 - 3 = 0$. The electron, ${}^{\ 0}_{-1}\beta$, is the particle in question.

(*f*) The reactants ${}^{43}_{20}$Ca and ${}^{4}_{2}$He have a combined nuclear charge of 22 and a mass number of 47. The ejected product will have a charge of $22 - 21 = 1$, and a mass number of $47 - 46 = 1$. This is a proton and should be represented within the parentheses by p.

21.3. What is the total binding energy of ^{12}C, and what is the average binding energy per nucleon?

Although “binding energy” is a term referring to the nucleus, it is more convenient to use the mass of the whole atom (nuclide) in calculations, since these are the masses that are given in tables. If $M(X)$ is the atomic mass of nuclide X,

$$M(\text{nucleus}) = M(X) - ZM(e^-) \tag{1}$$

The nucleus of X consists of Z protons and $A - Z$ neutrons. Then its binding energy, BE, is given by

$$\text{BE} = \{ZM(p) + (A - Z)M(n)\} - M(\text{nucleus}) \tag{2}$$

Applying (1) both to the nucleus of X and to the proton, which is a $^1_1$H nucleus, and substituting in (2),

$$\begin{aligned}\text{BE} &= \{Z[M(^1_1\text{H}) - M(e^-)] + (A - Z)M(n)\} - [M(X) - ZM(e^-)]\\ \text{BE} &= \{ZM(^1_1\text{H}\,) + (A - Z)M(n)\} - M(X)\end{aligned}$$

Then, nuclear masses can be replaced by atomic (nuclidic) masses when calculating the binding energy. Whole atom masses can, in fact, be used for mass-difference calculations in all nuclear reaction types discussed in this chapter, except for β^+ processes where there is a resulting annihilation of two electron masses (one β^+ and one β^-).

The data needed for ^{12}C are found in Tables 2-1 and 21-1. We cannot use *average* atomic masses from the periodic table for these calculations because our calculations call for the masses of single isotopes (^{1}H, ^{12}C, etc.).

$$\begin{aligned}&\text{Mass of } 6\,^1\text{H atoms} = 6 \times 1.00783 && = 6.04698\\ &\text{Mass of 6 neutrons} = 6 \times 10.00866 && = \underline{6.05196}\\ &\text{Total mass of component particles} && = 12.09894\,\text{u}\\ &\text{Mass of } ^{12}\text{C} && = \underline{12.00000}\\ &\text{Lost mass on formation of } ^{12}\text{C} && = 0.09894\,\text{u}\\ &\text{Binding energy} = \left(\frac{931.5\,\text{MeV}}{\text{u}}\right) 0.09894)\text{u} = 92.1\,\text{MeV}\end{aligned}$$

Since there are 12 nucleons (6 protons and 6 neutrons), the average binding energy per nucleon is

$$\frac{92.1\,\text{MeV}}{12} = 7.68\,\text{MeV}$$

21.4. Evaluate Q for the reaction ^{7}Li(p, n)^{7}Be.

The change in mass (u) for the reaction is calculated as follows:

Reactants		Products	
$^7_3$Li	7.01600	^1_0n	1.00866
$^1_1$H	$\underline{1.00783}$	$^7_4$Be	$\underline{7.01693}$
	8.02383 u		8.02559 u

$$\text{Increase in mass} = 8.02559 - 8.02383 = 0.00176\,\text{u}$$

A corresponding net amount of energy must be consumed. That energy is equal to

$$(931.5)(0.00176)\,\text{MeV} = 1.64\,\text{MeV} \qquad \text{or} \qquad Q = -1.64\,\text{MeV}$$

Note: The energy is supplied as kinetic energy from the bombarding proton and is *part* of the acceleration requirement for the proton supplied by the particle accelerator.

21.5. The Q-value for the $^{3}\text{He}(n, p)$ reaction is 0.76 MeV. What is the nuclidic mass of ^{3}He?

The reaction is ${}^{3}_{2}\text{He} + {}^{0}_{1}n \rightarrow {}^{1}_{1}\text{H} + {}^{3}_{1}\text{H}$. The mass loss must be 0.76/931.5 = 0.00082 u. And the mass balance can be calculated on the basis of whole atoms and the particles involved.

Reactants		Products	
${}^{3}_{2}\text{He}$	x	${}^{1}_{1}\text{H}$	1.00783
n	$\underline{1.00866}$	${}^{3}_{1}\text{H}$	$\underline{3.01605}$
	$(x + 1.00866)$u		4.02388 u

The calculation now becomes: $(x + 1.00866) - 4.02388 = 0.00082$. Solving: $x = 3.01604$ u.

21.6. Calculate the maximum kinetic energy of the beta particle emitted in the radioactive decay of ^{6}He. Assume that the beta particle has maximum energy when no other emission is involved.

The process referred to is ${}^{6}_{2}\text{He} \rightarrow {}^{6}_{3}\text{Li} + {}^{0}_{-1}\beta$. The calculation of the mass change only requires the whole number atomic masses of the elements since, if we add two electrons to each side, we would have enough for a whole helium atom on the left and a whole lithium atom on the right.

$$\begin{aligned} \text{Mass of } {}^{6}\text{He} &= 6.01889 \\ \text{Mass of } {}^{6}\text{LI} &= \underline{6.01512} \\ \text{Loss of mass} &= 0.00377\text{ u} \end{aligned}$$

$$\text{Energy equivalent} = (9.31.5)(0.00377) = 3.51\text{ MeV}$$

The maximum kinetic energy of the β^{-} is 3.51 MeV.

21.7. ^{13}N decays by positron emission. The maximum kinetic energy of β^{+} is 1.20 MeV. What is the nuclidic mass of ^{13}N?

The reaction is ${}^{13}_{7}\text{N} \rightarrow {}^{13}_{6}\text{C} + {}^{0}_{+1}\beta$. This is a process, mentioned in Problem 21.3, in which a simple difference of whole atom masses is *not* the desired quantity because we are not adding the same particle to both sides and cannot do so. The calculation for the mass difference is

$$\begin{aligned} \text{Mass difference} &= [M(\text{nucleus) for } {}^{13}\text{N}] - [M(\text{nucleus) for } {}^{13}\text{C}] - M(e^{-}) \\ &= [M({}^{13}\text{N}) - 7M(e^{-})] - [M({}^{13}\text{C}) - 6M(e^{-})] - M(e^{-}) \\ &= M({}^{13}\text{N}) - M({}^{13}\text{C}) - 2M(e^{-}) = M({}^{13}\text{N}) - 13.00335 - 2(0.00055) \\ &= M({}^{13}\text{N}) - 13.00445 \end{aligned}$$

This expression must equal the mass equivalent of the maximum kinetic energy of the β^{+}.

$$\frac{1.20\text{ MeV}}{931.5\text{ MeV/u}} = 0.00129\text{ u}$$

Then,

$$0.00129 = M({}^{13}\text{N}) - 13.00445 \qquad \text{or} \qquad M({}^{13}\text{N}) = 13.00574\text{ u}$$

21.8. Consider the two nuclides of mass number 7, ^{7}Li and ^{7}Be. Which of the two is the more stable? How does the unstable nuclide decay into the more stable one?

Table 2-1 shows that ^{7}Be has a larger mass than does ^{7}Li. This tells us that ${}^{7}_{4}\text{Be}$ can decay spontaneously into ${}^{7}_{3}\text{Li}$, but the reaction does not go the other way. There are two types of decay processes in which Z is decreased by one unit without a change in the mass number, A: β^{-} emission and electron capture. These two processes have different mass balance requirements.

Assume that the process is beta emission.

$$^{7}_{4}\text{Be} \rightarrow \,^{0}_{+1}\beta + \,^{7}_{3}\text{Li}$$

It was shown in Problem 21.7 (third line of mass difference equation) that a positron emission can occur (Q is + and the reaction is spontaneous) only if the *nuclidic* mass of the parent species exceeds the *nuclidic* mass of the daughter by at least twice the rest mass of the electron, $2(0.00055) = 0.00110$ u. In the present case, the actual mass difference between parent and daughter nuclides is $7.01693 - 7.01600 = 0.00093$ u. We can see that positron emission in this case is not possible. This means that ^{7}Be must undergo electron capture.

Note that we have predicted only that ^{7}Be *should* decay by electron capture into ^{7}Li. We have said nothing about the rate of the process. *Measurements* show the half-life to be 53 days.

21.9. Lithium hydride, LiH, composed of two isotopes, ^{6}Li and ^{2}H, is proposed as a potential nuclear fuel. The reaction involved is

$$^{6}_{3}\text{Li} + \,^{2}_{1}\text{H} \rightarrow 2\,^{4}_{2}\text{He}$$

Calculate the expected power production, in megawatts, associated with the consumption of 1.00 g of $^{6}\text{Li}^{2}\text{H}$ per day assuming 100% efficiency.

The change in mass for the reaction is first calculated.

$$\begin{array}{lll} \text{Mass of } ^{6}_{3}\text{Li} & = 6.01512 & \\ \text{Mass of } ^{2}_{1}\text{H} & = \underline{2.01410} & \\ \text{Total mass of reactants} & = 8.02922 & \\ \text{Mass of products} & = \underline{8.00520} & [2(4.00260)] \\ \text{Loss in mass} & = 0.02402\,\text{u} & [8.02922 - 8.00520] \end{array}$$

$$\text{Energy per atomic event} = (0.02402\,\text{u})(931.5 \times 10^{6}\,\text{eV/u})(1.6022 \times 10^{-12}\,\text{J/eV})$$

$$= 3.584 \times 10^{-12}\,\text{J}$$

$$\text{Energy per mol LiH} = (3.584 \times 10^{-12}\,\text{J})(6.02 \times 10^{23}\,\text{mol}^{-1}) = 2.16 \times 10^{12}\,\text{J/mol}$$

$$\text{Power production} = \frac{[(2.16 \times 10^{12}\,\text{J/mol})/(8.03\,\text{g/mol})](1.00\,\text{g/d})}{(24\text{h/d})(3.6 \times 10^{3}\,\text{s/h})} = 3.11 \times 10^{6}\,\text{W}$$

$$= 3.11\,\text{MW}$$

21.10. ^{18}F is found to undergo 90% radioactive decay in 366 min. What is its calculated half-life?

The rate constant for the decay can be found from (*20-2*). Ninety percent decay corresponds to 10% or 0.10, survival. In dealing with radioactive decay, the total population of radioactive element is used in place of its concentration. (Remember that in first-order reactions, the rate constant and the half-life, as well, are independent of the concentration units.) So, in place of the concentration ratio $[A]/[A]_0$, put the ratio of the numbers of atoms N/N_0, or moles, or masses, of radioactive element. The mass of radioactive element encountered in the laboratory is exceedingly small; a typical sample can be measured only by its activity. Since its activity is proportional to its population, the observed ratio of activities, A/A_0, can be used in place of the number ratio, N/N_0.

$$k = -\frac{2.303 \log \frac{N}{N_0}}{t} = -\frac{2.303 \log 0.10}{366\,\text{min}} = 6.29 \times 10^{-3}\,\text{min}^{-1}$$

Then, the half-life can be calculated from (*20-3*):

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.29 \times 10^{-3}\,\text{min}^{-1}} = 110\,\text{min}$$

21.11. A piece of the linen wrapping an Egyptian mummy was analyzed and found to have a ^{14}C activity of 8.1 counts (disintegrations) per minute for each gram of carbon. Estimate the age of the mummy.

The half-life of ^{14}C is 5730 years. It is generally assumed that over at least the past 30,000 years the ^{14}C content of the atmospheric carbon (as CO_2) has been roughly constant. Living plants, which obtained their carbon from the air by photosynthesis, have had over this period a constant activity whose value has been found to be 15.3 counts per minute, per gram of carbon.

After the flax was harvested and made into linen, there was no longer any absorption of ^{14}C from the atmosphere. From that point in time, the radioactivity dropped off at an assumed constant rate. Use (*20-3*) to find *k*, then (*20-2*) to find the time, *t*, for the activity to decay to its present level.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730\ \text{y}} = 1.209 \times 10^{-4}\ \text{y}^{-1}$$

$$t = \frac{-2.303}{k}\log\left(\frac{\text{A}}{\text{A}_0}\right) = \frac{-2.303}{1.209 \times 10^{-4}\ \text{y}^{-1}}\log\left(\frac{8.1}{15.3}\right) = \frac{(-2.303)(-0.276)}{1.209 \times 10^{-4}\ \text{y}^{-1}} = 5260\ \text{y}$$

21.12. A sample of uraninite, a uranium-containing mineral, was found on analysis to contain 0.214 g of lead for every gram of uranium. Assume that the lead all resulted from the radioactive disintegration of the uranium since the geological formation of the uraninite. Also, assume that all isotopes of uranium other than ^{238}U can be neglected. Estimate the date when the mineral was formed in the earth's crust. The half-life of ^{238}U is 4.5×10^9 years.

The radioactive decay of ^{238}U leads, after 14 steps, to the stable lead isotope, ^{206}Pb. The first of these steps is the α-decay of ^{238}U (4.5×10^9 years half-life), which is more than 10^4 times as slow (in terms of half-life) as any of the subsequent steps. As a result, the time required for the first step accounts for essentially all the time required for the entire 10-step process.

In a sample containing 1 g U, there is

$$\frac{0.214\ \text{g Pb}}{206\ \text{g/mol}} = 1.04 \times 10^{-3}\ \text{mol Pb} \qquad \text{and} \qquad \frac{1.000\ \text{g U}}{238\ \text{g/mol}} = 4.20 \times 10^{-3}\ \text{mol U}$$

If each atom of lead in the mineral today is the daughter of a uranium atom that existed at the time of the formation of the mineral, then the original number of moles of uranium in the sample would have been

$$(1.04 + 4.20) \times 10^{-3} = 5.24 \times 10^{-3}$$

Then the remaining fraction is

$$\frac{N}{N_0} = \frac{4.20 \times 10^{-3}}{5.24 \times 10^{-3}} = 0.802$$

Letting *t* be the elapsed time from the formation of the mineral to the present time, we have

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9\ \text{y}} = 1.54 \times 10^{-10}\ \text{y}$$

$$t = -\frac{2.303\log\left(\frac{N}{N_0}\right)}{k} = \frac{-2.303\log(0.802)}{1.54 \times 10^{-10}\ \text{y}^{-1}} = 1.4 \times 10^9\ \text{y}$$

21.13. A sample of $^{14}CO_2$ was to be mixed with ordinary CO_2 (containing ^{12}C) for a biological tracer experiment. In order that $10\ \text{cm}^3$ (S.T.P.) of the diluted gas should have 10^4 disintegrations per minute, how may microcuries of radioactive carbon are needed to prepare 60 L of the diluted gas?

$$\text{Total activity} = \frac{10^4\ \text{dis/min}}{10\ \text{cm}^3} \times \frac{(60\ \text{L})(10^3\ \text{cm}^3/\text{L})}{60\ \text{s/min}}$$

$$\text{Total activity} = (10^6\ \text{dis/s})\left(\frac{1\ \text{Ci}}{3.7 \times 10^{10}\ \text{dis/s}}\right)\left(\frac{10^6\ \mu\text{Ci}}{1\ \text{Ci}}\right) = 27\ \mu\text{Ci}$$

21.14. The half-life of ^{40}K is 1.25×10^9 years. What mass of this nuclide has an activity of 1 μCi?

Let us first calculate the rate constant and express it in s^{-1}.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{(1.25 \times 10^9\ \text{y})(365\ \text{d/y})(24\ \text{h/d})(3.6 \times 10^3\ \text{s/h})} = 1.76 \times 10^{-17}\ \text{s}^{-1}$$

The disintegration rate is an instantaneous rate measured under conditions of essential constancy of the concentration (i.e., the population) of ^{40}K atoms. The form of the rate equation is that used in Chapter 20, with the numerical value of the rate taken from the definition of the curie.

$$\begin{aligned}\text{Rate} &= -\frac{\Delta N}{\Delta t} = kN = (3.70 \times 10^{10}\ \text{dis} \cdot \text{s}^{-1} \cdot \text{Ci}^{-1})(10^{-6}\ \text{Ci} \cdot \mu\text{Ci}^{-1}) \\ &= 3.70 \times 10^4\ \text{dis} \cdot \text{s}^{-1} \cdot \mu\text{Ci}^{-1}\end{aligned}$$

Dividing the desired rate by the rate constant provides us with the total number of atoms needed to produce the desired rate.

$$N = \frac{\text{rate}}{k} = \frac{3.70 \times 10^4\ \text{atoms} \cdot \text{s}^{-1} \cdot \mu\text{Ci}^{-1}}{1.76 \times 10^{-17}\ \text{s}^{-1}} = 2.10 \times 10^{21}\ \text{atoms} \cdot \mu\text{Ci}^{-1}$$

and the corresponding mass is

$$\frac{(2.10 \times 10^{21}\ \text{atoms} \cdot \mu\text{Ci}^{-1})(40\ \text{g}\ ^{40}\text{K/mol})}{6.02 \times 10^{23}\ \text{atoms/mol}} = 0.140\ \text{g}\ ^{40}\text{K}/\mu\text{Ci}$$

21.15. The radioisotope ^{237}Ac has a half-life of 21.8 years. The decay follows two parallel paths: one leading to ^{227}Th, and one leading to ^{223}Fr. The percentage yields of these two daughter nuclides are 1.4% and 98.6%, respectively. What is the rate constant, in y^{-1}, for each of the separate paths?

The rate constant for the decay of Ac, k_{Ac}, can be calculated from the half-life.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{21.8\ \text{y}} = 3.18 \times 10^{-2}\ \text{y}^{-1}$$

The overall rate constant for a set of parallel first-order reactions must be equal to the sum of the separate rate constants.

$$k_{\text{Ac}} = k_{\text{Ac(Th)}} + k_{\text{Ac(Fr)}}$$

The fractional yield of either process is equal to the ratio of the rate constant for that process to the overall rate constant.

$$k_{\text{Ac(Th)}} = (\text{fractional yield of Th}) \times k_{\text{Ac}} = (0.014)(3.18 \times 10^{-2}\ \text{y}^{-1}) = 4.5 \times 10^{-4}\ \text{y}^{-1}$$

$$k_{\text{Ac(Fr)}} = (\text{fractional yield of Fr}) \times k_{\text{Ac}} = (0.986)(3.18 \times 10^{-2}\ \text{y}^{-1}) = 3.14 \times 10^{-2}\ \text{y}^{-1}$$

Supplementary Problems

21.16. Determine the number of protons, neutrons, and electrons in each of the following atoms: (*a*) ^{70}Ge; (*b*) ^{72}Ge; (*c*) ^{9}Be; (*d*) ^{235}U.

Ans. (*a*) 32 *p*, 38 *n*, 32 e^-; (*b*) 32 *p*, 40 *n*, 32 e^-;
(*c*) 4 *p*, 5 *n*, 4 e^-; (*d*) 92 *p*, 143 *n*, 92 e^-

21.17. Write the complete nuclear symbols for the most common isotope (by the mass number) of sodium, of phosphorus, and of iodine.

Ans. $^{23}_{11}\text{Na}$; $^{31}_{15}\text{P}$; $^{127}_{53}\text{I}$

21.18. An alpha particle is emitted from ^{238}U and the heavy residual nucleus is referred to as UX$_1$. UX$_1$ is also radioactive and emits a beta particle and its residual nucleus is referred to as UX$_2$. Determine the atomic numbers and mass numbers of (*a*) UX$_1$ and (*b*) UX$_2$.

Ans. (*a*) 90, 234; (*b*) 91, 234

21.19. $^{239}_{93}$Np emits one β^- and the residual heavy nucleus, also radioactive, gives rise to ^{235}U by its radioactive process. What small particle is emitted simultaneously with the formation of ^{235}U?

Ans. α-particle

21.20. Complete the following equations:

$$(a)\ {}^{23}_{11}\text{Na} + {}^{4}_{2}\text{He} \to {}^{26}_{12}\text{Mg} + ? \qquad (b)\ {}^{64}_{29}\text{Cu} \to {}^{0}_{+1}\beta + ?$$
$$(c)\ {}^{106}\text{Ag} \to {}^{106}\,\text{Cd} + ? \qquad (d)\ {}^{10}_{5}\text{B} + {}^{4}_{2}\text{He} \to {}^{13}_{7}\text{N} + ?$$

Ans. (*a*) $^{1}_{1}$H; (*b*) $^{64}_{28}$Ni; (*c*) $_{-1}^{\ 0}\beta$; (*d*) $^{0}_{1}n$

21.21. Complete the following equations:
(*a*) ^{24}Mg(d, α)? (*b*) ^{26}Mg(d, p)? (*c*) ^{40}Ar(α, p)? (*d*) ^{12}C(d, n)?
(*e*) ^{130}Te$(d, 2n)$? (*f*) ^{55}Mn(n, γ)? (*g*) ^{59}Co(n, α)?

Ans. (*a*) ^{22}Na; (*b*) ^{27}Mg; (*c*) ^{43}K; (*d*) ^{13}N; (*e*) ^{130}I; (*f*) ^{56}Mn; (*g*) ^{56}Mn

21.22. If a nuclide of an element in Group IA (alkali metals) of the periodic table undergoes radioactive decay by emitting positrons, what is the chemical nature of the resulting element?

Ans. Group VIIIA element (also referred to as an inert gas or noble gas)

21.23. An alkaline earth element is radioactive. It and its daughter elements decay by emitting 3 alpha particles in succession. In what group should the resulting element be found?

Ans. Group IVA

21.24. A nuclear power reactor gets its energy from neutron-induced fission (atom split when hit by a neutron), usually ^{235}U. The splitting is not symmetrical and different pairs of products result. Determine the missing fission product for the two examples given below.

(*a*) $n + {}^{235}\text{U} \to 4n + {}^{139}\text{Cs} + ?$ (*b*) $n + {}^{235}\text{U} \to 5n + {}^{135}\text{I} + ?$

Ans. (*a*) ^{93}Rb; (*b*) ^{96}Y

21.25. In the previous problem, notice how much higher the fission product's mass number, *A*, is when compared to the stable element's average atomic mass. All will decay by beta (e^-) emission to achieve a more normal *A* to *Z* ratio. Write the decay reactions for the four fission products above.

Ans. $^{139}\text{Cs} \to \beta^- + {}^{139}\text{Ba}$ $^{93}\text{Rb} \to \beta^- + {}^{93}\text{Sr}$ $^{135}\text{I} \to \beta^- + {}^{135}\text{Xe}$ $^{96}\text{Y} \to \beta^- + {}^{96}\text{Zr}$

21.26. Suppose an atom of ^{235}U, after absorption of a slow neutron, undergoes fission to form an atom of ^{139}Xe and an atom of ^{94}Sr. What other particles are produced? How many of the particles are produced?

Ans. 2 neutrons

21.27. Which is the more unstable of each of the following pairs: (*a*) ^{16}C or ^{16}N, (*b*) ^{18}F or ^{18}Ne? Also, indicate what type of process the unstable nucleus most likely undergoes to convert to the other nuclei?

Ans. (*a*) ^{16}C, β^--decay; (*b*) ^{18}Ne, both β^+-decay and electron capture are possibilities on the basis of the given data.

21.28. One of the most stable nuclei is ^{55}Mn. Its nuclidic mass is 54.938 u. Determine its total binding energy and average binding energy per nucleon.

Ans. 483 MeV, 8.78 MeV per nucleon

21.29. How much energy is released during each of the following fusion reactions?

(*a*) $^{1}_{1}\text{H} + {}^{7}_{3}\text{Li} \to 2\,{}^{4}_{2}\text{He}$ (*b*) $^{3}_{1}\text{H} + {}^{2}_{1}\text{H} \to {}_{2}^{4}\,\text{He} + {}^{1}_{0}n$

Ans. (*a*) 17.4 MeV; (*b*) 17.6 MeV

21.30. If the energy released in reaction (*a*) in the previous problem is divided equally between the two alpha particles, what is the velocity?

Ans. 2.0×10^7 m/s

21.31. ^{14}C is believed to be made in the upper atmosphere by an (n, p) process on ^{14}N. What is the Q for this reaction?

Ans. 0.62 MeV

21.32. In the reaction $^{32}S(n, \gamma)^{33}S$ with slow neutrons, the γ is produced with an energy of 8.65 MeV. What is the nuclidic mass of ^{33}S?

Ans. 32.97146 u

21.33. If a β^+ and a β^- annihilate each other and their rest masses are converted into two γ-rays of equal energy, what is the energy in MeV of each γ?

Ans. 0.51 MeV

21.34. ΔE for the combustion of a mole of ethylene in oxygen is -1.4×10^3 kJ. What would be the loss in mass (in u) accompanying the oxidation of one molecule of ethylene?

Ans. 1.6×10^{-8} u (This value is so small compared to the molecular mass that the change in mass, as in all chemical reactions, is ordinarily not taken into account.)

21.35. The sun's energy is believed to come from a series of nuclear reactions, the overall result of which is the transformation of four hydrogen atoms into one helium atom. How much energy is released in the formation of one helium atom? (*Hint*: Include the annihilation energy of the two positrons formed in the nuclear reaction with two electrons.)

Ans. 26.8 MeV

21.36. The nuclear fusion reaction, $2\,^2H \rightarrow {}^3H + {}^1H +$ energy, has been proposed as a way to produce the energy needed to generate electricity commercially. If the output is to be 50 MW and the energy of the above reaction is used with 30% efficiency, how many grams of deuterium fuel will be needed per day?

Ans. 149 g/d

21.37. A pure radiochemical preparation was observed to disintegrate at the rate of 4280 counts per minute at 1:35 p.m. At. 4:55 p.m. of the same day, the disintegration rate of the sample was only 1070 counts per minute. The disintegration rate is proportional to the number of radioactive atoms in the sample. What is the half-life of the substance?

Ans. 100 minutes

21.38. An atomic battery for pocket watches has been developed which uses the beta particles from ^{147}Pm as the primary energy source. The half-life of ^{147}Pm is 2.62 years. How long would it take for the rate of beta emission in the battery to be reduced to 10% of its initial value?

Ans. 8.7 years

21.39. A set of piston rings weighing 120 g was irradiated with neutrons in a nuclear reactor. Some of the cobalt present in the steel was converted to ^{60}Co, a radioisotope with a long enough half-life (5.3 y) so that there is essentially no mass loss during the investigation. Irradiation continued until the total ^{60}Co activity was 360 mCi. The rings were inserted into an automobile engine which was operated for 24 hours under average conditions, following which, 0.27 μCi of ^{60}Co activity was found in the oil filter. Calculate the rate of wear of the piston rings in mg/y based on the assumption that all the eroded metal was captured by the oil filter.

Ans. 33 mg/y

21.40. A charcoal sample taken from a fire pit in an archeological excavation of a rock shelter was believed to have been formed when early occupants of the shelter burned wood for cooking. A 100-mg sample of pure carbon from the charcoal was found in 1979 to have a disintegration rate of 0.25 counts per minute. How many millennia (1000 years) ago did the tree grow that was burned, producing the charcoal? (Use the data from Problem 21.11.)

Ans. 15 millennia ago

21.41. All naturally occurring rubidium cores contain ^{87}Sr, resulting from the beta decay of ^{87}Rb. In naturally occurring rubidium, 278 of every 1000 rubidium atoms are ^{87}Rb. A mineral containing 0.85% rubidium was analyzed and found to contain 0.0089% strontium. Assuming that all of the strontium originated by radioactive decay of ^{87}Rb, estimate the age of the mineral. Half-life for ^{87}Rb is 4.9×10^{10} y.

Ans. 2.6×10^9 years

21.42. Transuranium elements (above atomic number 92) were believed not to occur in nature because of their relatively short half-lives. Then ^{244}Pu was reported in natural ore. The half-life of ^{244}Pu is 8.0×10^7 years. If this element is more stable than any of its radioactive predecessors and has not been produced in this ore in significant amounts since the ore was deposited, what fraction of the original ^{244}Pu content would still be present? Assume the ore is 5×10^9 years old.

Ans. 10^{-19}

21.43. Before the use of nuclear weapons, the specific activity of ^{14}C in soluble ocean carbonates was found to be 16 disintegrations per minute per gram C. The amount of carbon in these carbonates has been estimated as 4.5×10^{16} kg. How many megacuries of ^{14}C did the ocean carbonates contain?

Ans. 320 MCi

21.44. Refer to Problems 21.13 and 21.11. Calculate the mass of pure ^{14}C needed to provide 17 μCi of beta activity. (*Note*: Refer to the procedure followed in Problem 21.14.)

Ans. 3.1×10^{-6} g

21.45. If the limit of a detection system is 0.002 disintegrations per second for a 1-g sample, what would be the maximum half-life that this system could detect for a 1-g sample of a nuclide whose mass number is around 200?

Ans. 3×10^{16} years

21.46. The activity of 30 μg of ^{247}Cm is 1.8 nCi. Calculate the disintegration rate constant and the half-life of ^{247}Cm.

Ans. 9.1×10^{-15} s^{-1}, 2.4×10^7 years

21.47. How much heat would be developed per hour from a 1-Ci ^{14}C source if we were able to capture all the energy of the β^--decay?

Ans. 3 J/h

21.48. ^{32}P has a 14.3-day half-life and emits an energetic β^- particle, making ^{21}P useful for nutritional studies in plants and animals. A 0.01-μCi sample of ^{32}P in the form of a soluble phosphate was added to a hydroponic bath containing a young tomato plant. Exactly three weeks later, the entire plant was rinsed, dried, and liquefied in a blender. A $\frac{1}{10}$ portion of the preparation was placed in a total activity counter. In a 1.00-min period an average of 625 counts was recorded. How efficient was the tomato plant in utilizing the phosphorus?

Ans. 78% efficient

21.49. Dr. Beaker had a solution which contained various sodium salts and wanted to determine the total sodium content. She added a quantity of HCl, which she judged to be in excess of the sodium ion equivalent. Then she added 0.4229 g of pure NaCl, which had a total ^{22}Na activity of 22,110 counts per minute. (^{22}Na is a positron emitter; its half-life is 2.6 years.) The solution was thoroughly mixed, then evaporated until crystals of NaCl were collected. The crystals were filtered off and repeatedly recrystallized until a small batch of pure NaCl was isolated. This NaCl sample had an activity of 483 counts/min per gram. What was the mass of sodium ion in Dr. Beaker's original solution?

Ans. 17.8 g

APPENDIX A

Exponents

A. The following is a partial list of powers of 10.

$$10^0 = 1$$
$$10^1 = 10$$
$$10^2 = 10 \times 10 = 100$$
$$10^3 = 10 \times 10 \times 10 = 1000$$
$$10^4 = 10 \times 10 \times 10 \times 10 = 10\,000$$
$$10^5 = 10 \times 10 \times 10 \times 10 \times 10 = 100\,000$$
$$10^6 = 10 \times 10 \times 10 \times 10 \times 10 \times 10 = 1\,000\,000$$

$$10^{-1} = \frac{1}{10} = 0.1$$
$$10^{-2} = \frac{1}{10^2} = \frac{1}{100} = 0.01$$
$$10^{-3} = \frac{1}{10^3} = \frac{1}{1000} = 0.001$$
$$10^{-4} = \frac{1}{10^4} = \frac{1}{10\,000} = 0.000\,1$$

In the expression 10^5, the *base* is 10 and the *exponent* is 5.

B. In multiplication, exponents of like bases are added.

(1) $a^3 \times a^5 = a^{3+5} = a^8$

(2) $10^2 \times 10^3 = 10^{2+3} = 10^5$

(3) $10 \times 10 = 10^{1+1} = 10^2$

(4) $10^7 \times 10^{-3} = 10^{7-3} = 10^4$

(5) $(4 \times 10^4)(2 \times 10^{-6}) = 8 + 10^{4-6} = 8 \times 10^{-2}$

(6) $(2 \times 10^5)(3 \times 10^{-2}) = 6 \times 10^{5-2} = 6 \times 10^3$

C. In division, exponents of like bases are subtracted.

(1) $\dfrac{a^5}{a^3} = a^{5-3} = a^2$

(2) $\dfrac{10^2}{10^5} = 10^{2-5} = 10^{-3}$

(3) $\dfrac{8 \times 10^2}{2 \times 10^{-6}} = \dfrac{8}{2} \times 10^{2+6} = 4 \times 10^8$

(4) $\dfrac{5.6 \times 10^{-2}}{1.6 \times 10^4} = \dfrac{5.6}{1.6} \times 10^{-2-4} = 3.5 \times 10^{-6}$

D. Any number may be expressed as an integral power of 10, or as the product of two numbers one of which is an integral power of 10 (e.g. $300 = 3 \times 10^2$).

(1) $22\,400 = 2.24 \times 10^4$

(2) $7\,200\,000 = 7.2 \times 10^6$

(3) $454 = 4.54 \times 10^2$

(4) $0.454 = 4.54 \times 10^{-1}$

(5) $0.045\,4 = 4.54 \times 10^{-2}$

(6) $0.000\,06 = 6 \times 10^{-5}$

(7) $0.003\,06 = 3.06 \times 10^{-3}$

(8) $0.000\,000\,5 = 5 \times 10^{-7}$

Moving the decimal point one place to the right is equivalent to multiplying a number by 10; moving the decimal point two places to the right is equivalent to multiplying by 100, and so on. Whenever the decimal point is moved to the right by n places, compensation can be achieved by *dividing* at the same time by 10^n; the value of the number remains unchanged. Thus

$$0.032\,5 = \frac{3.25}{10^2} = 3.25 \times 10^{-2}$$

Moving the decimal point one place to the left is equivalent to dividing by 10. Whenever the decimal point is moved to the left n places, compensation can be achieved by *multiplying* at the same time by 10^n; the value of the number remains unchanged. For example,

$$7\,296 = 72.96 \times 10^2 = 7.296 \times 10^3$$

E. An expression with an exponent of zero is equal to 1.

(1) $a^0 = 1$ **(2)** $10^0 = 1$ **(3)** $(3 \times 10)^0 = 1$ **(4)** $7 \times 10^0 = 7$ **(5)** $8.2 \times 10^0 = 8.2$

F. A factor may be transferred from the numerator to the denominator of a fraction, or vice versa, by changing the sign of the exponent.

(1) $10^{-4} = \dfrac{1}{10^4}$ **(2)** $5 \times 10^{-3} = \dfrac{5}{10^3}$ **(3)** $\dfrac{7}{10^{-2}} = 7 \times 10^2$ **(4)** $-5a^{-2} = -\dfrac{5}{a^2}$

G. The meaning of the fractional exponent is illustrated by the following.

(1) $10^{2/3} = \sqrt[3]{10^2}$ **(2)** $10^{3/2} = \sqrt{10^3}$ **(3)** $10^{1/2} = \sqrt{10}$ **(4)** $4^{3/2} = \sqrt{4^3} = \sqrt{64} = 8$

H. **(1)** $(10^3)^2 = 10^{3\times 2} = 10^6$ **(2)** $(10^{-2})^3 = 10^{-2\times 3} = 10^{-6}$ **(3)** $(a^3)^{-2} = a^{-6}$

I. To extract the square root of a power of 10, divide the exponent by 2. If the exponent is an odd number it should be increased or decreased by 1, and the coefficient adjusted accordingly. To extract the cube root of a power of 10, adjust so that the exponent is divisible by 3; then divide the exponent by 3. The coefficients are treated independently.

(1) $\sqrt{90\,000} = \sqrt{9 \times 10^4} = \sqrt{9} \times \sqrt{10^4} = 3 \times 10^2$ or 300

(2) $\sqrt{3.6 \times 10^3} = \sqrt{36 \times 10^2} = \sqrt{36} \times \sqrt{10^2} = 6 \times 10^1$ or 60

(3) $\sqrt{4.9 \times 10^{-5}} = \sqrt{49 \times 10^{-6}} = \sqrt{49} \times \sqrt{10^{-6}} = 7 \times 10^{-3}$ or 0.007

(4) $\sqrt[3]{8 \times 10^9} = \sqrt[3]{8} \times \sqrt[3]{10^9} = 2 \times 10^3$ or 2000

(5) $\sqrt[3]{1.25 \times 10^5} = \sqrt[3]{125 \times 10^3} = \sqrt[3]{125} \times \sqrt[3]{10^3} = 5 \times 10$ or 50

J. Multiplication and division of numbers expressed as powers of ten.

(1) $8\,000 \times 2\,500 = (8 \times 10^3)(2.5 \times 10^3) = 20 \times 10^6 = 2 \times 10^7$ or 20 000 000

(2) $\dfrac{48\,000\,000}{1\,200} = \dfrac{48 \times 10^6}{12 \times 10^2} = 4 \times 10^{6-2} = 4 \times 10^4$ or 40 000

(3) $\dfrac{0.007\,8}{120} = \dfrac{7.8 \times 10^{-3}}{1.2 \times 10^2} = 6.5 \times 10^{-5}$ or 0.000 065

(4) $(4 \times 10^{-3})(5 \times 10^4)^2 = (4 \times 10^{-3})(5^2 \times 10^8) = 4 \times 5^2 \times 10^{-3+8} = 100 \times 10^5 = 1 \times 10^7$

(5)
$$\frac{(6\,000\,000)(0.000\,04)^2}{(800)^2(0.000\,2)^3} = \frac{(6 \times 10^6)(4 \times 10^{-5})^4}{(8 \times 10^2)^2(2 \times 10^{-4})^3} = \frac{6 \times 4^4}{8^2 \times 2^3} \times \frac{10^6 \times 10^{-20}}{10^4 \times 10^{-12}}$$
$$= \frac{6 \times 256}{64 \times 8} \times \frac{10^{6-20}}{10^{4-12}} = 3 \times \frac{10^{-14}}{10^{-8}} = 3 \times 10^{-6}$$

(6) $$\begin{aligned}(\sqrt{4.0\times 10^{-6}})(\sqrt{8.1\times 10^{3}})(\sqrt{1.001\,6}) &= (\sqrt{4.0\times 10^{-6}})(\sqrt{81\times 10^{2}})(\sqrt{16\times 10^{-4}})\\ &= (2\times 10^{-3})(9\times 10^{1})(4\times 10^{-2})\\ &= 72\times 10^{-4} = 7.2\times 10^{-3} \text{ or } 0.007\,2\end{aligned}$$

(7) $$\begin{aligned}(\sqrt[3]{6.4\times 10^{-2}})(\sqrt[3]{27\,000})(\sqrt[3]{2.16\times 10^{-4}}) &= (\sqrt[3]{64\times 10^{-3}})(\sqrt[3]{27\times 10^{3}})(\sqrt[3]{216\times 10^{-6}})\\ &= (4\times 10^{-1})(3\times 10^{1})(6\times 10^{-2})\\ &= 72\times 10^{-2} \text{ or } 0.72\end{aligned}$$

APPENDIX B

Significant Figures

INTRODUCTION

The numerical value of every observed measurement is an approximation. No physical measurement, such as mass, length, time, volume, velocity, is ever absolutely correct. The accuracy (reliability) of every measurement is limited by the reliability of the measuring instrument, which is never absolutely reliable.

Consider that the length of an object is recorded as 15.7 cm. By convention, this means that the length was measured to the *nearest* tenth of a centimeter and that its exact value lies between 15.65 and 15.75 cm. If this measurement were exact to the nearest hundredth of a centimeter, it would have been recorded as 15.70 cm. The value 15.7 cm represents *three significant figures* (1, 5, 7), while 15.70 cm represents *four significant figures* (1, 5, 7, 0). A significant figure is one which is known to be reasonably reliable.

Similarly, a recorded mass of 3.406 2 g, observed with an analytical balance, means that the mass of the object was determined to the nearest tenth of a milligram and represents five significant figures (3, 4, 0, 6, 2), the last figure (2) being reasonably correct and guaranteeing the certainty of the preceding four figures.

A 50-mL buret has markings 0.1 ml apart, and the hundredths of a milliliter are estimated. A recorded volume of 41.83 cm^3 represents four significant figures. The last figure (3), being estimated, may be in error by one or two digits in either direction. The preceding three figures (4, 1, 8) are completely certain.

In elementary measurements in chemistry and physics, the last digit is an estimated figure and is considered as a significant figure.

ZEROS

A recorded volume of 28 mL represents two significant figures (2, 8). If this same volume were written as 0.028 L, it would still contain only two significant figures. Zeros appearing as the first figures of a number are not significant, since they merely locate the decimal point. However, the values 0.028 0 L and 0.280 L represent three significant figures (2, 8, and the last zero); the value 1.028 L represents four significant figures (1, 0, 2, 8); and the value 1.028 0 L represents five significant figures (1, 0, 2, 8, 0). Similarly, the value 19.00 for the atomic mass of fluorine contains four significant figures.

The statement that a body of ore weighs 9 800 lb does not indicate definitely the accuracy of the weighing. The last two zeros may have been used merely to locate the decimal point. If it was weighed to the nearest hundred pounds, the weight contains only two significant figures and may be written exponentially as 9.8×10^3 lb. If weighed to the nearest ten pounds it may be written as 9.80×10^3 lb, which indicates that the value is accurate to three significant figures. Since the zero in this case is not needed to locate the decimal point, it must be a significant figure. If the object was weighed to the nearest pound, the weight could be written as 9.800×10^3 lb (four significant figures). Likewise, the statement that the velocity of light is 186 000 mi/s is accurate to three significant figures, since this value is accurate only to the nearest thousand miles per second; to avoid confusion, it may be written as 1.86×10^5 mi/s. (Normally the decimal point is placed after the first significant figure.)

EXACT NUMBERS

Some numerical values are exact to as many significant figures as necessary, by definition. Included in this category are the numerical equivalents of prefixes used in unit definition. For example, 1 cm = 0.01 m by definition, and the units conversion factor, 1.0×10^{-2} m/cm, is exact to an infinite number of significant figures.

Other numerical values are exact by definition. For example, the atomic mass scale was established by fixing the mass of one atom of ^{12}C as 12.000 0 u. As many more zeros could be added as desired. Other examples include the definition of the inch (1 in = 2.540 0 cm) and the calorie (1 cal = 4.184 00 J).

ROUNDING OFF

A number is rounded off to the desired number of significant figures by dropping one or more digits to the right. When the first digit dropped is less than 5, the last digit retained should remain unchanged; when it is greater than 5, 1 is added to the last digit retained. When it is exactly 5, 1 is added to the last digit retained if that digit is odd. Thus the quantity 51.75 g may be rounded off to 51.8 g; 51.65 g to 51.6 g; 51.85 g to 51.8 g. When more than one digit is to be dropped, rounding off should be done in a block, not one digit at a time.

ADDITION AND SUBTRACTION

The answer should be rounded off after adding or subtracting, so as to retain digits only as far as the first column containing estimated figures. (Remember that the last significant figure is estimated.)

EXAMPLES Add the following quantities expressed in grams.

(1)	**(2)**	**(3)**	**(4)**
25.340	58.0	4.20	415.5
5.465	0.003 8	1.652 3	3.64
0.322	0.000 01	0.015	0.238
31.127 g (*Ans.*)	58.003 81	5.867 3	419.378
	= 58.0 g (*Ans.*)	= 5.87 g (*Ans.*)	= 419.4 g (*Ans.*)

An alternative procedure is to round off the individual numbers before performing the arithmetic operation, retaining only as many columns to the right of the decimal as would give a digit in every item to be added or subtracted. Examples **(2)**, **(3)**, and **(4)** above would be done as follows:

(2)	**(3)**	**(4)**
58.0	4.20	415.5
0.0	1.65	3.6
0.0	0.02	0.2
58.0 g	5.87 g	419.3 g

Note that the answer to **(4)** differs by one in the last place from the previous answer. The last place, however, is known to have some uncertainty in it.

MULTIPLICATION AND DIVISION

The answer should be rounded off to contain only as many significant figures as are contained in the least exact factor. For example, when multiplying 7.485×8.61, or when dividing $0.164\,2 \div 1.52$, the answer should be given in three significant figures.

This rule is an approximation to a more exact statement that the fractional or percentage error of a product or quotient cannot be any less than the fractional or percentage error of any one factor. For this reason, numbers whose first significant figure is 1 (or occasionally 2) must contain an additional significant figure to have a given fractional error in comparison with a number beginning with 8 or 9.

Consider the division

$$\frac{9.84}{9.3} = 1.06$$

By the approximate rule, the answer should be 1.1 (two significant figures). However, a difference of 1 in the last place of 9.3 (9.3 ± 0.1) results in an error of about 1 percent, while a difference of 1 in the last place of 1.1 (1.1 ± 0.1) yields an error of roughly 10 percent. Thus the answer 1.1 is of much lower percentage accuracy than 9.3. Hence in this case the answer should be 1.06, since a difference of 1 in the last place of the least exact factor used in the calculation (9.3) yields a percentage of error about the same (about 1 percent) as a difference of 1 in the last place of 1.06 (1.06 ± 0.01). Similarly, $0.92 \times 1.13 = 1.04$.

In nearly all practical chemical calculations, a precision of only two to four significant figures is required. Therefore the student need not perform multiplications and divisions manually. Even if an electronic calculator is not available, an inexpensive 10-in slide rule is accurate to three significant figures, and a table of 4-place logarithms is accurate to four significant figures.

Since not all electronic calculators are alike, detailed instructions cannot be given here. Read your instruction manual. You should purchase a calculator which, in addition to $+$, $-$, $\times$, and $\div$ functions, provides at least the following: scientific notation (powers of ten); logarithms and antilogarithins (inverse logarithms) both natural and common (base ten); and exponentials (y^x). If it has these functions, it will probably have reciprocals ($1/x$), squares, square roots, and trigonometric functions as well.

The use of the arithmetic functions is fairly obvious, but you should use powers of ten except in trivial cases. To enter "96 500" for instance, consider it 9.65×10^4 and enter 9.65 EE4. (On most calculators "EE4" means $\times 10^4$). The calculator keeps track of the decimal point and provides an answer between one and ten times the appropriate power of ten. It will usually display many more figures than are significant, and you will have to round off the final result. If at least one factor was entered as a power of ten, the power-of-ten style will prevail in the display, and you need not fear running "off scale," nor will any significant figures disappear off scale.

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Figures in **bold**; tables in *italics*

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TABLE OF ATOMIC MASSES

Scaled to the relative atomic mass A_r (^{12}C)=12

Name	Symbol	Atomic Number	Atomic Mass	Name	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	(227)	Hassium	Hs	108	(265)
Aluminum	Al	13	26.981 54	Helium	He	2	4.002 60
Americium	Am	95	(243)	Holmium	Ho	67	164.930 32
Antimony	Sb	51	121.760	Hydrogen	H	1	1.007 94
Argon	Ar	18	39.948	Indium	In	49	114.818
Arsenic	As	33	74.921 60	Iodine	I	53	126.904 47
Astatine	At	85	(210)	Iridium	Ir	77	192.217
Barium	Ba	56	137.327	Iron	Fe	26	55.845
Berkelium	Bk	97	(247)	Krypton	Kr	36	83.80
Beryllium	Be	4	9.012 18	Lanthanum	La	57	138.905 5
Bismuth	Bi	83	208.980 38	Lawrencium	Lr	103	(262)
Bohrium	Bh	107	(264)	Lead	Pb	82	207.2
Boron	B	5	10.811	Lithium	Li	3	6.941
Bromine	Br	35	79.904	Lutetium	Lu	71	174.967
Cadmium	Cd	48	112.411	Magnesium	Mg	12	24.305 0
Calcium	Ca	20	40.078	Manganese	Mn	25	54.938 05
Californium	Cf	98	(251)	Meitnerium	Mt	109	(268)
Carbon	C	6	12.010 7	Mendelevium	Md	101	(258)
Cerium	Ce	58	140.116	Mercury	Hg	80	200.59
Cesium	Cs	55	132.905 45	Molybdenum	Mo	42	95.94
Chlorine	Cl	17	35.452 7	Neodymium	Nd	60	144.24
Chromium	Cr	24	51.996 1	Neon	Ne	10	20.179 7
Cobalt	Co	27	58.933 20	Neptunium	Np	93	(237)
Copper	Cu	29	63.546	Nickel	Ni	28	58.693 4
Curium	Cm	96	(247)	Niobium	Nb	41	92.906 38
Dubnium	Db	105	(262)	Nitrogen	N	7	14.006 74
Dysprosium	Dy	66	162.50	Nobelium	No	102	(259)
Einsteinium	Es	99	(252)	Osmium	Os	76	190.23
Erbium	Er	68	167.26	Oxygen	O	8	15.999 4
Europium	Eu	63	151.964	Palladium	Pd	46	106.42
Fermium	Fm	100	(257)	Phosphorus	P	15	30.973 76
Fluorine	F	9	18.998 40	Platinum	Pt	78	195.078
Francium	Fr	87	(223)	Plutonium	Pu	94	(244)
Gadolinium	Gd	64	157.25	Polonium	Po	84	(209)
Gallium	Ga	31	69.723	Potassium	K	19	39.098 3
Germanium	Ge	32	72.61	Praseodymium	Pr	59	140.907 65
Gold	Au	79	196.966 55	Promethium	Pm	61	(145)
Hafnium	Hf	72	178.49	Protactinium	Pa	91	231.035 88

Name	Symbol	Atomic Number	Atomic Mass	Name	Symbol	Atomic Number	Atomic Mass
Radium	Ra	88	(226)	Technetium	Tc	43	(98)
Radon	Rn	86	(222)	Tellurium	Te	52	127.60
Rhenium	Re	75	186.207	Terbium	Tb	65	158.925 34
Rhodium	Rh	45	102.905 50	Thallium	Tl	81	204.383 3
Rubidium	Rb	37	85.467 8	Thorium	Th	90	232.038 1
Ruthenium	Ru	44	101.07	Thulium	Tm	69	168.934 21
Rutherfordium	Rf	104	(261)	Tin	Sn	50	118.710
Samarium	Sm	62	150.36	Titanium	Ti	22	47.867
Scandium	Sc	21	44.955 91	Tungsten (Wolfram)	W	74	183.84
Seaborgium	Sg	106	(263)				
Selenium	Se	34	78.96	Uranium	U	92	238.028 9
Silicon	Si	14	28.085 5	Vanadium	V	23	50.941 5
Silver	Ag	47	107.868 2	Xenon	Xe	54	131.29
Sodium	Na	11	22.989 77	Ytterbium	Yb	70	173.04
Strontium	Sr	38	87.62	Yttrium	Y	39	88.905 85
Sulfur	S	16	32.066	Zinc	Zn	30	65.39
Tantalum	Ta	73	180.947 9	Zirconium	Zr	40	91.224

A value in parentheses for an element without any stable nuclides is the atomic mass number of the isotope of that element of longest known half-life.

NUCLIDIC MASSES OF SELECTED RADIONUCLIDES

Name	Symbol	Atomic Number	Nuclidic Mass	Name	Symbol	Atomic Number	Nuclidic Mass
Actinium	Ac	89	227.027 7	Mendelevium	Md	101	258.098 4
Americium	Am	95	243.0614	Neptunium	Np	93	237.048 2
Astatine	At	85	209.987 1	Nobelium	No	102	259.101 1
Berkelium	Bk	97	247.070 3	Plutonium	Pu	94	244.064 2
Bohrium	Bh	107	264.12	Polonium	Po	84	208.982 4
Californium	Cf	98	251.079 6	Promethium	Pm	61	144.912 7
Curium	Cm	96	247.070 3	Protactinium	Pa	91	231.035 9
Dubnium	Db	105	262.114 4	Radium	Ra	88	226.025 4
Einsteinium	Es	99	252.083 0	Radon	Rn	86	222.017 6
Fermium	Fm	100	257.095 1	Rutherfordium	Rf	104	261.108 9
Francium	Fr	87	223.019 7	Seaborgium	Sg	106	263.118 6
Hassium	Hs	108	265.130 6	Technetium	Tc	43	97.907 2
Lawrencium	Lr	103	262.110	Thorium	Th	90	232.038 0
Meitnerium	Mt	109	---	Uranium	U	92	238.050 8

The listed mass is that for the longest-lived isotope of the listed element.