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AQUEOUS SOLUTIONS AND ACID-BASE CHEMISTRY

A. AQUEOUS SOLUTIONS

The majority of reactions studied by biochemists occur in solution. Consequently, it is appropriate to begin our mathematical survey by reviewing the various ways of expressing and interconverting concentrations of solutions.

CONCENTRATIONS BASED ON VOLUME

Concentrations based on the amount of dissolved solute per unit volume are the most widely used in biochemistry laboratories. The most common conventions are defined below.

$$\boxed{\textit{Molarity } (M) = \text{the number of moles of solute per liter of solution}} \qquad (1)$$

Molar concentrations are usually given in square brackets, for example, $[H^+]$ = molarity of H^+ ion. To calculate M, we need to know the weight of dissolved solute and its molecular weight, MW.

$$\boxed{\frac{\mathrm{wt}_g}{\mathrm{MW}} = \text{moles}} \qquad (2)$$

Dilute solutions are often expressed in terms of millimolarity, micromolarity, and so on, where:

$$1 \text{ mmole} = 10^{-3} \text{ moles}$$
$$1\ \mu\text{mole} = 10^{-6} \text{ moles}$$
$$1 \text{ nmole} = 1 \text{ m}\mu \text{ mole} = 10^{-9} \text{ moles}$$
$$1 \text{ pmole} = 1\ \mu\mu\text{mole} = 10^{-12} \text{ moles}$$

Therefore:

$$1 \text{ m}M = 10^{-3}\,M = 1 \text{ mmole/liter} = 1\ \mu\text{mole/ml}$$
$$1\ \mu M = 10^{-6}\,M = 1\ \mu\text{mole/liter} = 1 \text{ nmole/ml}$$
$$1 \text{ n}M = 10^{-9}\,M = 1 \text{ nmole/liter} = 1 \text{ pmole/ml}$$

A 1 M solution contains one Avogadro's number of molecules per liter.

$$\begin{aligned}\text{Avogadro's number} &= \text{number of molecules per g-mole}\\ &= \text{number of atoms per g-atom}\\ &= \text{number of ions per g-ion}\\ &= 6.023 \times 10^{23}\end{aligned}$$

In general practice, one Avogadro's number of particles (i.e., 1 g-mole or 1 g-atom or 1 g-ion) is frequently called a "mole" regardless of whether the substance is ionic, monoatomic, or molecular in nature. For example, 35.5 g of Cl^- ions may be called a "mole" instead of a "gram-ion."

$$\boxed{\textit{Activity (a)} = \text{the effective or apparent molarity of a solute}} \quad (3)$$

Activity and actual molarity are related by:

$$\boxed{a = \gamma[M]} \quad (4)$$

where γ = activity coefficient (i.e., the fraction of the actual concentration that is active). Because of interactions between solute molecules that prevent their full expression, γ is usually less than unity. For example, HCl in a 0.1 M solution is fully ionized, yet the solution behaves as if it contains only 0.086 M H^+. Thus, $\gamma = 0.86$.

$$\boxed{\textit{Normality (N)} = \text{the number of equivalents of solute per liter of solution}} \quad (5)$$

To calculate N, we need to know the weight of dissolved solute and its equivalent weight, EW.

$$\boxed{\frac{\mathrm{wt_g}}{\mathrm{EW}} = \text{equivalents}} \quad (6)$$

One equivalent (i.e., the EW) of an acid or base is the weight that contains 1 g-atom (1 mole) of replaceable hydrogen, or 1 g-ion (1 mole) of replaceable hydroxyl. The EW of a compound involved in an oxidation-reduction reaction is the weight that provides or accepts 1 faraday (1 mole) of electrons. In general:

$$\boxed{\mathrm{EW} = \frac{\mathrm{MW}}{n}} \quad (7)$$

where n = the number of replaceable H^+ or OH^- per molecule (for acids and bases)

or n = the number of electrons lost or gained per molecule (for oxidizing and reducing agents).

The molarity and normality are related by:

$$\boxed{N = nM} \tag{8}$$

For example, a 0.01 M solution of H_2SO_4 is 0.02 N.

Weight/Volume Percent (% w/v) = the weight in g of a solute per 100 ml of solution (9)

Weight/volume percent is often used for routine laboratory solutions where exact concentrations are not too important.

Milligram Percent (mg %) = the weight in mg of a solute per 100 ml of solution (10)

Milligram percent is often used in clinical laboratories. For example, a clinical blood sugar value of 225 means 225 mg of glucose per 100 ml of blood serum.

Osmolarity = the molarity of particles in a solution (11)

A 1 M solution of a nondissociable solute is also 1 Osmolar. (The solution contains 6.023×10^{23} particles per liter.) A 1 M solution of a dissociable salt is n Osmolar, where n is the number of ions produced per molecule. Thus, a 0.03 M solution of KCl is 0.06 Osmolar. Osmolarity is often considered in physiological studies where tissues or cells must be bathed in a solution of the same osmolarity as the cytoplasm in order to prevent the uptake or release of water. Blood plasma is 0.308 Osmolar. Thus, red blood cells suspended in a 0.308 Osmolar NaCl solution (0.154 M) would neither shrink nor swell. The 0.154 M NaCl solution is said to be *isotonic* with respect to the red blood cells.

Problem 1-1

(a) How many grams of solid NaOH are required to prepare 500 ml of a 0.04 M solution? (b) Express the concentration of this solution in terms of N, g/liter, % w/v, mg %, and osmolarity.

Solution

(a)
$$\text{liters} \times M = \text{number of moles NaOH required}$$
$$0.5 \times 0.04 = 0.02 \text{ mole NaOH required}$$
$$\text{number of moles} = \frac{\text{wt}_g}{\text{MW}} \qquad 0.02 = \frac{\text{wt}_g}{40}$$
$$\boxed{\textbf{wt} = \textbf{0.8 g}}$$

∴ Weigh out 0.8 g, dissolve in water, and dilute to 500 ml.

(b) NaOH contains one OH per molecule.

$$\therefore \quad M = N \text{ and the solution is } \boxed{\mathbf{0.04}\ \boldsymbol{N}}$$

$$\text{The solution contains 0.8 g/500 ml, or } \boxed{\textbf{1.6 g/liter}}$$

$$\text{\% (w/v)} = \text{g per 100/ml} \qquad 1.6 \text{ g/liter} = 0.16 \text{ g/100 ml} = \boxed{\textbf{0.16\%}}$$ [illegible]

$$\text{mg \%} = \text{mg per 100 ml} \qquad 0.16 \text{ g/100} = 160 \text{ mg/100 ml} = \boxed{\textbf{160 mg \%}}$$

NaOH yields two particles (Na^+ and OH^-)

$$\therefore \quad \text{osmolarity} = 2 \times M = \boxed{\textbf{0.08 Osmolar}}$$

· **Problem 1-2**

How many milliliters of 5 M H_2SO_4 are required to make 1500 ml of a 0.002 M H_2SO_4 solution?

Solution

The number of moles of H_2SO_4 in the dilute solution equals the number of moles of H_2SO_4 taken from the concentrated solution.

$$\text{liters} \times M \text{ (dilute solution)} = \text{liters} \times M \text{ (concentrated solution)}$$
$$1.5 \times 0.002 = \text{liters} \times 5$$
$$\frac{1.5 \times 0.002}{5} = \text{liters concentrated solution required}$$
$$\frac{3 \times 10^{-3}}{5} = 0.6 \times 10^{-3} \text{ liters} = \boxed{\textbf{0.6 ml}}$$

∴ Take 0.6 ml of the concentrated solution and dilute to 1.5 liters.

$$\text{Ionic Strength } \left(\frac{\Gamma}{2}\right) = 1/2\, \Sigma\, M_iZ_i^2$$

where M_i = the molarity of the ion (12)

Z_i = the net charge of the ion (regardless of sign)

Σ = a symbol meaning "the sum of"

Ionic strength measures the concentration of charges in solution. As the ionic strength of a solution increases, the activity coefficient of an ion decreases. The relationship between the ionic strength and the molarity of a solution of ionizable salt depends on the number of ions produced and their net charge, as summarized below.

Salt		Ionic Strength
Type	Example	
1:1	KCl, NaBr	M
2:1	$CaCl_2$, Na_2HPO_4	$3 \times M$
2:2	$MgSO_4$	$4 \times M$
3:1	$FeCl_3$, Na_3PO_4	$6 \times M$
2:3	$Fe_2(SO_4)_3$	$15 \times M$

"Type" refers to the net charge on the ions. Thus $MgSO_4$, which yields Mg^{2+} and SO_4^{2-}, is called a 2:2 salt. Na_2HPO_4, which yields HPO_4^{2-} and Na^+ ions, is called a 2:1 salt.

Only the *net* charge on an ion is used in calculating ionic strength. Thus, un-ionized compounds (e.g., un-ionized acetic acid) or species carrying an equal number of positive and negative charges (e.g., a neutral amino acid) do not contribute toward the ionic strength of a solution.

Problem 1-3

Calculate the ionic strength of a 0.02 M solution of $\overset{+3}{Fe_2}(\overset{-2}{SO_4})_3$.

Solution

$$\frac{\Gamma}{2} = \tfrac{1}{2}\sum M_iZ_i^2 = \tfrac{1}{2}[M_{Fe^{3+}}Z^2_{Fe^{3+}} + M_{SO_4^{2-}}Z^2_{SO_4^{2-}}]$$

The 0.02 M $Fe_2(SO_4)_3$ yields 0.04 M Fe^{3+} and 0.06 M SO_4^{2-}.

$$\frac{\Gamma}{2} = \frac{(0.04)(3)^2 + (0.06)(-2)^2}{2} = \frac{(0.04)(9) + (0.06)(4)}{2}$$

$$= \frac{(0.36) + (0.24)}{2} = \frac{0.60}{2}$$

$$\boxed{\frac{\Gamma}{2} = 0.30}$$

Or, from the precalculated relationship for 2:3 salts:

$$\frac{\Gamma}{2} = 15 \times M = (15)(0.02) = \boxed{0.30}$$

CONCENTRATIONS BASED ON WEIGHT

$$\boxed{\textit{Weight/Weight Percent } (\%\ w/w) = \text{the weight in g of a solute per 100 g of solution}} \qquad (13)$$

The concentrations of many commercial acids are given in terms of % w/w. In order to calculate the volume of the stock solution required for a given preparation, we must know its *density* or *specific gravity* where:

ρ = density = weight per unit volume

SG = specific gravity = density relative to water. Since the density of water is 1 g/ml, specific gravity is numerically equal to density.

Problem 1-4

Describe the preparation of 2 liters of 0.4 M HCl starting with a concentrated HCl solution (28% w/w HCl, SG = 1.15).

Solution

$$\text{liters} \times M = \text{number of moles} \qquad \boxed{\mathbf{2 \times 0.4 = 0.80\ mole\ HCl\ needed}}$$

$$\text{wt}_g = \text{number of moles} \times \text{MW} \qquad \text{wt}_g = 0.80 \times 36.5$$

$$\boxed{\mathbf{wt_g = 29.2\ g\ pure\ HCl\ needed}}$$

The stock solution is not pure HCl but only 28% HCl by weight.

$$\therefore\ \frac{29.2}{0.28} = \boxed{\mathbf{104.3\ g\ stock\ solution\ needed}}$$

Instead of weighing out 104.3 g of stock solution, we can calculate the *volume* required.

$$\text{vol}_{\text{ml}} = \frac{\text{wt}_g}{\rho_{g/\text{ml}}} = \frac{104.3}{1.15} = \boxed{\mathbf{90.7\ ml\ stock\ solution\ needed}}$$

$\therefore$ Measure out 90.7 ml of stock solution and dilute to 2 liters with water.

All of the above relationships (between weight, density, and percent w/w) can be combined into a single expression.

$$\boxed{\mathbf{wt_g = vol_{ml} \times \rho_{g/ml} \times \%\ (as\ decimal)}}$$

where wt_g = weight of *pure* substance required in g
vol_{ml} = volume of stock solution needed in ml
% = fraction of total weight that is pure substance

$$\therefore\quad \text{vol} = \frac{\text{wt}}{\rho \times \%} = \frac{29.2}{1.15 \times 0.28} = 90.7\ \text{ml}$$

As an alternate method, we can calculate the molarity of the stock solution. First calculate the weight of pure HCl in 1 liter of stock solution.

$$\text{wt} = \text{vol} \times \rho \times \%$$
$$\text{wt}_g = 1000\ \text{ml} \times 1.15\ \text{g/ml} \times 0.28$$
$$\text{wt} = 322\ \text{g}$$

In other words, 1000 ml (1 liter) of stock solution contains 322 g of pure HCl.

$$\text{number of moles} = \frac{\text{wt}_g}{\text{MW}} = \frac{322}{36.5} = 8.82$$

$\therefore$ The concentrated stock solution is 8.82 *M*.
We need 0.80 mole.

$$\text{liters} = \frac{\text{number of moles}}{M} = \frac{0.80}{8.82} = 0.0907\ \text{liter}$$

$\therefore$ Take 0.0907 liter (90.7 ml) of stock and dilute to 2 liters.

Molality (m) = the number of moles of solute per 1000 g of solvent (14)

Molality is used in certain physical chemical calculations (e.g., calculations of boiling-point elevation and freezing-point depression). For dilute aqueous solutions, *m* and *M* will be quite close. In order to interconvert *m* and *M*, we need to know % w/w.

Mole Fraction = the fraction of the total number of moles present represented by the compound in question (15)

For example, in a solution containing n_1 moles of compound 1, n_2 moles of compound 2, and n_3 moles of compound 3, the mole fraction of compound 2,

MF_2, is given by:

$$MF_2 = \frac{n_2}{n_1 + n_2 + n_3}$$

The mole fraction of a compound is important in certain physical chemical calculations, but is not often used in biochemistry.

Problem 1-5

Calculate (a) the molality of the concentrated stock HCl solution described in Problem 1-4. (b) Calculate the mole fraction of HCl in the solution.

Solution

(a) The solution contains 28% w/w HCl, or 28 g HCl per 100 g total, or 28 g HCl per (100 − 28) = 72 g water.

$$\frac{28 \text{ g HCl}}{72 \text{ g } H_2O} \times 1000 = 388.9 \text{ g HCl}/1000 \text{ g } H_2O$$

$$\frac{wt_g}{MW} = \text{moles} \qquad \frac{388.9}{36.5} = 10.65 \text{ moles HCl}/1000 \text{ g } H_2O$$

$$\therefore \quad \boxed{\textbf{the solution is 10.65 } m}$$

(b) In 100 g of solution, for example, we have:

$$\frac{28 \text{ g HCl}}{36.5 \text{ g/mole}} = 0.767 \text{ moles of HCl}$$

and

$$\frac{72 \text{ g } H_2O}{18 \text{ g/mole}} = 4.0 \text{ moles of } H_2O$$

$$MF_{HCl} = \frac{n_{HCl}}{n_{HCl} + n_{H_2O}} = \frac{0.767}{4.767}$$

$$\boxed{MF_{HCl} = 0.161}$$

CONCENTRATION BASED ON DEGREE OF SATURATION

Proteins are often purified by differential precipitation with neutral salts. Ammonium sulfate is the most common salt used for this purpose, although occasionally NaCl is used. The concentration of ammonium sulfate used to "salt out" proteins is almost always expressed in terms of "percent saturation."

Percent Saturation = the concentration of salt in solution as a percent of the maximum concentration possible at the given temperature (16)

In order to take into account volume changes that occur when a large amount of salt is added to an aqueous solution we need to know the *specific volume* of the salt, where:

$$\begin{aligned}\bar{v} = \text{specific volume} &= \text{volume occupied by 1 g of salt (ml/g)}\\ &= \text{the reciprocal of the density}\end{aligned}$$

· Problem 1-6

The specific volume of solid ammonium sulfate is 0.565 ml/g. The solubility of ammonium sulfate at 0°C is 706 g/1000 g water*. Calculate (a) the concentration of ammonium sulfate in a saturated solution at 0°C and (b) the amount of solid ammonium sulfate that must be added at 0°C to 500 ml of a "40% saturated" solution to bring it to "60% saturation."

Solution

(a) A saturated solution at 0°C prepared by adding 706 g of ammonium sulfate (AS) to 1000 g of H_2O occupies:

$$1000 \text{ ml} + (706)(0.565) \text{ ml} = 1399 \text{ ml}$$

The concentration of AS in the solution is:

$$\frac{706}{1399} = \boxed{0.505 \text{ g/ml}} = \boxed{505 \text{ g/liter}}$$

The MW of AS is 132.14. Therefore the molarity of the solution is:

$$\frac{505}{132.14} = \boxed{3.82\ M}$$

(b) We can derive a simple equation giving the amount of solid AS that must be added to 1000 ml of solution at an initial degree of saturation, S_1, in order to bring the solution to a different degree of saturation, S_2. Knowing that 0.505 g/ml = 100% saturation, or 1.00 saturation:

$$\begin{aligned}S_2 &= \frac{(\text{initial wt}_g \text{ of AS present}) + (\text{wt}_g \text{ AS added})}{(\text{final vol. of solution in ml})(0.505 \text{ g/ml})}\\ &= \frac{(1000 \text{ ml})(0.505 \text{ g/ml})(S_1) + (\text{wt}_g)}{[1000 \text{ ml} + 0.565\,(\text{wt}_g)]0.505 \text{ g/ml}}\end{aligned}$$

$$\boxed{\text{wt}_g = \frac{505(S_2 - S_1)}{1 - 0.285 S_2}} \qquad (17)$$

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* Different sources give slightly different values. For example, Appendix II gives 697 g/liter at 0°C; Appendix III gives 706.8 g/liter.

where wt_g = wt of solid AS to be added to 1000 milliliters
S_2 = the final saturation (as a decimal)
S_1 = the initial saturation (as a decimal)
505 = g AS per 1000 ml for 100% saturation

$$\therefore \quad \text{wt}_g = \frac{505(0.60-0.40)}{1-0.285(0.60)} = \frac{101}{0.829}$$

$$= 121.8\ \text{g/liter} \qquad \text{or} \qquad \boxed{\mathbf{60.9\ g/500\ ml}}$$

Problem 1-7

How many milliliters of a saturated ammonium sulfate solution must be added to 40 ml of a 20% saturated solution to make the final solution 70% saturated? Assume that the volumes are additive.

Solution

$$(40\ \text{ml})(0.20) + (X\ \text{ml})(1.00) = (40 + X\ \text{ml})(0.70)$$
$$8 + X = 28 + 0.70X$$
$$0.3X = 20$$

$$\boxed{\mathbf{X = 66.7\ ml}}$$

In general, the volume of saturated ammonium sulfate solution to be added to 100 ml of solution at saturation S_1 (as a decimal) to produce a final saturation, S_2, is given by:

$$\boxed{\mathbf{vol_{ml} = \frac{100(S_2 - S_1)}{(1 - S_2)}}} \tag{1-8}$$

(Usually, the tables shown in Appendices II and III are used for enzyme purification by fractional precipitation with ammonium sulfate.)

B. EQUILIBRIUM CONSTANTS

A great many reactions that occur in nature are *reversible* and do not proceed to completion. Instead, they come to an apparent halt or *equilibrium* at some point between 0 and 100% completion. At equilibrium, the net velocity is zero because the absolute velocity in the forward direction exactly equals the absolute velocity in the reverse direction. The position of equilibrium is conveniently described by an *equilibrium constant*, K_{eq}. For example, consider the dissociation of a weak acid (which we will examine in more detail in the following pages).

$$\mathrm{HA} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{H^+} + \mathrm{A^-}$$

The forward velocity, v_f, is proportional to the concentration of HA:

$$v_f \propto [\mathrm{HA}] \qquad \text{or} \qquad v_f = k_1[\mathrm{HA}]$$

where k_1 is a proportionality constant, known as a *rate constant* (specifically, a *first-order rate constant* because v_f is proportional to the concentration of a single substance raised to power one). The reverse velocity, v_r, is proportional to the concentration of H^+ and A^-, and, therefore, to the products of the concentration of A^- and H^+:

$$v_r \propto [\mathrm{H^+}] \qquad \text{and} \qquad v_r \propto [\mathrm{A^-}]$$

$$\therefore \quad v_r \propto [\mathrm{H^+}][\mathrm{A^-}] \qquad \text{or} \qquad v_r = k_{-1}[\mathrm{H^+}][\mathrm{A^-}]$$

where k_{-1} is a *second-order rate constant.* Thus, doubling $[H^+]$ doubles v_r. Doubling $[A^-]$ doubles v_r. Doubling both $[H^+]$ and $[A^-]$ increases v_r fourfold. At equilibrium:

$$v_f = v_r$$

or

$$k_1[\mathrm{HA}] = k_{-1}[\mathrm{H^+}][\mathrm{A^-}] \qquad \text{or} \qquad \frac{k_1}{k_{-1}} = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

The ratio of the two constants k_1/k_{-1} is itself a constant and is defined as K_{eq}:

$$\boxed{K_{eq} = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}} \tag{19}$$

In this particular case, K_{eq} is an acid dissociation constant and would be indicated as K_a.

If the reaction in question is $\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\mathrm{C}$, then:

$$v_f = k_1[\mathrm{A}][\mathrm{B}] \qquad \text{and} \qquad v_r = k_{-1}[\mathrm{C}][\mathrm{C}] = k_{-1}[\mathrm{C}]^2$$

$$\therefore \quad \boxed{K_{eq} = \frac{[\mathrm{C}]^2}{[\mathrm{A}][\mathrm{B}]}}$$

The dimensions of K_{eq} depend on the number of components in the system.

Strictly speaking, it is not the concentrations of the reaction components that are considered, but instead, their *activities* or *effective* or *apparent* concentrations. For most of the calculations in the following chapters, we will assume that $\gamma = 1$, that is, activity is equivalent to molar concentration. This assumption is reasonably valid for the dilute aqueous solutions of monovalent and divalent ions employed in biochemical studies. Appendix V lists some activity coefficients.

Problem 1-8

Consider the reaction $E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$. What are the units of (a) k_1, (b) k_{-1}, and (c) K_{eq}?

Solution

(a) $v_f = k_1[E][S]$

Let v_f = moles of ES formed per liter per minute

$= \text{moles} \times \text{liter}^{-1} \times \text{min}^{-1} = M \times \text{min}^{-1}$

and [E] and [S] = moles × liter^{-1} = M

$$\therefore \quad k_1 = \frac{v_f}{[E][S]} = \frac{M \times \text{min}^{-1}}{(M)^2} = \frac{\text{min}^{-1}}{M}$$

or

$$\boxed{k_1 = \text{min}^{-1} \times M^{-1}}$$

(b) $v_r = k_{-1}[ES]$

$$k_{-1} = \frac{v_r}{[ES]} = \frac{M \times \text{min}^{-1}}{M} \qquad \therefore \qquad \boxed{k_{-1} = \text{min}^{-1}}$$

(c) $$K_{eq} = \frac{k_1}{k_{-1}} = \frac{\text{min}^{-1} \times M^{-1}}{\text{min}^{-1}} \qquad \therefore \qquad \boxed{K_{eq} = M^{-1}}$$

or

$$K_{eq} = \frac{[ES]}{[E][S]} = \frac{M}{(M)^2} = M^{-1}$$

Additional problems on chemical equilibria are found in Chapter 3.

C. ACIDS AND BASES

An understanding of acid-base chemistry is essential if we are to appreciate the properties of biological molecules. A great many of the low-molecular-weight metabolites and macromolecular components of living cells are acids and bases, and thus, have the potential to ionize. The electrical charges on these molecules are important factors in the rate of enzyme-catalyzed reactions, the stability and conformation of proteins, the interactions of macromolecules with each other and with small ions, and the analytical and purification techniques used in the laboratory.

BRONSTED CONCEPT OF CONJUGATE ACID-CONJUGATE BASE PAIRS

The most useful way of discussing acids and bases in general biochemistry is to define an "acid" as a substance that donates protons (hydrogen ions) and a "base" as a substance that accepts protons. This concept is generally referred to as the Bronsted concept of acids and bases. When a Bronsted acid loses a proton, a Bronsted base is produced. The original acid and resulting base are referred to as a conjugate acid-conjugate base pair. The substance that accepts the proton is a different Bronsted base; by accepting the proton, another Bronsted acid is produced. Thus, in every ionization of an acid or base, two conjugate acid-conjugate base pairs are involved.

$$\underset{[\text{conjugate acid}]_1}{HA} + \underset{[\text{conjugate base}]_2}{B^-} \rightleftharpoons \underset{[\text{conjugate base}]_1}{A^-} + \underset{[\text{conjugate acid}]_2}{HB}$$

IONIZATION OF STRONG ACIDS AND BASES

A "strong" acid is a substance that ionizes almost 100% in aqueous solution. For example, HCl in solution is essentially 100% ionized to H_3O^+ and Cl^-:

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

H_3O^+ (the hydronium ion, or conjugate acid of water) is the actual form of the hydrogen ion (proton) in solution. The ionization of HCl could just as easily be represented as a simple dissociation:

$$HCl \longrightarrow H^+ + Cl^-$$

Thus, for all practical purposes, H_3O^+ and H^+ mean the same thing. We will use the two conventions for "hydrogen ion" interchangeably, depending on which is the more convenient.

A "strong" base is a substance that ionizes extensively in solution to yield OH^- ions. Sodium and potassium hydroxides are examples of strong inorganic bases.

$$KOH \longrightarrow K^+ + OH^-$$

IONIZATION OF WATER

The ionization of water itself can be considered in two ways: (1) as a simple dissociation to yield H^+ and OH^- ions and (2) in terms of Bronsted conjugate acid-conjugate base pairs. In either case, it is obvious that water is amphoteric—it yields both H^+ and OH^- ions; it can both donate and accept protons.

The ionization of water can be described by a "dissociation constant," K_d, an "ionization constant," K_i, and a specific constant for water, K_w, as shown below.

Simple Dissociation	Conjugate Acid-Conjugate Base
$HOH \rightleftharpoons H^+ + OH^-$	$HOH + HOH \rightleftharpoons H_3O^+ + OH^-$
$K_d = \frac{[H^+][OH^-]}{[HOH]}$	$K_i = \frac{[H_3O^+][OH^-]}{[HOH]^2}$

Note that water produces two conjugate acid-conjugate base pairs: HOH/OH^- and H_3O^+/HOH.

For every mole of H^+ (or H_3O^+), 1 mole of OH^- is produced. In pure water $[H^+] = 10^{-7}\,M$. $\therefore$ $[OH^-] = 10^{-7}\,M$. The molarity of HOH can be calculated as follows:

$$M = \frac{\text{number of moles } H_2O}{\text{liter}} \qquad \text{number of moles} = \frac{\text{wt}_g}{\text{MW}}$$

A liter of water weighs 1000 g. The MW of H_2O is 18.

$$\therefore \quad M = \frac{1000/18\text{ g}}{1\text{ liter}} = 55.6$$

The M of H_2O is actually 55.6 M (original concentration), minus 10^{-7} M (the amount that ionized). However, this amount is so close to 55.6 that we may neglect the 10^{-7} M. We can now substitute the above values into the K_d and K_i expressions.

$$K_d = \frac{(10^{-7})(10^{-7})}{55.6} = \frac{10^{-14}}{55.6}$$

$$\boxed{K_d = 1.8 \times 10^{-16}}$$

$$K_i = \frac{(10^{-7})(10^{-7})}{(55.6)^2} = \frac{10^{-14}}{3.09 \times 10^3}$$

$$\boxed{K_i = 3.24 \times 10^{-18}}$$

The molarity of H_2O is essentially constant in the dilute solutions considered in most biochemical problems. Consequently, we can define a new constant for the dissociation or ionization of water, K_w, which combines the two constants (K_d and $[H_2O]$ or K_i and $[H_2O]^2$).

$$K_w = K_d \times [H_2O]$$
$$K_w = (1.8 \times 10^{-16})(55.6)$$

$$\boxed{K_w = 1 \times 10^{-14} = [H^+][OH^-]}$$

$$K_w = K_i \times [H_2O]^2$$
$$K_w = (3.24 \times 10^{-18})(55.6)^2$$
$$= (3.24 \times 10^{-18})(3.09 \times 10^3)$$

$$\boxed{K_w = 1 \times 10^{-14} = [H_3O^+][OH^-]} \tag{20}$$

pH *AND* pOH

pH is a shorthand way of designating the hydrogen ion activity of a solution. By definition pH is the negative logarithm of the hydrogen ion activity. Similarly, pOH is the negative logarithm of the hydroxyl ion activity.

$$\begin{aligned} \text{pH} &= -\log a_{H^+} = \log \frac{1}{a_{H^+}} \\ &= -\log \gamma_{H^+}[H^+] \\ &= \log \frac{1}{\gamma_{H^+}[H^+]} \end{aligned}$$

$$\begin{aligned} \text{pOH} &= -\log a_{OH^-} = \log \frac{1}{a_{OH^-}} \\ &= -\log \gamma_{OH^-}[OH^-] \\ &= \log \frac{1}{\gamma_{OH^-}[OH^-]} \end{aligned}$$

In dilute solutions of acids and bases and in pure water, the activities of H^+ and OH^- may be considered to be the same as their concentrations.

$$\boxed{\text{pH} = -\log [H^+] = \log \frac{1}{[H^+]}} \qquad \boxed{\text{pOH} = -\log [OH^-] = \log \frac{1}{[OH^-]}} \tag{21}$$

In all aqueous solutions the equilibrium for the ionization of water must be satisfied, that is, $[H^+][OH^-] = K_w = 10^{-14}$. Thus, if $[H^+]$ is known, we can easily calculate $[OH^-]$. Furthermore, we can derive the following relationship between pH and pOH:

$$[H^+][OH^-] = K_w$$

Taking logarithms:

$$\log [H^+] + \log [OH^-] = \log K_w$$

$$-\log [H^+] - \log [OH^-] = -\log K_w$$

$$-\log [H^+] = \text{pH} \qquad -\log [OH^-] = \text{pOH} \qquad -\log K_w = \text{p}K_w$$

$$\therefore \quad \text{pH} + \text{pOH} = \text{p}K_w$$

$$K_w = 10^{-14} \qquad \text{p}K_w = -\log 10^{-14} = +14$$

$$\therefore \quad \boxed{\textbf{pH} + \textbf{pOH} = \textbf{14}} \tag{22}$$

Thus, if any one of the values $[H^+]$, $[OH^-]$, pH, or pOH is known, the other three can be calculated easily. At concentrations of H^+ and OH^- greater than 0.1 *M*, the activity coefficients must be taken into account.

· Problem 1-9

What are the (a) H^+ ion concentration, (b) pH, (c) OH^- ion concentration, and (d) pOH of a 0.001 *M* solution of HCl?

Solution

(a) HCl is a "strong" inorganic acid; that is, it is essentially 100% ionized in dilute solution. Consequently, when 0.001 mole of HCl is introduced into 1 liter of H_2O, it immediately dissociates into 0.001 *M* H^+ and 0.001 *M* Cl^-.

Note that when we are dealing with strong acids, the H^+ contribution from the ionization of water is neglected.

(b)

$$\text{pH} = -\log [H^+]$$

$$= -\log 10^{-3}$$

$$= -(-3) = +3$$

$$\boxed{\textbf{pH} = \textbf{3}}$$

or

$$\text{pH} = \log \frac{1}{[H^+]}$$

$$= \log \frac{1}{10^{-3}}$$

$$= \log 10^{3}$$

$$\boxed{\textbf{pH} = \textbf{3}}$$

(c)

$$[H^+][OH^-] = K_w \qquad [OH^-] = \frac{K_w}{[H^+]}$$

$$[OH] = \frac{1 \times 10^{-14}}{1 \times 10^{-3}} \qquad \boxed{[\textbf{OH}^-] = \textbf{1} \times \textbf{10}^{-11}}$$

(d)
$$\mathrm{pOH} = -\log\,[\mathrm{OH^-}]$$
$$= -\log\,(10^{-11})$$
$$= -(-11)$$
$$\boxed{\mathbf{pOH = 11}}$$

or

$$\mathrm{pOH} = \log \frac{1}{[\mathrm{OH^-}]}$$
$$= \log \frac{1}{10^{-11}}$$
$$= \log 10^{11}$$
$$\boxed{\mathbf{pOH = 11}}$$

or:

$$\mathrm{pH} + \mathrm{pOH} = 14, \qquad \mathrm{pOH} = 14 - \mathrm{pH}$$
$$\mathrm{pOH} = 14 - 3 \qquad \boxed{\mathbf{pOH = 11}}$$

· **Problem 1-10**

What are the (a) $[\mathrm{H^+}]$, (b) $[\mathrm{OH^-}]$, (c) pH, and (d) pOH of a 0.002 *M* solution of $\mathrm{HNO_3}$?

Solution

(a) $\mathrm{HNO_3}$ is a strong inorganic acid.

$$\boxed{[\mathrm{H^+}] = 0.002\ M = 2 \times 10^{-3}\ M}$$

(b)
$$[\mathrm{H^+}][\mathrm{OH^-}] = 1 \times 10^{-14}$$
$$[\mathrm{OH^-}] = \frac{1 \times 10^{-14}}{2 \times 10^{-3}} = 0.5 \times 10^{-11}$$
$$\boxed{[\mathrm{OH^-}] = 5 \times 10^{-12}\ M}$$

(c)
$$\mathrm{pH} = \log \frac{1}{[\mathrm{H^+}]}$$
$$= \log \frac{1}{2 \times 10^{-3}}$$
$$= \log 0.5 \times 10^{3}$$
$$= \log 5 \times 10^{2}$$
$$= \log 5 + \log 10^{2}$$
$$= 0.699 + 2$$
$$\boxed{\mathbf{pH = 2.699}}$$

or

$$\mathrm{pH} = \log 500$$
$$\log 500 = 2.699$$
$$\boxed{\mathbf{pH = 2.699}}$$

where 2 = the number of places between the first significant figure and the decimal point and 0.699 = log of "5."

Check:

$$10^{-2}\,M\,[\mathrm{H^+}] = \mathrm{pH}\ 2$$
$$10^{-3}\,M\,[\mathrm{H^+}] = \mathrm{pH}\ 3$$
$$\therefore\quad 2\times10^{-3}\,M\,[\mathrm{H^+}] = \mathrm{pH\ between\ 2\ and\ 3}$$

(d) $\mathrm{pH} + \mathrm{pOH} = 14$

$$\mathrm{pOH} = 14.000 - 2.699$$

$$\boxed{\mathbf{pOH = 11.301}}$$

or

$$\mathrm{pOH} = \log\frac{1}{[\mathrm{OH^-}]}$$
$$= \log\frac{1}{5\times10^{-12}}$$
$$= \log 0.2\times10^{12}$$
$$= \log 2\times10^{11}$$
$$= \log 2 + \log 10^{11}$$
$$= 0.301 + 11$$

$$\boxed{\mathbf{pOH = 11.301}}$$

Problem 1-11

What is the concentration of HNO_3 in a solution that has a pH of 3.4?

Solution

$$\mathrm{pH} = \log\frac{1}{[\mathrm{H^+}]} = 3.4$$

where 3 = number of places between first significant figure and the decimal point. Look up antilog of "4."

antilog of 4 = "2512"

$$\therefore\quad [\mathrm{H^+}] = \frac{1}{2512}$$
$$= \frac{1}{2.512\times10^{3}}$$
$$= 0.398\times10^{-3}$$

$$\boxed{\mathbf{[H^+] = 3.98\times10^{-4}}\ M}$$

or

$$[\mathrm{H^+}] = 10^{-\mathrm{pH}}$$
$$= 10^{-3.4}$$
$$= 10^{-4}\times10^{+0.6}$$

Look up antilog of 0.6

antilog of 0.6 = "398"
= 3.98

$$\boxed{\mathbf{[H^+] = 3.98\times10^{-4}}\ M}$$

$$\therefore\quad HNO_3 = 3.98\times10^{-4}\,M \text{ assuming 100\% ionization}$$

Check:

$$\mathrm{pH}\ 3 = 10^{-3}\,M\,[HNO_3]$$
$$\mathrm{pH}\ 4 = 10^{-4}\,M\,[HNO_3]$$
$$\therefore\quad \mathrm{pH}\ 3.4 = [HNO_3] \text{ between } 10^{-4} \text{ and } 10^{-3}\,M$$

Problem 1-12

How many (a) H^+ ions and (b) OH^- ions are present in 250 ml of a solution of pH 3?

Solution

(a)

$$pH = 3$$
$$\therefore \quad [H^+] = 10^{-3}\,M \ (10^{-3} \text{ g-ions/liter})$$
$$1 \text{ g-ion/liter} = 6.023 \times 10^{23} \text{ ions/liter}$$
$$\therefore \quad 10^{-3} \text{ g-ions/liter} = 6.023 \times 10^{20} \text{ ions/liter}$$
$$\therefore \quad \frac{6.023 \times 10^{20}}{4} = \boxed{1.506 \times 10^{20} \text{ ions/250 ml}}$$

(b)

$$pH + pOH = 14$$
$$pOH = 14 - 3 = 11$$
$$[OH^-] = 10^{-11}\,M \text{ or } 10^{-11} \text{ g-ions/liter}$$
$$10^{-11} \text{ g-ions/liter} \times 6.023 \times 10^{23} \text{ ions/g-ion} = 6.023 \times 10^{12} \text{ ions/liter}$$
$$\frac{6.023 \times 10^{12}}{4} = \boxed{1.506 \times 10^{12} \text{ ions/250 ml}}$$

Problem 1-13

What is the pH of a $10^{-8}\,M$ solution of HCl?

Solution

The first tendency of many students is to say "pH = 8." This is obviously incorrect. No matter how much one dilutes a strong acid, the solution will never become alkaline. In this dilute solution, the contribution of H^+ ions from H_2O is actually greater than the amount contributed by HCl. As a *first approximation*, therefore, the H^+ ions from the HCl may be neglected. The pH then is around 7.

As a *second approximation*, we can solve for pH while taking into account the H^+ ions from both sources.

$$pH = -\log [H^+]$$
$$[H^+] = 10^{-7} \text{ (from } H_2O) + 10^{-8} \text{ (from HCl)}$$
$$pH = -\log (1 \times 10^{-7} + 0.1 \times 10^{-7})$$
$$= \log \frac{1}{1.1 \times 10^{-7}} = \log 0.909 \times 10^{7}$$
$$= \log 9.09 \times 10^{6} = \log 9.09 + \log 10^{6}$$
$$= 0.959 + 6 \qquad \boxed{pH = 6.959}$$

The above solution is still not completely correct. It assumes that the contribution of H^+ ions from water is still $10^{-7}\,M$ in the presence of $10^{-8}\,M$ HCl. Actually, the slight increase in H^+ ions from HCl tends to depress the ionization of H_2O, that is, shift the equilibrium of the $HOH \rightleftharpoons H^+ + OH^-$

reaction back to the left. An exact solution to the problem can be obtained in the following manner: Both HOH and HCl ionize to form H^+ ions.

$$HOH \leftrightharpoons H^+ + OH^-$$
$$HCl \rightarrow H^+ + Cl^-$$
$$\text{Let}\quad X = [H^+] \text{ from } H_2O$$
$$\therefore\quad [OH^-] = X$$
$$[H^+] \text{ from HCl} = 10^{-8}\,M$$
$$\therefore\quad [H^+] = X + 10^{-8}, [OH^-] = X$$
$$[H^+][OH^-] = 10^{-14}$$
$$(X + 10^{-8})(X) = 10^{-14}$$
$$X^2 + 10^{-8}X = 10^{-14}$$
$$X^2 + 10^{-8}X - 10^{-14} = 0$$

The above equation can be solved by substituting into the general solution for a quadratic equation:

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where $a = 1$, $b = 10^{-8}$ and $c = -10^{-14}$.

$$X = \frac{-10^{-8} \pm \sqrt{(10^{-8})^2 - 4(-10^{-14})}}{2} = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4 \times 10^{-14}}}{2}$$
$$= \frac{-10^{-8} \pm \sqrt{4.01 \times 10^{-14}}}{2} = \frac{-10^{-8} \pm 2.0025 \times 10^{-7}}{2}$$
$$= \frac{-10^{-8} \pm 20.025 \times 10^{-8}}{2}$$
$$= \frac{19.025 \times 10^{-8}}{2} \quad \text{and} \quad \frac{-21.025 \times 10^{-8}}{2}$$
$$X = 9.5125 \times 10^{-8} \quad \text{(neglecting the negative value)}$$
$$[H^+] = X + 10^{-8}$$
$$= 9.5125 \times 10^{-8} + 10^{-8} = 10.5125 \times 10^{-8}$$
$$pH = \log \frac{1}{10.5125 \times 10^{-8}}$$
$$= \log 0.09512 \times 10^8 = \log 9.512 \times 10^6$$
$$= \log 9.512 + \log 10^6 = 0.978 + 6$$

$$\boxed{pH = 6.978}$$

· Problem 1-14

What are the (a) a_{H^+} and (b) γ_{H^+} in a 0.010 M solution of HNO_3 if the pH is 2.08?

Solution

In this problem we can no longer assume that $a_{H^+} = [H^+]$. It is obvious that if $a_{H^+} = [H^+]$ and $pH = -\log [H^+]$, the pH would be 2.0 and not 2.08. $\therefore \gamma \neq 1$.

(a)

$$\text{pH} = \log \frac{1}{a_{H^+}}$$

$$2.08 = \log \frac{1}{a_{H^+}}$$

$$\text{antilog of } 0.08 = \text{“}120\text{”}$$

$$\frac{1}{a_{H^+}} = 120$$

$$a_{H^+} = \frac{1}{120}$$

$$a_{H^+} = 0.0083$$

$$\boxed{a_{H^+} = 8.3 \times 10^{-3}}$$

or

$$a_{H^+} = 10^{-\text{pH}}$$

$$a_{H^+} = 10^{-2.08}$$

$$= 10^{-3} \times 10^{+0.92}$$

$$= 10^{-3} \times 8.3$$

$$\boxed{a_{H^+} = 8.3 \times 10^{-3}}$$

(b)

$$a_{H^+} = \gamma_{H^+}[H^+] \quad \text{where } \gamma = \text{the activity coefficient}$$

$$0.0083 = \gamma_{H^+}(0.010)$$

$$\boxed{\gamma_{H^+} = 0.83}$$

Although the *actual* concentration of HNO_3 is 0.01 *M*, the solution behaves as if only 83% of the HNO_3 molecules are dissociated; the *effective* or *apparent* concentration (a_{H^+}) is 0.0083 *M*. The HNO_3 is actually 100% ionized. Interactions of ion clouds, however, prevent full expression of the H^+ ions; that is, the shielding effects of NO_3^- ions surrounding the H^+ ions make it seem as if some of the H^+ ions are not there.

NEUTRALIZATION AND TITRATION OF STRONG ACIDS AND BASES

Problem 1-15

(a) How many milliliters of 0.025 *M* H_2SO_4 are required to neutralize exactly 525 ml of 0.06 *M* KOH? (b) What is the pH of the "neutralized" solution?

Solution

(a) number of moles (equivalents) of H^+ required = number of moles (equivalents) of OH^- present

$$\text{liters} \times N = \text{number of equivalents}$$

$$\text{liters}_{\text{acid}} \times N_{\text{acid}} = \text{liters}_{\text{base}} \times N_{\text{base}}$$

$$H_2SO_4 = 0.025\ M = 0.05\ N$$

$$\text{liters}_{\text{acid}} \times 0.05 = 0.525 \times 0.06$$

$$\text{liters}_{\text{acid}} = \frac{0.525 \times 0.06}{0.05} = 0.63$$

$$\boxed{\textbf{acid required} = \mathbf{630\ ml}}$$

(b) The neutralized solution contains only K_2SO_4 that, being a salt of a strong acid and strong base, has no effect on pH.

$$\therefore \quad \boxed{\mathbf{pH = 7}}$$

Problem 1-16

How many milliliters of 0.05 N HCl are required to neutralize exactly 8.0 g of NaOH?

Solution

At the equivalence point, the number of moles H^+ added equals the number of moles OH^- present.

$$\text{liters}_{\text{acid}} \times N_{\text{acid}} = \text{number of moles (equivalents) of } H^+ \text{ added}$$

$$\frac{\text{wt}_{\text{g NaOH}}}{\text{MW}_{\text{NaOH}}} = \text{number of moles of NaOH (and } OH^-\text{) present}$$

$$\text{liters} \times N = \frac{\text{wt}_g}{\text{MW}} \qquad \text{liters} \times 0.05 = \frac{8.0}{40}$$

$$\text{liters} = \frac{8.0}{40 \times 0.05} = \frac{8.0}{2}$$

$$= 4.0 \text{ liters} = \boxed{\mathbf{4000\ ml}}$$

Problem 1-17

Calculate the appropriate values and draw the curve for the titration of 500 ml of 0.01 N HCl with 0.01 N KOH.

Solution

A titration curve is a plot of pH versus milliliters (or equivalents or moles) of standard titrant added. For the titration of a given amount of acid, the curve is a plot of pH versus milliliters (or equivalents) of base added. The pH at any position up to the equivalence point is calculated from the concentration of excess (untitrated) H^+ remaining (taking the increased volume into account). At the equivalence point, the solution contains only KCl, a salt of a strong acid and strong base that has no effect on the pH. Therefore, pH = 7.0. The pH at positions beyond the equivalence point is calculated from the concentration of excess OH^-. The titration curve is shown in Figure 1-1.

IONIZATION OF WEAK ACIDS

In an aqueous solution a weak acid ionizes to a limited extent as follows:

$$\underset{[\text{conjugate acid}]_1}{HA} + \underset{[\text{conjugate base}]_2}{H_2O} \rightleftharpoons \underset{[\text{conjugate acid}]_2}{H_3O^+} + \underset{[\text{conjugate base}]_1}{A^-}$$

The proton released from HA is accepted by water to form the hydronium ion H_3O^+. The reversible ionization reaction can be described by an equilib-

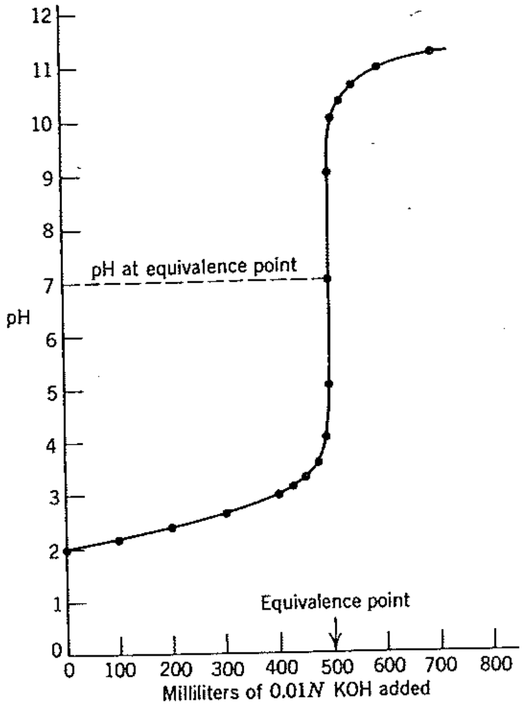


Figure 1-1 Titration of a strong acid (e.g., HCl) with a strong base (e.g., KOH).

rium constant, K_i:

$$K_i = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

Because $[H_2O]$ is itself a constant, we can define a new constant, K_a, that combines K_i and $[H_2O]$.

$$K_i[H_2O] = K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Because $[H_3O^+]$ is the same as the "hydrogen ion concentration," $[H^+]$, the K_a expression is usually written as shown below.

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

It is not surprising that the above K_a expression is identical to the expression that we would obtain if we assumed that the weak acid dissociates directly to yield H^+ and A^-:

$$HA \rightleftharpoons H^+ + A^-$$

IONIZATION OF WEAK BASES

In an aqueous solution, inorganic bases yield OH^- ions directly by dissociation.

$$KOH \rightarrow K^+ + OH^-$$

Organic bases such as amines R-NH_2, contain no OH to dissociate. However, if we assume that the R-NH_2 reacts with H_2O to form "R-NH_3OH," then we can consider the "dissociation" of organic bases to yield OH^- ions directly just as we do for inorganic bases. In fact, this is frequently done when we consider aqueous ammonia, NH_3; we assume that the dissociable substance present is "NH_4OH."

$$\text{“R-NH}_3\text{OH”} \rightleftharpoons \text{R-NH}_3^+ + \text{OH}^-$$
$$\text{“NH}_4\text{OH”} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$

We should bear in mind that "R-NH_3OH" refers to the sum of R-NH_2 plus any small amount of R-NH_3OH that might exist.

It usually makes little difference whether we consider the ionization of an acid as a simple dissociation or as the true ionization involving water as a conjugate base. However, in dealing with organic bases, it is usually more fruitful to consider the ionization as it actually occurs.

$$\underset{\text{[conjugate base]}_1}{\text{R-NH}_2} + \underset{\text{[conjugate acid]}_2}{\text{HOH}} \rightleftharpoons \underset{\text{[conjugate acid]}_1}{\text{R-NH}_3^+} + \underset{\text{[conjugate base]}_2}{\text{OH}^-}$$

The two conjugate acid-conjugate base pairs involved are R-NH_3^+/R-NH_2 and HOH/OH^-. The ionization can be described by an ionization constant, K_i.

$$K_i = \frac{[\text{R-NH}_3^+][\text{OH}^-]}{[\text{R-NH}_2][\text{H}_2\text{O}]}$$

Again, we can define a new constant, K_b, that combines the two constants, K_i and $[H_2O]$.

$$K_i[\text{H}_2\text{O}] = K_b = \frac{[\text{R-NH}_3^+][\text{OH}^-]}{[\text{R-NH}_2]}$$

The K_b expression is exactly the same as that which we obtain if we assume that R-NH_2 is actually R-NH_3OH, which dissociates directly to yield R-NH_3^+ and OH^-.

RELATIONSHIP BETWEEN K_a AND K_b FOR WEAK ACIDS AND BASES

When a weak acid, HA, is dissolved in water, it ionizes as shown previously to form H_3O^+ and the corresponding conjugate base, A^-. A K_a expression can be written for the ionization.

$$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \qquad K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

If we *start* with the conjugate base, A^-, and dissolve it in water, it ionizes as a typical base; it accepts a proton from H_2O to form OH^- and the corresponding conjugate acid, HA. A K_b expression can be written for this ionization.

$$\text{A}^- + \text{HOH} \rightleftharpoons \text{HA} + \text{OH}^- \qquad K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

Solving the K_a and K_b expressions for $[H_3O^+]$ and $[OH^-]$:

$$[H_3O^+] = \frac{[HA]K_a}{[A^-]} \qquad [OH^-] = \frac{[A^-]K_b}{[HA]}$$

Substituting into $[H_3O^+][OH^-] = K_w$:

$$\frac{[HA]K_a}{[A^-]} \times \frac{[A^-]K_b}{[HA]} = K_w$$

$$\text{or} \quad \boxed{K_a \times K_b = K_w} \qquad (23)$$

Taking logarithms:

$$\log K_a + \log K_b = \log K_w$$
$$-\log K_a - \log K_b = -\log K_w$$

Just as $-\log[H^+]$ has been defined as pH, we can define $-\log K_a$ as pK_a, $-\log K_b$ as pK_b, and $-\log K_w$ as pK_w (which equals 14).

$$\therefore \quad \boxed{pK_a + pK_b = 14} \qquad (23a)$$

For polyprotic acids, the K_a values are numbered in order of decreasing acid strength (K_{a_1}, K_{a_2}, etc.). The K_b values are numbered in order of decreasing base strength. However, remember that the conjugate base of the strongest acid group is the weakest basic group, and vice versa. The K_a and K_b values are numbered accordingly as shown below.

$$\begin{tikzcd}
H_2A \arrow[r, shift left, "K_{a_1}"] & H^+ + HA^- \arrow[l, shift left, "K_{b_2}"] \arrow[d, shift right, "K_{a_2}"'] \\
& H^+ + A^{2-} \arrow[u, shift right, "K_{b_1}"']
\end{tikzcd}$$

We must be sure to use the K_a and K_b (or pK_a and pK_b) of *the same ionization.* For the diprotic acid illustrated above, the correct expressions are as follows:

$$K_{a_1} \times K_{b_2} = K_w \qquad pK_{a_1} + pK_{b_2} = pK_w$$
$$K_{a_2} \times K_{b_1} = K_w \qquad pK_{a_2} + pK_{b_1} = pK_w$$

pH *OF SOLUTIONS OF WEAK ACIDS*

The dissociation of a weak monoprotic acid, HA, yields H^+ and A^- in equal concentrations. If K_a and the initial concentration of HA are known, H^+ can be calculated easily:

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]^2}{[HA]}$$

$$\boxed{[H^+]=\sqrt{K_a[HA]}} \tag{24}$$

Equation 24 assumes that the degree of ionization is small so that [HA] remains essentially unchanged. To obtain an expression giving pH, we put the above equation in logarithmic form:

$$\log[H^+]=\tfrac{1}{2}\log K_a[HA]=\tfrac{1}{2}(\log K_a+\log[HA])$$

$$-\log[H^+]=\frac{-\log K_a-\log[HA]}{2}$$

$$\text{or}\quad \boxed{pH=\frac{pK_a+p[HA]}{2}} \tag{25}$$

where p[HA] is the negative logarithm of the HA concentration. Similar relationships can be derived for weak bases, A^- or RNH_2.

$$\boxed{[OH^-]=\sqrt{K_b[A^-]}}\quad \text{and}\quad \boxed{pOH=\frac{pK_b+p[A^-]}{2}} \tag{26}$$

Problem 1-18

The weak acid, HA, is 0.1% ionized (dissociated) in a 0.2 *M* solution. (a) What is the equilibrium constant for the dissociation of the acid (K_a)? (b) What is the pH of the solution? (c) How much "weaker" is the active acidity of the HA solution compared to a 0.2 *M* solution of HCl? (d) How many milliliters of 0.1 *N* KOH would be required to neutralize completely 500 ml of the 0.2 *M* HA solution?

Solution

(a)	HA	$\rightleftharpoons$	H^+	+	A^-
Start:	0.2 *M*		0		0
Change:	−(0.1% of 0.2 *M*) =				
	$-2\times10^{-4}\,M$		$+2\times10^{-4}\,M$		$+2\times10^{-4}\,M$
Equilibrium:	$0.2-2\times10^{-4}\,M$		$2\times10^{-4}\,M$		$2\times10^{-4}\,M$

$$K_a=\frac{[H^+][A^-]}{[HA]}=\frac{(2\times10^{-4})(2\times10^{-4})}{0.2-2\times10^{-4}}$$

When the amount of HA that has dissociated is small compared to the original concentration of HA, (e.g., 10% or less) the K_a expression may be simplified by ignoring the subtraction in the denominator.

$$K_a=\frac{(2\times10^{-4})(2\times10^{-4})}{0.2}=\frac{4\times10^{-8}}{2\times10^{-1}}$$

$$\boxed{K_a=2\times10^{-7}}$$

(b)

$$\begin{aligned}\mathrm{pH} &= \log\frac{1}{[\mathrm{H^+}]} = \log\frac{1}{2\times10^{-4}}\\ &= \log 0.5\times10^{4} = \log 5\times10^{3}\\ &= \log 5 + \log 10^{3} = 0.7+3\end{aligned}$$

$$\boxed{\mathrm{pH} = 3.7}$$

(c) A 0.2 M solution of HCl would be 100% ionized and yield 0.2 M H^+.

$$\mathrm{pH} = \log\frac{1}{[\mathrm{H^+}]} = \log\frac{1}{2\times10^{-1}} = \log 0.5\times10^{1} = \log 5$$

$$\boxed{\mathrm{pH} = 0.7} \quad \text{(assuming } \gamma = 1\text{)}$$

∴ The weak acid is 3 pH units less acid than a comparable HCl solution. Remember the pH scale is a *logarithmic* scale, not a linear scale. The HA then is 10^3 or 1000 times less acid than the HCl (*not* 3 times).

(d) Although the *active* acidity $[H^+]$ of the weak acid is 1000 times less than that of the HCl solution, the *total* acidity (free H^+ plus the undissociated hydrogen in HA) is the same. When OH^- is added, it reacts with the free H^+ to form H_2O. Some HA then immediately dissociates to H^+ and A^- to reestablish the equilibrium. This H^+ is also neutralized by further additions of OH^- and so on until all the HA is neutralized. Neutralization calculations for weak acids then may be conducted in the same manner as for strong acids.

$$\text{number of moles of OH}^- \text{ required} = \text{total number of moles H}^+ \text{ available}$$

$$\text{liters}_{\text{base}} \times N_{\text{base}} = \text{liters}_{\text{acid}} \times N_{\text{acid}}$$

HA is monoprotic.

$$\therefore\ N = M$$

$$\text{liters}_{\text{base}} \times 0.1 = 0.5 \times 0.2$$

$$\text{liters}_{\text{base}} = \frac{0.5\times0.2}{0.1} = \frac{0.1}{0.1} = \boxed{\textbf{1 liter of base required}}$$

Problem 1-19

The K_a for a weak acid, HA, is 1.6×10^{-6}. What are the (a) pH and (b) degree of ionization of the acid in a 10^{-3} M solution? (c) Calculate pK_a and pK_b.

Solution

(a) Let $x = M$ of HA that dissociates. ∴ $x = M$ of H^+ and also M of A^- produced.

	HA $\rightleftharpoons$	H^+ +	A^-
Start:	$10^{-3}\,M$	0	0
Change:	$-x\,M$	$+x\,M$	$+x\,M$
Equilibrium:	$10^{-3} - x\,M$	$x\,M$	$x\,M$

$$K_a = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} = \frac{(x)(x)}{10^{-3}-x} = 1.6\times10^{-6}$$

First calculate x assuming that x is very much smaller than the concentration of un-ionized acid, that is, assuming that the acid is less than 10% ionized. The denominator of the K_a expression may then be simplified.

$$1.6\times10^{-6}=\frac{x^2}{10^{-3}}$$

$$x^2=1.6\times10^{-9}=16\times10^{-10}$$

$$x=\sqrt{16\times10^{-10}}=\sqrt{16}\times\sqrt{10^{-10}}=4.0\times10^{-5}$$

$$\boxed{[\mathrm{H}^+]=4\times10^{-5}\,M}$$

or using equation 24:

$$[\mathrm{H}^+]=\sqrt{K_a[\mathrm{HA}]}=\sqrt{(1.6\times10^{-6})(10^{-3})}$$

$$=\sqrt{16\times10^{-10}}=4\times10^{-5}\,M$$

$$\mathrm{pH}=\log\frac{1}{[\mathrm{H}^+]}$$

$$=\log\frac{1}{4\times10^{-5}}=\log 0.25\times10^{5}=\log 2.5\times10^{4}$$

$$=\log 2.5+\log 10^{4}=0.398+4$$

$$\boxed{\mathrm{pH}=4.398}$$

(b)

$$\text{degree of ionization}=\frac{[\mathrm{H}^+]}{[\mathrm{HA}]_{\mathrm{orig}}}\times100$$

$$=\frac{4\times10^{-5}}{10^{-3}}\times100=\frac{4\times10^{-3}}{10^{-3}}=\boxed{4\%}$$

The acid is indeed less than 10% ionized. Therefore, the simplification of the denominator term in the expression for K_a is reasonably valid.

(c) The pK_a is the negative logarithm of K_a.

$$\mathrm{p}K_a=-\log K_a=\log\frac{1}{K_a}$$

$$\mathrm{p}K_a=\log\frac{1}{1.6\times10^{-6}}=\log 6.25\times10^{5}$$

$$\mathrm{p}K_a=\log 6.25+\log 10^{5}=0.796+5$$

$$\boxed{\mathrm{p}K_a=5.796}$$

$$\mathrm{p}K_a+\mathrm{p}K_b=14\qquad \mathrm{p}K_b=14-\mathrm{p}K_a=14-5.796$$

$$\boxed{\mathrm{p}K_b=8.204}$$

• Problem 1-20

Calculate (a) the H^+ ion concentration in a 0.02 M solution of a moderately strong acid, HA, where $K_a = 3 \times 10^{-2}\ M$, and (b) the degree of dissociation of the acid.

Solution

(a) Let:

$x = M$ of HA dissociated
$= M$ of H^+ produced

	HA	$\rightleftharpoons$	H^+	+	A^-
Start:	$0.02\ M$		0		0
Change:	$-x\ M$		$+x\ M$		$+x\ M$
Equilibrium:	$0.02 - x\ M$		$x\ M$		$x\ M$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad 3 \times 10^{-2} = \frac{(x)(x)}{0.02 - x}$$

The relatively large $K_a (>10^{-3})$ suggests that the acid is more than 10% dissociated. Therefore, the denominator term in the K_a expression should not be simplified.

$$(3 \times 10^{-2})(0.02 - x) = x^2$$
$$6 \times 10^{-4} - 3 \times 10^{-2}x = x^2$$
$$x^2 + 3 \times 10^{-2}x - 6 \times 10^{-4} = 0$$

Solve for x using the general solution for quadratic equations.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where $a = 1 \quad b = 3 \times 10^{-2} \quad c = -6 \times 10^{-4}$.

$$x = \frac{-3 \times 10^{-2} \pm \sqrt{(3 \times 10^{-2})^2 - 4(-6 \times 10^{-4})}}{2}$$

$$= \frac{-3 \times 10^{-2} \pm \sqrt{(9 \times 10^{-4}) + 24 \times 10^{-4}}}{2}$$

$$= \frac{-3 \times 10^{-2} \pm \sqrt{33 \times 10^{-4}}}{2} = \frac{-3 \times 10^{-2} \pm 5.74 \times 10^{-2}}{2}$$

$$= \frac{+2.74 \times 10^{-2}}{2} \quad \text{(neglecting the negative answer)}$$

$$\boxed{[H^+] = 1.37 \times 10^{-2}\ M}$$

(b)
$$\text{degree of dissociation} = \frac{[H^+]}{[HA]_{\text{orig}}} \times 100$$
$$= \frac{0.0137}{0.0200} \times 100 \quad \boxed{= 68.5\%}$$

• Problem 1-21

What is the pH of a $3.5 \times 10^{-2}\ M$ solution of an amine with a pK_a of 9.6?

Solution

$$\begin{aligned} pK_b &= pK_w - pK_a \\ &= 14 - 9.6 \\ pK_b &= 4.4 \end{aligned}$$

$$\begin{aligned} p[RNH_2] &= -\log[RNH_2] \\ &= \log\frac{1}{3.5\times10^{-2}} \\ &= \log 28.57 \\ p[RNH_2] &= 1.456 \end{aligned}$$

$$\begin{aligned} pOH &= \frac{pK_b + p[RNH_2]}{2} = \frac{4.4 + 1.456}{2} \\ &= \frac{5.86}{2} = 2.93 \\ pH &= 14 - pOH = 14 - 2.93 \end{aligned}$$

$$\boxed{\mathbf{pH = 11.07}}$$

· Problem 1-22

Calculate the ionic strength of a 0.1 M solution of butyric acid. $K_a = 1.5\times10^{-5}$.

Solution

Butyric acid is only partially ionized. The undissociated molecules have no effect on the ionic strength of the solution. First calculate M_{H^+} and M_{butyrate^-}.

$$K_a = \frac{[H^+][\text{butyrate}^-]}{[\text{butyric acid}]} = \frac{(X)(X)}{0.1 - X} = \frac{X^2}{0.1} = 1.5\times10^{-5}$$

$$X^2 = 1.5\times10^{-6}$$

$$X = \sqrt{150\times10^{-8}} = 12.25\times10^{-4}$$

$$[H^+] = 1.225\times10^{-3}\,M, \quad [\text{butyrate}^-] = 1.225\times10^{-3}\,M$$

$$\frac{\Gamma}{2} = \frac{1}{2}\sum M_i Z_i^2 = \frac{1}{2}[M_{H^+}Z_{H^+}^2 + M_{\text{butyrate}^-}Z_{\text{butyrate}^-}^2]$$

$$= \frac{(1.225\times10^{-3})(1)^2 + (1.225\times10^{-3})(-1)^2}{2}$$

$$\boxed{\frac{\Gamma}{2} = 1.225\times10^{-3}}$$

EFFECT OF CONCENTRATION ON DEGREE OF DISSOCIATION

As a consequence of the law of mass action, the degree of dissociation of a weak acid varies with concentration. A dissociating system of the type $HA \rightleftharpoons H^+ + A^-$ has an unequal number of particles on the two sides of the equilibrium. As the total concentration of all species increases, the equilibrium shifts to the left (i.e., to the side with the fewer particles). As the total concentration of all species decreases, the equilibrium shifts to the right (i.e., to the side with the greater number of particles). The equilibrium constant remains constant. Only the relative proportions of the various species change.

A simple example will illustrate why the relative proportions must change upon dilution if K_{eq} is to remain constant. Consider the reaction $A \rightleftharpoons B + C$. At equilibrium, the concentrations of A, B, and C are related by:

$$K_{eq} = \frac{[B][C]}{[A]} = 1.0$$

Let the letters A, B, and C stand for some equilibrium concentrations, for example, 1 *M*. Now dilute the solution tenfold. If the relative proportions of A, B, and C remain constant:

$$\text{New concentration of A} = 0.1\,[A] = 0.1\,M$$
$$\text{New concentration of B} = 0.1\,[B] = 0.1\,M$$
$$\text{New concentration of C} = 0.1\,[C] = 0.1\,M$$

But $$\frac{(0.1)(0.1)}{0.1} \text{ does } \textit{not} \text{ equal } 1.0$$

Therefore, the relative concentrations must change to reestablish equilibrium. B and C increase while A decreases.

A mathematical relationship between concentration, K_a, and the degree of dissociation can be derived easily.

	HA	$\rightleftharpoons$	H^+	$+$	A^-
Start:	C		0		0
Change:	$-nC$		$+nC$		$+nC$
Equilibrium:	$C - nC$		nC		nC

where C = the original total concentration of HA
n = the fraction dissociated (as a decimal)

$$K_a = \frac{(nC)(nC)}{(C - nC)} \qquad K_aC - K_anC = n^2C^2$$

$$K_a - K_an = n^2C \qquad K_a(1 - n) = n^2C$$

$$\boxed{C = \frac{1-n}{n^2}K_a} \tag{27}$$

If nC is very small compared to C, the expression for K_a simplifies to:

$$K_a = \frac{(nC)(nC)}{C} = \frac{n^2C^2}{C} = n^2C$$

Solving for C or n:

$$\boxed{C = \frac{K_a}{n^2}} \quad \text{and} \quad \boxed{n = \sqrt{\frac{K_a}{C}}} \tag{28}$$

Problem 1-23

At what concentration (in terms of K_a) of a weak acid, HA, will the acid be (a) 10% dissociated, (b) 50% dissociated, and (c) 90% dissociated?

Solution

(a) $$C = \frac{1-n}{n^2} K_a = \frac{1-0.1}{(0.1)^2} K_a = \frac{0.9}{0.01} K_a \qquad \boxed{C = 90K_a}$$

(b) $$C = \frac{1-0.5}{(0.5)^2} K_a = \frac{0.5}{0.25} K_a \qquad \boxed{C = 2K_a}$$

(c) $$C = \frac{1-0.9}{(0.9)^2} K_a = \frac{0.1}{0.81} K_a \qquad \boxed{C = 0.123K_a}$$

Thus, we see that the degree of dissociation increases as the initial concentration of HA decreases.

"HYDROLYSIS" OF SALTS OF WEAK ACIDS AND BASES

Salts of weak acids (the conjugate base anion of weak acids) react with water to produce the weak parent acid (conjugate acid) and OH^- ions.

$$A^- + HOH \rightleftharpoons HA + OH^-$$

We can see that the "hydrolysis" is nothing more than the ionization of the conjugate base as described earlier. The "hydrolysis constant," K_h, is identical to K_b.

$$K_{eq} = \frac{[HA][OH^-]}{[A^-][HOH]} \qquad K_{eq}[HOH] = K_h = \frac{[HA][OH^-]}{[A^-]} = K_b$$

Similarly, salts of weak bases (the conjugate acid of weak bases) react with water to produce the weak parent base and H^+ ions.

$$R\text{-}NH_3^+ + HOH \rightleftharpoons R\text{-}NH_2 + H_3O^+$$
$$NH_4^+ + HOH \rightleftharpoons NH_3 + H_3O^+$$

or

$$NH_4^+ + HOH \rightleftharpoons \text{"}NH_4OH\text{"} + H^+$$

Again, we see that the "hydrolysis" is nothing more than the usual ionization of the conjugate acid. In this instance, the K_h that is defined is identical to K_a for the conjugate acid.

$$K_{eq} = \frac{[R\text{-}NH_2][H_3O^+]}{[R\text{-}NH_3^+][HOH]} \qquad K_{eq}[HOH] = K_h = \frac{[R\text{-}NH_2][H_3O^+]}{[R\text{-}NH_3^+]} = K_a$$

⊛ **Problem 1-24**

(a) Calculate the pH of a 0.1 *M* solution of NH_4Cl. The K_b for NH_4OH is 1.8×10^{-5}. (b) What is the degree of hydrolysis of the salt?

Solution

(a) NH_4Cl is a salt of a weak base and a strong acid. Therefore a solution of NH_4Cl will be acidic because of "hydrolysis" of the NH_4^+ ion.

$$NH_4^+ + HOH \rightleftharpoons NH_4OH + H^+$$

$$K_h = K_a = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} = 5.56 \times 10^{-10}$$

Let

$$y = M \text{ of } NH_4OH \text{ produced upon hydrolysis}$$

$$\therefore \quad y = M \text{ of } H^+ \text{ produced upon hydrolysis}$$

$$\frac{(y)(y)}{(0.1 - y)} = 5.56 \times 10^{-10}$$

Simplifying:

$$y^2 = 5.56 \times 10^{-11} \qquad y = \sqrt{55.6} \times \sqrt{10^{-12}}$$

$$[H^+] = 7.46 \times 10^{-6} \qquad pH = \log \frac{1}{7.46 \times 10^{-6}}$$

$$\boxed{pH = 5.13}$$

(b)

$$\text{degree of hydrolysis} = \frac{[H^+]}{[NH_4^+]} \times 100\% = \frac{7.46 \times 10^{-6}}{10^{-1}} \times 100$$

$$= \frac{7.46 \times 10^{-4}}{10^{-1}} = \boxed{7.46 \times 10^{-3}\%}$$

Because the NH_4^+ is less than 10% hydrolyzed (ionized), our substitution of 0.1 M for $0.1 - y\,M$ is reasonably valid.

HENDERSON-HASSELBALCH EQUATION

A useful expression relating the (a) K_a of a weak acid, HA, and the pH of a solution of the weak acid or (b) K_b of a weak base and the pOH of a solution of the weak base can be derived.

(a)

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Rearranging terms:

$$[H^+] = K_a \frac{[HA]}{[A^-]}$$

Taking logarithms of both sides:

$$\log [H^+] = \log K_a + \log \frac{[HA]}{[A^-]}$$

Multiplying both sides by -1:

$$-\log[\mathrm{H}^+] = -\log K_a - \log\frac{[\mathrm{HA}]}{[\mathrm{A}^-]}$$

$$\mathrm{pH} = \mathrm{p}K_a - \log\frac{[\mathrm{HA}]}{[\mathrm{A}^-]}$$

$$\boxed{\mathbf{pH} = \mathbf{p}K_a + \mathbf{log}\frac{[\mathbf{A}^-]}{[\mathbf{HA}]}} \qquad (29)$$

(b)

$$K_b = \frac{[\mathrm{M}^+][\mathrm{OH}^-]}{[\mathrm{MOH}]}$$

$$[\mathrm{OH}^-] = K_b\frac{[\mathrm{MOH}]}{[\mathrm{M}^+]}$$

$$\log[\mathrm{OH}^-] = \log K_b + \log\frac{[\mathrm{MOH}]}{[\mathrm{M}^+]}$$

$$-\log[\mathrm{OH}^-] = -\log K_b - \log\frac{[\mathrm{MOH}]}{[\mathrm{M}^+]}$$

$$\mathrm{pOH} = \mathrm{p}K_b - \log\frac{[\mathrm{MOH}]}{[\mathrm{M}^+]}$$

$$\boxed{\mathbf{pOH} = \mathbf{p}K_b + \mathbf{log}\frac{[\mathbf{M}^+]}{[\mathbf{MOH}]}}$$

$$K_b = \frac{[\mathrm{R\text{-}NH_3^+}][\mathrm{OH}^-]}{[\mathrm{R\text{-}NH_2}]}$$

$$[\mathrm{OH}^-] = K_b\frac{[\mathrm{R\text{-}NH_2}]}{[\mathrm{R\text{-}NH_3^+}]}$$

$$\log[\mathrm{OH}^-] = \log K_b + \log\frac{[\mathrm{R\text{-}NH_2}]}{[\mathrm{R\text{-}NH_3^+}]}$$

$$-\log[\mathrm{OH}^-] = -\log K_b - \log\frac{[\mathrm{R\text{-}NH_2}]}{[\mathrm{R\text{-}NH_3^+}]}$$

$$\mathrm{pOH} = \mathrm{p}K_b - \log\frac{[\mathrm{R\text{-}NH_2}]}{[\mathrm{R\text{-}NH_3^+}]}$$

$$\boxed{\mathbf{pOH} = \mathbf{p}K_b + \mathbf{log}\frac{[\mathbf{R\text{-}NH_3^+}]}{[\mathbf{R\text{-}NH_2}]}} \qquad (30)$$

Note that when the concentrations of conjugate acid and conjugate base are equal, $\mathrm{pH} = \mathrm{p}K_a$ and $\mathrm{pOH} = \mathrm{p}K_b$. This same relationship can be seen from the original K_a or K_b expressions; when $[\mathrm{A}^-] = [\mathrm{HA}]$, $[\mathrm{H}^+] = K_a$ and when $[\mathrm{R\text{-}NH_2}] = [\mathrm{R\text{-}NH_3^+}]$, $[\mathrm{OH}^-] = K_b$.

According to the above equations, the pH of a solution containing HA and A^- is independent of concentration; the pH is established solely by the *ratio* of conjugate base to conjugate acid. This is not quite true, as we will see. For the moment, we will assume that the conjugate base/conjugate acid ratio is the determining factor. The assumption is valid as long as $[\mathrm{A}^-]$ and $[\mathrm{HA}]$ are high compared to K_a, but not so high as to warrant corrections for activity coefficients. Under the usual laboratory conditions, the concentrations might be 0.1 M or less with K_a values of 10^{-3} or less, so this condition is met.

D. LABORATORY BUFFERS

TITRATION OF A WEAK ACID

When a strong acid is titrated with a strong base the pH at any point is determined solely by the concentration of untitrated acid or excess base (Problem 1-17). The conjugate base that is formed (e.g., Cl^-) has no effect on pH. The situation is quite different when a weak acid is titrated with a strong base. A weak acid dissociates in an aqueous solution to yield a small amount of H^+ ions.

1. $$HA \rightleftharpoons H^+ + A^-$$

When OH^- ions are added, they are neutralized by the H^+ ions to form H_2O.

2. $$OH^- + H^+ \rightarrow H_2O$$

The removal of H^+ ions disturbs the equilibrium between the weak acid and its ions. Consequently, more HA ionizes to reestablish the equilibrium. The newly produced H^+ ions can then be neutralized by more OH^- and so on until all of the hydrogen originally present is neutralized. The overall result, the sum of reactions 1 and 2, is the titration of HA with OH^-.

3. $$HA + OH^- \rightleftharpoons H_2O + A^-$$

The number of equivalents of OH^- required equals the total number of equivalents of hydrogen present (as H^+ plus HA).

The pH at the exact end (equivalence) point of the titration is not 7 but higher because of the hydrolysis of the A^- ion; that is, because reaction 3 itself is an equilibrium reaction. In the absence of any remaining HA, the A^- ion reacts with H_2O to produce OH^- ions and the undissociated weak acid, HA. Because equilibrium conditions must always be satisfied in solutions of weak acids and bases, the H^+ ion concentration and pH during the titration can be calculated from the K_a expression or from the Henderson-Hasselbalch equation, provided the concentration of conjugate acid and conjugate base (or the ratio of their concentrations) is known. When calculating the values for [HA] and [A^-] during a titration, it is safe to assume that moles HA_{remain} = moles HA_{orig} − moles $HA_{titrated}$, and moles A^- = moles $HA_{titrated}$ throughout *most* of the titration curve. Significant errors (resulting from hydrolysis of the salt) arise only when an equivalence point is approached. The weaker the acid (in terms of K_a as well as original concentration), the sooner (in terms of percent of the original acid titrated) anomalous answers result from ignoring hydrolysis.

In other words, if A^- is 10% ionized (to $HA + OH^-$), then the Henderson-Hasselbalch equation cannot be used to estimate the pH of a solution of HA that has been 99% titrated.

· **Problem 1-25**

Calculate the appropriate values and draw the curve for the titration of 500 ml of 0.1 *M* weak acid, HA, with 0.1 *M* KOH. $K_a = 10^{-5}$ ($pK_a = 5.0$).

Solution

The titration curve is shown in Figure 1-2. The values were calculated as shown below.

(a) At the start, the pH depends solely on the concentration of HA and the value of K_a.

$$pH = \frac{pK_a + p[HA]}{2} = \frac{5+1}{2} = 3.0$$

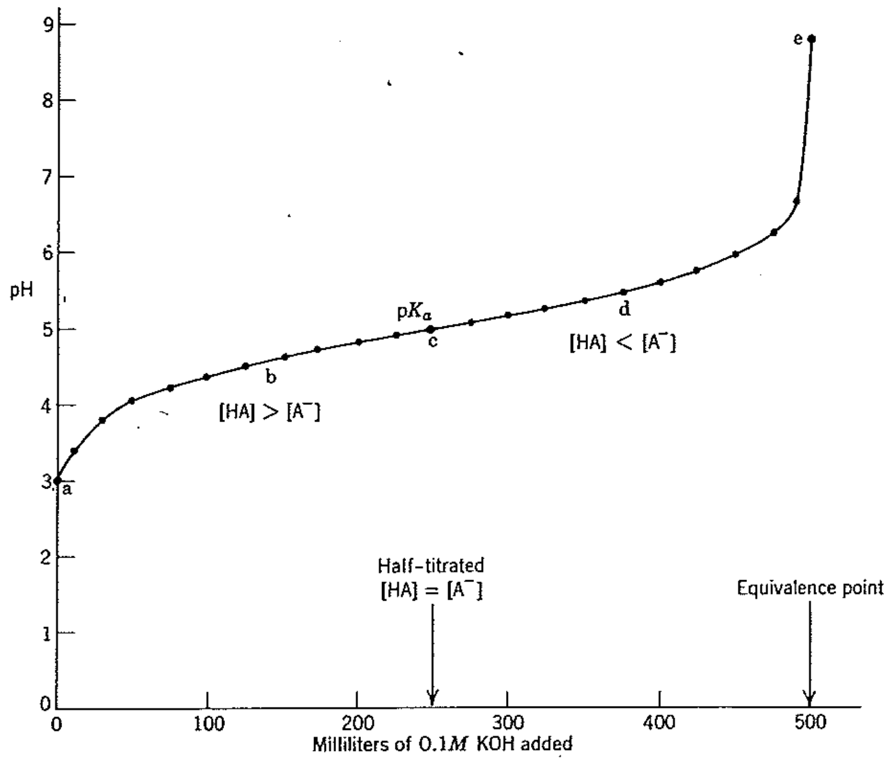


Figure 1-2 Titration of a weak monoprotic acid, HA, with a strong base (e.g., KOH). $pK_a = 5.0$; [HA] at the start = 0.1 *M*.

(b) At any point during the titration the pH can be calculated from:

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

For example, after adding 100 ml of 0.1 *M* KOH:

$$0.1 \text{ liter} \times 0.1\ M = 0.01 \text{ moles of OH}^- \text{ have been added}$$

$$\therefore\ 0.01 \text{ moles of HA have been converted to } 0.01 \text{ moles of A}^-$$

$$\begin{aligned} \text{moles HA remaining} &= \text{moles HA originally present} \\ &\quad - \text{moles of HA titrated to A}^- \\ &= (0.5 \text{ liter} \times 0.1\ M) - 0.01 \\ &= 0.05 - 0.01 = 0.04 \text{ moles} \end{aligned}$$

The volume has changed, but the ratio of moles A^-/moles HA is the same as the ratio of $[\mathrm{A}^-]/[\mathrm{HA}]$.

$$\mathrm{pH} = 5.0 + \log \frac{0.01}{0.04} = 5.0 + \log 0.25$$

To avoid dealing with the log of a number smaller than unity, the Henderson-Hasselbalch equation can be written as

$$\text{pH} = \text{p}K_a - \log\frac{[\text{HA}]}{[\text{A}]} = 5.0 - \log\frac{0.04}{0.01}$$
$$= 5.0 - \log 4 = 5.0 - 0.602$$

$$\boxed{\textbf{pH} = \mathbf{4.40}}$$

(c) When 250 ml of 0.1 *M* KOH has been added, the original HA is half titrated.

$$\text{pH} = \text{p}K_a + \log\frac{[\text{A}^-]}{[\text{HA}]}$$

$$[\text{A}^-] = [\text{HA}] \qquad \frac{[\text{A}^-]}{[\text{HA}]} = 1 \qquad \log 1 = 0$$

$$\therefore\ \text{pH} = \text{p}K_a \qquad \text{or} \qquad \boxed{\textbf{pH} = \mathbf{5.0}}$$

(d) Beyond the halfway point, the pH is still given by:

$$\text{pH} = \text{p}K_a + \log\frac{[\text{A}^-]}{[\text{HA}]}$$

For example, after adding 375 ml of 0.1 *M* KOH:

$$0.375 \text{ liter} \times 0.1\ M = 0.0375 \text{ moles OH}^- \text{ added}$$
$$\therefore\ 0.0375 \text{ moles of HA have been converted to } 0.0375 \text{ moles of A}^-$$
$$\text{HA remaining} = 0.0500 - 0.0375 = 0.0125$$
$$\text{pH} = 5.0 + \log\frac{0.0375}{0.0125} = 5.0 + \log 3$$

$$= 5.0 + 0.477 \qquad \boxed{\textbf{pH} = \mathbf{5.48}}$$

Note that when the acid is less than half titrated, the pH is less than pK_a. When the acid is exactly half titrated, the pH equals pK_a. When the acid is more than half titrated, the pH is greater than pK_a.

(e) When exactly 500 ml of 0.1 *M* KOH have been added, we have theoretically titrated all the HA to A^-. However, the pH at the endpoint is not 7 because A^-, the salt or conjugate base of HA, ionizes:

$$\text{A}^- + \text{HOH} \rightleftharpoons \text{HA} + \text{OH}^-$$

Note that the ionization equation read backwards is the equation for the titration of HA with OH^-. Thus, the titration is an equilibrium reaction that does not go to completion. The addition of 1 mole of OH^- to 1 mole of HA does not produce exactly 1 mole of A^-. The pH at the endpoint can be calculated from K_b. First note that the concentration of A^- is $5 \times 10^{-2}\ M$ at the endpoint (500 ml of 0.1 *M* KOH have been added to 500 ml of 0.1 *M* HA yielding 1 liter of solution containing 0.05 moles of A^-).

$$K_b = \frac{[\mathrm{HA}][\mathrm{OH}^-]}{[\mathrm{A}^-]} = \frac{K_w}{K_a} = \frac{10^{-14}}{10^{-5}} = 10^{-9}$$

$$\mathrm{pOH} = \frac{\mathrm{p}K_b + \mathrm{p}[\mathrm{A}^-]}{2} = \frac{9 + \log \frac{1}{0.05}}{2}$$

$$= \frac{9 + 1.30}{2} = \frac{10.30}{2}$$

$$\boxed{\mathrm{pOH} = 5.15}$$

$$\mathrm{pH} = \mathrm{p}K_w - \mathrm{pOH} \qquad \mathrm{pH} = 14 - 5.15$$

$$\boxed{\mathrm{pH} = 8.85}$$

If we started with A^- and titrated with HCl, the curve would be essentially identical to that shown in Figure 1-2 with the horizontal axis reading (from right to left) "ml of 0.1 *M* HCl added."

WHAT IS A BUFFER? HOW DOES A BUFFER WORK?

A "buffer" is something that resists change. In common chemical usage, a pH buffer is a substance, or mixture of substances, that permits solutions to resist *large changes* in pH upon the addition of small amounts of H^+ or OH^- ions. To put it another way, a buffer helps maintain a *near constant* pH upon the addition of small amounts of H^+ or OH^- ions to a solution.

Common buffer mixtures contain two substances, a conjugate acid and a conjugate base. An "acidic" buffer contains a weak acid and a salt of the weak acid (conjugate base). A "basic" buffer contains a weak base and a salt of the weak base (conjugate acid). Together the two species (conjugate acid plus conjugate base) resist large changes in pH by *partially* absorbing additions of H^+ or OH^- ions to the system. If H^+ ions are added to the buffered solution, they react partially with the conjugate base present to form the conjugate acid. Thus, some H^+ ions are taken out of circulation. If OH^- ions are added to the buffered solution, they react partially with the conjugate acid present to form water and the conjugate base. Thus, some OH^- ions are taken out of circulation. Buffered solutions *do* change in pH upon the addition of H^+ or OH^- ions. However, the change is much less than that which would occur if no buffer were present. The amount of change depends on the strength of the buffer and the $[A^-]/[HA]$ ratio (see Buffer Capacity). The solution obtained by titrating HA with KOH (Problem 1-25) is a buffer. If we examine the titration curve, we see that in the region of $\mathrm{p}K_a$ the pH changes only slightly as OH^- is added. Thus $HA + A^-$ provides good buffering action in the neighborhood of pH 5. However, this particular weak acid plus its salt is a poor buffer at pH 7. If we wished to prepare a solution that would buffer at pH 7, we would use a weak acid whose $\mathrm{p}K_a$ is around 7.

· Problem 1-26

(a) Describe the components of an "acetate" buffer. (b) Show the reactions by which an acetate buffer resists changes in pH upon the addition of OH^- and H^+ ions.

Solution

(a) An "acetate" buffer contains un-ionized acetic acid (HOAc) as the conjugate acid and acetate ions (OAc^-) as the conjugate base. The OAc^- may be provided directly by NaOAc, KOAc, and the like, or by neutralizing a portion of the HOAc with KOH or NaOH.

(b) In a solution containing a weak acid such as HOAc, a certain condition must be met—namely, the product of $[H^+][OAc^-]$ divided by [HOAc] must be constant:

$$K_a = \frac{[H^+][OAc^-]}{[HOAc]}$$

A change in the concentration of any one of the three components of the K_a expression causes the concentrations of the other two to alter appropriately so that $[H^+][OAc^-]$ divided by [HOAc] is still the same constant value (K_a).

For example, if OH^- ions are added to the system, they react with the H^+ ions present to form H_2O.

$$\boxed{OH^- + H^+ \rightarrow H_2O}$$

The reduction in $[H^+]$ disturbs the equilibrium momentarily. Consequently, more HOAc dissociates to reestablish the equilibrium condition.

$$\boxed{HOAc \rightleftharpoons H^+ + OAc^-}$$

The net result (as well as the sum of the above two reactions) is as if the OH^- ions react directly with the conjugate acid of the acetate buffer to yield H_2O plus more conjugate base $[OAc^-]$.

$$\boxed{OH^- + HOAc \rightleftharpoons H_2O + OAc^-}$$

All of this, of course, happens almost instantaneously.

Similarly, if H^+ ions are added to the system, the equilibrium again shifts. This time the conjugate base $[OAc^-]$ reacts with some of the excess H^+ ions to form un-ionized HOAc.

$$\boxed{H^+ + OAc^- \rightleftharpoons HOAc}$$

It should be emphasized that the excess H^+ or OH^- ions are not *completely* neutralized by the buffer; that is, the pH does not remain absolutely constant upon addition of H^+ or OH^- ions to a buffer. The reactions by which H^+ and OH^- ions are absorbed are themselves equilibrium reactions and do not go to completion.

PREPARATION OF BUFFERS

· Problem 1-27

What are the concentrations of HOAc and OAc^- in a 0.2 *M* "acetate" buffer, pH 5.00? The K_a for acetic acid is 1.70×10^{-5} ($pK_a = 4.77$).

Solution

A "0.2 *M* acetate" buffer contains a *total* of 0.2 mole of "acetate" per liter. Some of the total acetate is in the conjugate acid form, HOAc, and some is in the conjugate base form, OAc^-. The proportions (hence, the concentrations) of each form may be solved by using either the K_a expression or the Henderson-Hasselbalch equation.

$$K_a = \frac{[H^+][OAc^-]}{[HOAc]}$$

Let

$$y = M \text{ of } OAc^-$$

$$\therefore \quad 0.2 - y = M \text{ of } HOAc$$

$$pH = 5$$

$$\therefore \quad [H^+] = 10^{-5}$$

$$1.7 \times 10^{-5} = \frac{(10^{-5})(y)}{(0.2 - y)}$$

$$3.4 \times 10^{-6} - 1.7 \times 10^{-5}y = 1 \times 10^{-5}y$$

$$3.4 \times 10^{-6} = 2.7 \times 10^{-5}y$$

$$y = \frac{3.4 \times 10^{-6}}{27 \times 10^{-6}}$$

$$y = 0.126$$

$$\boxed{[OAc^-] = \mathbf{0.126}\ M}$$

$$[HOAc] = 0.200 - 0.126$$

$$\boxed{[HOAc] = \mathbf{0.074}\ M}$$

$$pH = pK_a + \log \frac{[OAc^-]}{[HOAc]}$$

Let

$$y = M \text{ of } OAc^-$$

$$\therefore \quad 0.2 - y = M \text{ of } HOAc$$

$$5.00 = 4.77 + \log \frac{y}{0.2 - y}$$

$$0.23 = \log \frac{y}{0.2 - y}$$

$$\frac{y}{0.2 - y} = \text{antilog of } 0.23$$

$$\frac{y}{0.2 - y} = 1.70$$

$$0.34 - 1.70y = y$$

$$0.34 = 2.7y$$

$$y = 0.126$$

$$\boxed{[OAc^-] = \mathbf{0.126}\ M}$$

$$[HOAc] = 0.2 - y\ M$$

$$[HOAc] = 0.2 - 0.126$$

$$\boxed{[HOAc] = \mathbf{0.074}\ M}$$

or $$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{OAc^-}]}{[\mathrm{HOAc}]} \qquad 5 = 4.77 + \log\frac{[\mathrm{OAc^-}]}{[\mathrm{HOAc}]}$$

$$0.23 = \log\frac{[\mathrm{OAc^-}]}{[\mathrm{HOAc}]} \qquad \frac{[\mathrm{OAc^-}]}{[\mathrm{HOAc}]} = \text{antilog of } 0.23$$

$$\frac{[\mathrm{OAc^-}]}{[\mathrm{HOAc}]} = 1.70 = \frac{1.70}{1}$$

$$\therefore \quad \frac{1.70}{2.70} \text{ of total} = \mathrm{OAc^-} \qquad \text{and} \qquad \frac{1.00}{2.70} \text{ of total} = \mathrm{HOAc}$$

$$\frac{1.70}{2.7} \times 0.2\ M = 0.126 \qquad \boxed{[\mathrm{OAc^-}] = 0.126\ M}$$

$$\frac{1.00}{2.70} \times 0.2\ M = 0.074 \qquad \boxed{[\mathrm{HOAc}] = 0.074\ M}$$

Check: The pH is higher than the pK_a. ∴ The solution should contain more conjugate base than conjugate acid. Conjugate base = 0.126 M. Conjugate acid = 0.074 M.

· Problem 1-28

Describe the preparation of 3 liters of a 0.2 M acetate buffer, pH 5.00, starting from solid sodium acetate trihydrate (MW 136) and a 1 M solution of acetic acid.

Solution

First calculate the molarities of $\mathrm{OAc^-}$ and HOAc present. Any of the three methods shown in Problem 1-27 may be used to obtain $[\mathrm{OAc^-}] = 0.126\ M$ and $[\mathrm{HOAc}] = 0.074\ M$. We need 3 liters of the 0.2 M buffer.

$$3 \text{ liters} \times 0.2\ M = 0.6 \text{ mole } \textit{total} \ (\mathrm{HOAc} \text{ plus } \mathrm{OAc^-})$$

The total of 0.6 mole is obtained from two sources:

$$3 \text{ liters} \times 0.126\ M = 0.378 \text{ mole } \mathrm{OAc^-}$$
$$3 \text{ liters} \times 0.074\ M = 0.222 \text{ mole } \mathrm{HOAc}$$

The 0.378 mole of $\mathrm{OAc^-}$ comes from solid NaOAc.

$$\text{number of moles} = \frac{\mathrm{wt_g}}{\mathrm{MW}} \qquad 0.378 = \frac{\mathrm{wt_g}}{136}$$

$$\boxed{\mathrm{wt_g} = 51.4\ \mathrm{g}}$$

The 0.222 mole of HOAc comes from a 1 M stock solution.

$$\text{number of moles} = \text{liters} \times M \qquad 0.222 = \text{liters} \times 1$$

$$\text{liters} = 0.222 \qquad \text{or} \qquad \boxed{222\ \mathrm{ml}}$$

Therefore, to prepare 3 liters of the buffer, dissolve 51.4 g of the sodium acetate in some water, add 222 ml of the 1 M acetic acid, and then dilute to a total final volume of 3.0 liters.

· Problem 1-29

Describe the preparation of 5 liters of a 0.3 M acetate buffer, pH 4.47, starting from a 2 M solution of acetic acid and a 2.5 M solution of KOH.

Solution

As in the previous problem, first calculate the proportions of the two acetate species present.

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{OAc^-}]}{[\mathrm{HOAc}]} \qquad 4.47 = 4.77 + \log\frac{[\mathrm{OAc^-}]}{[\mathrm{HOAc}]}$$

$$-0.30 = \log\frac{[\mathrm{OAc^-}]}{[\mathrm{HOAc}]} \quad \text{or} \quad +0.30 = \log\frac{[\mathrm{HOAc}]}{[\mathrm{OAc^-}]}$$

$$\frac{[\mathrm{HOAc}]}{[\mathrm{OAc^-}]} = \text{antilog of } 0.3 = 2 = \frac{2}{1} \text{ ratio}$$

$\therefore$ $\frac{2}{3}$ of the total acetate is present as HOAc and $\frac{1}{3}$ of the total acetate is present as $\mathrm{OAc^-}$. The final solution contains:

$$\tfrac{2}{3} \times 0.3\,M = 0.2\,M \text{ HOAc (1 mole in 5 liters)}$$

$$\tfrac{1}{3} \times 0.3\,M = 0.1\,M \text{ OAc}^- \text{ (0.5 mole in 5 liters)}$$

In this buffer, *all* of the acetate must be provided by the HOAc. The buffer is prepared by converting the *proper proportion* of the HOAc to $\mathrm{OAc^-}$ by adding KOH. We need 5 liters × 0.3 M = 1.5 moles *total* acetate. Calculate how much stock 2 M HOAc is needed to obtain 1.5 moles.

$$\text{liters} \times M = \text{number of moles}$$

$$\text{liters} \times 2 = 1.5 \qquad \text{liters} = \frac{1.5}{2} = 0.75$$

$\therefore$ 750 ml of the 2 M HOAc is required.

Next, convert $\frac{1}{3}$ of the 1.5 moles to $\mathrm{OAc^-}$ by adding the proper amount of 2.5 M KOH.

$$\tfrac{1}{3} \times 1.5 \text{ moles} = 0.5 \text{ mole KOH needed}$$

$$\text{liters} \times M = \text{number of moles}$$

$$\text{liters} \times 2.5 = 0.5 \text{ mole}$$

$$\text{liters} = \frac{0.5}{2.5} = 0.2 \text{ liter}$$

$\therefore$ Add 200 ml of 2.5 M KOH.

The solution now contains 1 mole of HOAc and 0.5 mole of $\mathrm{OAc^-}$. Finally, add sufficient water to bring the volume up to 5 liters. The final solution contains 0.2 M HOAc and 0.1 M $\mathrm{OAc^-}$.

pH *CHANGES IN BUFFERS*

In general, a buffer is used to maintain the pH relatively constant during the course of a reaction that produces or utilizes $\mathrm{H^+}$ ions. As we shall see in a following section, the ability of a buffer to maintain a near-constant pH increases as the concentration of the buffer increases. However, it is not always possible to use a relatively concentrated buffer. The enzyme, tissue, or cells under investigation may be sensitive to high ionic strength, or the assay may require that the pH be adjusted easily to some higher or lower value at the end of the reaction. Thus, a compromise is necessary. The concentration and pH of the buffer are chosen so that the pH will remain as near constant as possible without introducing complications due to high ionic strength. There are some circumstances where we want the pH to change significantly (e.g., when the extent of a reaction is measured by the pH change). In this case, we would use the lowest concentration of buffer possible without allowing the pH to move out of a range optional for the reaction under investigation.

· Problem 1-30

Show mathematically why an acetate buffer cannot maintain an absolutely constant pH upon the addition of H^+.

Solution

Suppose we have a buffer containing 0.01 M HA and 0.01 M A^-. Assume that the K_a of the weak acid is also 10^{-5}. Consequently, the H^+ ion concentration must also be 10^{-5} M.

$$\frac{[H^+][A^-]}{[HA]} = K_a \qquad \frac{(10^{-5})(10^{-2})}{(10^{-2})} = 10^{-5}$$

Now suppose 10^{-3} M H^+ is added to the buffer. If *all* of the H^+ reacts with A^- to yield HA (thus maintaining $[H^+]$ at 10^{-5} M), the new concentration of [HA] would be 1.1×10^{-2} M and the new concentration of $[A^-]$ would be 0.9×10^{-2} M. Substituting these values into the K_a expression, we can see that the $[H^+][A^-]$ divided by [HA] is *not* constant and equal to 10^{-5}.

$$\frac{(10^{-5})(0.9 \times 10^{-2})}{(1.1 \times 10^{-2})} \neq 10^{-5}$$

· Problem 1-31

Consider a 0.002 M acidic buffer containing 10^{-3} M HA and 10^{-3} M A^-. The $pH = pK_a = 5$ ($K_a = 10^{-5}$). Suppose that 5×10^{-4} moles of H^+ are added to 1 liter of the buffer (assume that the volume remains at 1 liter). (a) Calculate the *exact* concentrations of A^- and HA and the pH of the solution after addition of the HCl. (b) Calculate the concentrations of A^- and HA and the pH of the solution assuming that the increase in the amount of HA (and the decrease in the amount of A^-) is equal to the amount of H^+ added.

Solution

The added H^+ is partially utilized by reacting with A^- to form un-ionized HA.

$$H^+ + A^- \rightleftharpoons HA$$

(a) Let

$$y = M \text{ of } H^+ \text{ utilized by the buffer}$$

$$[A^-] = 10^{-3} - y\,M \qquad [HA] = 10^{-3} + y\,M$$

$$[H^+] = 10^{-5} + 5\times10^{-4} - y = 51\times10^{-5} - y$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(51\times10^{-5} - y)(10^{-3} - y)}{(10^{-3} + y)} = 10^{-5}$$

Cross multiplying:

$$10^{-8} + 10^{-5}y = 51\times10^{-8} - 51\times10^{-5}y - 10^{-3}y + y^2$$

Rearranging and collecting terms:

$$y^2 - 10^{-3}y - 51\times10^{-5}y - 10^{-5}y + 51\times10^{-8} - 10^{-8} = 0$$

$$y^2 - 100\times10^{-5}y - 51\times10^{-5}y - 1\times10^{-5}y + 50\times10^{-8} = 0$$

$$y^2 - 152\times10^{-5}y + 50\times10^{-8} = 0$$

$$y = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where $a = 1$ $b = -152\times10^{-5}$ $c = 50\times10^{-8}$.

$$y = \frac{+152\times10^{-5} \pm \sqrt{(-15.2\times10^{-4})^2 - 4(50\times10^{-8})}}{2}$$

$$y = \frac{15.2\times10^{-4} \pm \sqrt{231\times10^{-8} - 200\times10^{-8}}}{2}$$

$$y = \frac{15.2\times10^{-4} \pm \sqrt{31\times10^{-8}}}{2} = \frac{15.20\times10^{-4} \pm 5.57\times10^{-4}}{2}$$

$$y = \frac{20.77\times10^{-4}}{2} \quad \text{and} \quad \frac{9.63\times10^{-4}}{2}$$

$$y = 10.39\times10^{-4} \quad \text{and} \quad 4.815\times10^{-4}\,M$$

The higher value is obviously incorrect because only $5\times10^{-4}\,M$ H^+ was added.

$$\therefore \quad y = 4.815\times10^{-4}\,M$$

Thus, of the $5\times10^{-4}\,M$ H^+ originally added, $4.815\times10^{-4}\,M$ was utilized by the buffer. The final H^+ ion concentration was increased by $0.185\times10^{-4}\,M$.

$$[H^+]_{\text{final}} = (1\times10^{-5}) + (1.85\times10^{-5}) \qquad \boxed{[H^+]_{\text{final}} = 2.85\times10^{-5}\,M}$$

$$[A^-]_{\text{final}} = (10\times10^{-4}) - (4.82\times10^{-4}) \qquad \boxed{[A^-]_{\text{final}} = 5.18\times10^{-4}\,M}$$

$$[HA]_{\text{final}} = (10\times10^{-4}) + (4.82\times10^{-4}) \qquad \boxed{[HA]_{\text{final}} = 14.82\times10^{-4}\,M}$$

$$\mathrm{pH_{final}} = \log \frac{1}{[\mathrm{H^+}]_{\mathrm{final}}} = \log \frac{1}{2.85 \times 10^{-5}}$$
$$= \log 0.351 \times 10^{5} = \log 3.51 \times 10^{4}$$

$$\boxed{\mathbf{pH = 4.545}}$$

In other words, the pH decreased by 0.455 unit.

(b) If we assume that virtually *all* the H^+ reacts with A^- to form HA, in order to simplify the calculations:

$$[\mathrm{A^-}]_{\mathrm{final}} = (10 \times 10^{-4}) - (5 \times 10^{-4}) \qquad \boxed{[\mathrm{A^-}]_{\mathrm{final}} = \mathbf{5.0 \times 10^{-4}}\ M}$$

$$[\mathrm{HA}]_{\mathrm{final}} = (10 \times 10^{-4}) + (5 \times 10^{-4}) \qquad \boxed{[\mathrm{HA}]_{\mathrm{final}} = \mathbf{15 \times 10^{-4}}\ M}$$

The estimated new $[H^+]$ is that which is in equilibrium with $15 \times 10^{-4}\ M$ HA and $5 \times 10^{-4}\ M$ A^-. The estimated value will be slightly high because, as shown in part a, the $[HA]/[A^-]$ ratio is actually a little less than 3:1.

$$K_a = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

Let $y = M$ of H^+ present

$$10^{-5} = \frac{(y)(5 \times 10^{-4})}{(15 \times 10^{-4})}$$
$$15 \times 10^{-9} = (5 \times 10^{-4})y$$
$$y = \frac{15 \times 10^{-9}}{5 \times 10^{-4}}$$
$$y = 3 \times 10^{-5}$$

$$\boxed{[\mathrm{H^+}] = \mathbf{3 \times 10^{-5}}\ M}$$

The calculated H^+ ion concentration increase is $2 \times 10^{-5}\ M$ (compared to the true value of $1.85 \times 10^{-5}\ M$).

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$
$$\mathrm{pH} = 5.00 + \log \frac{(5 \times 10^{-4})}{(15 \times 10^{-4})}$$
$$\mathrm{pH} = 5.00 - \log \frac{(15 \times 10^{-4})}{(5 \times 10^{-4})}$$
$$\mathrm{pH} = 5.00 - \log 3$$
$$\mathrm{pH} = 5.00 - 0.477$$

$$\boxed{\mathbf{pH = 4.523}}$$

The calculated pH decrease is 0.477 unit (compared to the true value of 0.455).

We can see that the error introduced by assuming that the buffer reacts *completely* with the added H^+ is small. In the above problem, the buffer is relatively weak and the amount of H^+ ion added is of the same order of magnitude as the original A^- concentration. In practice, the concentration of the buffer employed would be high compared to the expected change in H^+ (or OH^-) ion concentration. Consequently, buffer calculations may be simplified greatly, as shown in part b above, without undue error.

· Problem 1-32

An enzyme-catalyzed reaction was carried out in a 0.2 *M* "Tris" buffer, pH 7.8. As a result of the reaction, 0.03 mole/liter of H^+ was produced. (a) What was the ratio of $Tris^+$ (conjugate acid)/$Tris^0$ (conjugate base) at the start of the reaction? (b) What are the concentrations of $Tris^+$ and $Tris^0$ at the start of the reaction? (c) Show the reaction by which the buffer maintained a near constant pH. (d) What were the concentrations of $Tris^0$ and $Tris^+$ at the end of the reaction? (e) What was the pH at the end of the reaction? The pK_a of Tris is 8.1. (f) What would the final pH be if no buffer were present?

Solution

(a)

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{\mathrm{Tris}^0}{\mathrm{Tris}^+} \qquad 7.8 = 8.1 + \log\frac{\mathrm{Tris}^0}{\mathrm{Tris}^+}$$

$$-0.3 = \log\frac{\mathrm{Tris}^0}{\mathrm{Tris}^+} \quad \text{or} \quad +0.3 = \log\frac{\mathrm{Tris}^+}{\mathrm{Tris}^0}$$

$$\frac{\mathrm{Tris}^+}{\mathrm{Tris}^0} = \text{antilog of } 0.3 = 2 \qquad \boxed{\frac{\mathrm{Tris}^+}{\mathrm{Tris}^0} = \frac{2}{1}}$$

(b)

$$\tfrac{2}{3}\times 0.2\,M = \boxed{0.133\,M\ \mathrm{Tris}^+} \quad \text{and} \quad \tfrac{1}{3}\times 0.2\,M = \boxed{0.067\,M\ \mathrm{Tris}^0}$$

Check: The pH is less than the pK_a; ∴ [conjugate acid] > [conjugate base]; 0.133 *M* > 0.067 *M*.

(c) The conjugate base reacts with the excess H^+.

$$\boxed{\mathrm{Tris}^0 + \mathrm{H}^+ \rightarrow \mathrm{Tris}^+}$$

(d) As a result of the reaction, the amounts of $Tris^+$ and $Tris^0$ change as shown below.

$$[\mathrm{Tris}^+] = 0.133 + 0.030 = \boxed{0.163\,M}$$

$$[\mathrm{Tris}^0] = 0.067 - 0.030 = \boxed{0.037\,M}$$

(e)

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{\mathrm{Tris}^0}{\mathrm{Tris}^+} = 8.1 + \log\frac{0.037}{0.163}$$

$$= 8.1 - \log\frac{0.163}{0.037} = 8.1 - \log 4.4$$

$$\mathrm{pH} = 8.1 - 0.644 \qquad \boxed{\mathrm{pH} = 7.456}$$

(f) If no buffer were present, the production of 0.03 M H^+ would bring the pH to:

$$\mathrm{pH} = \log\frac{1}{[\mathrm{H}^+]} = \log\frac{1}{0.03} = \log 33.33$$

$$\boxed{\mathbf{pH = 1.52}}$$

(The enzyme would very likely be denatured before the pH decreased to 1.52.)

BUFFER CAPACITY—THEORETICAL AND PRACTICAL

The ability of a buffer to resist changes in pH is referred to as the "buffer capacity." "Buffer capacity" can be defined in two ways: (1) the number of moles per liter of H^+ or OH^- required to cause a given change in pH (e.g., 1 unit), or (2) the pH change that occurs upon addition of a given amount of H^+ or OH^- (e.g., 1 mole/liter). The first definition is better because it can be applied to buffers of any concentration.

An expression for instantaneous buffer capacity, β, can be derived using calculus. Essentially, β is the reciprocal of the slope of the titration curve at any point. Starting with the Henderson-Hasselbalch equation:

$$\begin{aligned}\mathrm{pH} &= \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} = \mathrm{p}K_a + \log[\mathrm{A}^-] - \log[\mathrm{HA}]\\ &= \mathrm{p}K_a + \log[\mathrm{A}^-] - \log([C] - [\mathrm{A}^-])\\ &= \mathrm{p}K_a + \frac{\ln[\mathrm{A}^-]}{2.3} - \frac{\ln([C]-[\mathrm{A}^-])}{2.3}\end{aligned}$$

where C = the total concentration of buffer components
$= [\mathrm{A}^-] + [\mathrm{HA}]$

Differentiating with respect to $[\mathrm{A}^-]$:

$$\frac{d\mathrm{pH}}{d[\mathrm{A}^-]} = \frac{1}{2.3[\mathrm{A}^-]} + \frac{1}{2.3([C]-[\mathrm{A}^-])} = \frac{[C]}{2.3[\mathrm{A}^-]([C]-[\mathrm{A}^-])}$$

$d[\mathrm{A}^-]$ is the same as $d[\mathrm{H}^+]$ or $d[\mathrm{OH}^-]$ because for every mole of H^+ added a mole of A^- is utilized; for every mole of OH^- added a mole of A^- is produced. Substituting and inverting:

$$\frac{d[\mathrm{H}^+]}{d\mathrm{pH}} = \frac{d[\mathrm{OH}^-]}{d\mathrm{pH}} = \frac{2.3[\mathrm{A}^-]([C]-[\mathrm{A}^-])}{[C]} = \beta$$

or

$$\boxed{\beta = \frac{2.3[\mathrm{A}^-][\mathrm{HA}]}{[\mathrm{A}^-]+[\mathrm{HA}]}} \qquad (31)$$

Further substitution from the expression for K_a yields:

$$\boxed{\beta = \frac{2.3\,K_a[\mathrm{H^+}][C]}{(K_a + [\mathrm{H^+}])^2}} \quad \text{and} \quad \boxed{\beta_{\max} = 0.575\,[C]} \tag{32}$$

where $[\mathrm{H^+}]$ = the hydrogen ion concentration of the buffer.

We see that β increases as the concentration of the buffer increases. We might have arrived at this conclusion intuitively. It seems logical that a 0.25 M buffer should resist a pH change better than a 0.01 M buffer. It can also be shown (by calculus or by trial and error) that β will be maximum when $[\mathrm{A^-}] = [\mathrm{HA}]$ or $[\mathrm{H^+}] = K_a$, that is, the slope of the titration curve is minimal at $\mathrm{pH} = \mathrm{p}K_a$. Also, when $[\mathrm{H^+}] = K_a$, $\beta = 2.3[\mathrm{H^+}]^2[C]/(2[\mathrm{H^+}])^2 = 2.3[\mathrm{H^+}]^2[C]/4[\mathrm{H^+}]^2$ or $\beta = 0.575[C]$.

Since β is related to the slope of the titration curve at one point, its value is the same whether $\mathrm{H^+}$ or $\mathrm{OH^-}$ is added to the buffer. A more practical definition of buffer capacity is:

Buffer capacity$_a$ = the number of moles of $\mathrm{H^+}$ that must be added to one liter of the buffer in order to decrease the pH by 1 unit.
= the buffer capacity in the acid direction. (33)
and Buffer capacity$_b$ = the number of moles of $\mathrm{OH^-}$ that must be added to one liter of the buffer in order to increase the pH by 1 unit.
= the buffer capacity in the alkaline direction.

Biochemical reactions seldom produce $\mathrm{OH^-}$ ions. However, many reactions consume $\mathrm{H^+}$ ions. The utilization of n moles/liter of $\mathrm{H^+}$ ions during a reaction has the same effect on a buffer as the addition of n moles/liter of $\mathrm{OH^-}$ ions.

Problem 1-33

Calculate (a) the instantaneous and (b) the practical buffer capacity in both directions of a 0.05 M Tricine buffer, pH 7.5. Tricine is N-tris-(hydroxymethyl)-methylglycine. $\mathrm{p}K_a = 8.15$. ($K_a = 7.08 \times 10^{-9}$.)

Solution

The titration curve for Tricine (base) showing the position of the buffer is sketched in Figure 1-3. The curve is shown for the titration of Tricine conjugate base with $\mathrm{H^+}$. The curve for the titration of Tricine conjugate acid with $\mathrm{OH^-}$ would be the mirror image of that shown. The pH of the buffer is less than $\mathrm{p}K_a$. Therefore, $[\mathrm{Tricine^+}] > [\mathrm{Tricine^0}]$, as shown below.

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{Tricine^0}]}{[\mathrm{Tricine^+}]} \qquad 7.50 = 8.15 + \log\frac{[\mathrm{Tricine^0}]}{[\mathrm{Tricine^+}]}$$

$$7.50 = 8.15 - \log\frac{[\mathrm{Tricine^+}]}{[\mathrm{Tricine^0}]} \qquad 0.65 = \log\frac{[\mathrm{Tricine^+}]}{[\mathrm{Tricine^0}]}$$

$$\frac{[\mathrm{Tricine^+}]}{[\mathrm{Tricine^0}]} = \frac{4.47}{1}$$

$$[\text{Tricine}^+] = \frac{4.47}{5.47} \times 0.05 = 0.041\ M$$

$$[\text{Tricine}^0] = \frac{1}{5.47} \times 0.05 = 0.009\ M$$

$$\text{At pH 7.5, } [\text{H}^+] = 3.16 \times 10^{-8}\ M$$

(a)

$$\beta = \frac{2.3\ K_a[\text{H}^+][C]}{(K_a + [\text{H}^+])^2} = \frac{(2.3)(7.08 \times 10^{-9})(3.16 \times 10^{-8})(0.05)}{(7.08 \times 10^{-9} + 3.16 \times 10^{-8})^2} = \frac{2.57 \times 10^{-17}}{(3.87 \times 10^{-8})^2} = \frac{2.57 \times 10^{-17}}{1.50 \times 10^{-15}}$$

$$\boxed{\beta = 0.017\ M}$$

or

$$\beta = \frac{2.3[\text{Tricine}^0][\text{Tricine}^+]}{[\text{Tricine}^0] + [\text{Tricine}^+]} = \frac{2.3[\text{Tricine}^0][\text{Tricine}^+]}{C} = \frac{(2.3)(0.041)(0.009)}{0.05} = \frac{8.49 \times 10^{-4}}{5 \times 10^{-2}}$$

$$\boxed{\beta = 0.017\ M}$$

(b) We can see from the titration curve that the practical buffer capacity in the alkaline direction is greater than the practical buffer capacity in the acid direction. To calculate BC$_a$, we start by calculating the concentrations of Tricine$^+$ and Tricine^0 at pH 6.5 (one pH unit less than the pH of the buffer).

$$\text{pH} = \text{p}K_a + \log\frac{[\text{Tricine}^0]}{[\text{Tricine}^+]} \qquad 6.50 = 8.15 + \log\frac{[\text{Tricine}^0]}{[\text{Tricine}^+]}$$

$$1.65 = \log\frac{[\text{Tricine}^+]}{[\text{Tricine}^0]} \qquad \frac{[\text{Tricine}^+]}{[\text{Tricine}^0]} = \frac{44.7}{1}$$

$$\therefore \text{ at pH 6.5: } [\text{Tricine}^+] = \frac{44.7}{45.7} \times 0.05 = 0.049\ M$$

$$[\text{Tricine}^0] = \frac{1}{45.7} \times 0.05 = 0.001\ M$$

Next, calculate the [H$^+$] required to change the original concentrations of conjugate acid and conjugate base to the final concentrations.

$$[\text{Tricine}^+]_{\text{final}} = [\text{Tricine}^+]_{\text{orig}} + [\text{H}^+]$$
$$0.049 = 0.041 + [\text{H}^+]$$

$$[\text{H}^+] = 0.008\ M \quad \therefore \quad \boxed{\text{BC}_a = 0.008\ M}$$

or

$$[\text{Tricine}^0]_{\text{final}} = [\text{Tricine}^0]_{\text{orig}} - [\text{H}^+]$$
$$0.001 = 0.009 - [\text{H}^+]$$

$$[\text{H}^+] = 0.008\ M \quad \therefore \quad \boxed{\text{BC}_a = 0.008\ M}$$

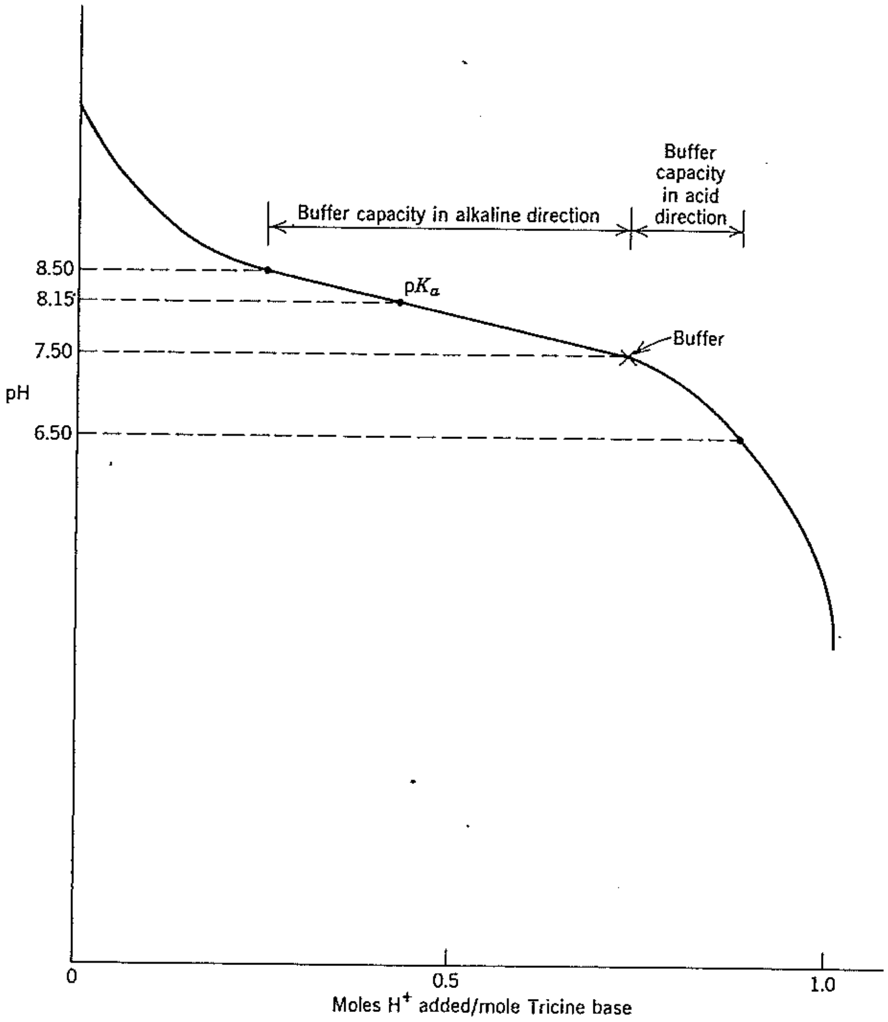


Figure 1-3 Titration of a weak monoprotic base (e.g., Tricine) with a strong acid (e.g., HCl). pK_a of Tricine = 8.15.

To calculate BC_b, we proceed in the same manner to obtain the concentrations of Tricine^0 and Tricine^+ at pH 8.5.

$$8.5 = 8.15 + \log \frac{[\text{Tricine}^0]}{[\text{Tricine}^+]}$$

$$0.35 = \log \frac{[\text{Tricine}^0]}{[\text{Tricine}^+]} \qquad \frac{[\text{Tricine}^0]}{[\text{Tricine}^+]} = \frac{2.24}{1}$$

$$[\text{Tricine}^0] = \frac{2.24}{3.24} \times 0.05\ M = 0.035\ M$$

$$[\text{Tricine}^+] = \frac{1}{3.24} \times 0.05\ M = 0.015\ M$$

Now, calculate the amount of OH^- that must be added (or H^+ that must be removed) to change the original concentrations to the final concentrations.

$$[\text{Tricine}^0]_{\text{final}} = [\text{Tricine}^0]_{\text{orig}} + [\text{OH}^-]$$
$$0.035 = 0.009 + [\text{OH}^-]$$
$$[\text{OH}^-] = 0.026\ M \quad \therefore \quad \boxed{\mathbf{BC}_b = \mathbf{0.026}\ \boldsymbol{M}}$$

or

$$[\text{Tricine}^+]_{\text{final}} = [\text{Tricine}^+]_{\text{orig}} - [\text{OH}^-]$$
$$0.015 = 0.041 - [\text{OH}^-]$$
$$[\text{OH}^-] = 0.026\ M \quad \therefore \quad \boxed{\mathbf{BC}_b = \mathbf{0.026}\ \boldsymbol{M}}$$

Thus, the practical buffer capacity in the alkaline direction is more than three times the practical buffer capacity in the acid direction. At pH 7.5, $BC_b > \beta$, but $BC_a < \beta$. If the pH of the buffer were 8.15 (i.e., $pH = pK_a$):

$$BC_a = BC_b \simeq 0.020\ M$$

and

$$\beta \simeq 0.029\ M$$

That is, the slope of the line between pK_a and $pK_a + 1$ (or pK_a and $pK_a - 1$) is greater than the slope of the line drawn tangent to the titration curve at $pH = pK_a$.

Instead of proceeding stepwise as outlined above, we can derive a general equation for practical buffer capacity. For example, for BC_a where pH_1 is the initial pH and pH_2 is the final (lower) pH:

$$pH_1 = pK_a + \log\frac{[A^-]_1}{[HA]_1} \qquad \text{and} \qquad pH_2 = pK_a + \log\frac{[A^-]_2}{[HA]_2}$$

$$\therefore \qquad pH_1 - pH_2 = 1 = \left(pK_a + \log\frac{[A^-]_1}{[HA]_1}\right) - \left(pK_a + \log\frac{[A^-]_2}{[HA]_2}\right)$$

or

$$1 = \log\frac{[A^-]_1}{[HA]_1} - \log\frac{[A^-]_2}{[HA]_2}$$

or

$$1 = \log\frac{[A^-]_1[HA]_2}{[HA]_1[A^-]_2} \quad \therefore \quad \frac{[A^-]_1[HA]_2}{[HA]_1[A^-]_2} = 10$$

Substituting $[HA]_2 = [HA]_1 + [H^+]$ and $[A^-]_2 = [A^-]_1 - [H^+]$, multiplying out, separating terms, and solving for $[H^+]$:

$$\boxed{[\mathbf{H}^+] = \mathbf{BC}_a = \frac{9[\mathbf{HA}]_1[\mathbf{A}^-]_1}{10[\mathbf{HA}]_1 + [\mathbf{A}^-]_1}} \tag{34}$$

Similarly, we can derive the equation for BC_b:

$$\boxed{[\mathbf{OH}^-] = \mathbf{BC}_b = \frac{9[\mathbf{HA}]_1[\mathbf{A}^-]_1}{10[\mathbf{A}^-]_1 + [\mathbf{HA}]_1}} \tag{35}$$

For Tricine, $HA = \text{Tricine}^+$, $A^- = \text{Tricine}^0$.

· Problem 1-34

In the preceding problem, we saw that it takes 8×10^{-3} moles H^+/liter to decrease the pH of a 0.05 *M* Tricine buffer, pH 7.5, by one unit. (a) Will the addition of 4×10^{-3} *M* H^+ decrease the pH by 0.5 unit? (b) What is the ΔpH caused by adding 4×10^{-3} *M* H^+?

Solution

(a) A titration curve is not a straight line and the pH scale is logarithmic, not linear. Hence, there is no direct proportionality between H^+ added and ΔpH. Thus, it does *not* take half as much H^+ to decrease the pH by 0.5 unit as it took to decrease the pH by 1.0 unit. The exact amount of H^+ required can easily be calculated as shown in the previous problem but substituting pH 7.0 for the final pH. We will find that at pH 7.0:

$$[\text{Tricine}^+] = 0.047\ M \qquad \therefore \quad [H^+]_{\text{added}} = 0.006\ M$$

Thus, more than half as much H^+ is required to reduce the pH by 0.5 unit as it took to reduce the pH by 1.0 unit.

(b)

$$\text{pH} = 8.15 + \log\frac{0.009 - 0.004}{0.041 + 0.004}$$

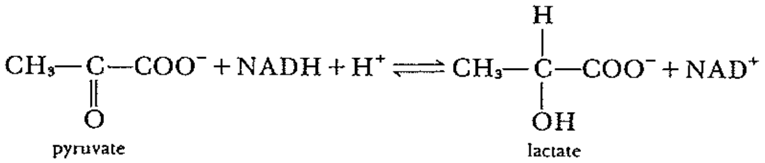
$$= 8.15 + \log\frac{0.005}{0.045} = 8.15 - \log 9 = 8.15 - 0.95$$

$$\text{pH} = 7.2 \qquad \boxed{\Delta\text{pH} = 0.3}$$

Thus, half as much H^+ decreased the pH by less than 0.5 unit.

· Problem 1-35

Lactic dehydrogenase catalyzes the reversible reaction shown below.



$$\underset{\text{pyruvate}}{CH_3{-}\underset{\underset{O}{\|}}{C}{-}COO^-} + NADH + H^+ \rightleftharpoons \underset{\text{lactate}}{CH_3{-}\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}{-}COO^-} + NAD^+$$

Suppose the enzyme that you are interested in has a relatively flat pH plateau (optimum) between pH 7.9 and pH 8.3. Beyond these limits, the reaction rate decreases markedly. The enzyme is also rapidly inactivated at high ionic strength. You wish to assay the enzyme in the direction of lactate production. The reaction will be allowed to proceed until 0.05 *M* lactate is produced. In order to minimize inactivation of the enzyme you must use the lowest concentration of buffer possible that will still maintain the pH within the limits of 7.9 to 8.4. You decide to use Tris as a buffer.

Describe in detail the characteristics of your buffer; that is, indicate the starting pH of the assay mixture, the final pH, the concentrations of conjugate acid and conjugate base at the beginning and end of the reaction, and the total buffer concentration (conjugate acid plus conjugate base). The pK_a value of Tris is 8.1.

Solution

The reaction utilizes H$^+$ ions. Therefore, we would start at the lowest pH permissible (7.9). The pH will rise as the reaction proceeds, but the final pH cannot be greater than 8.4. The problem is to calculate the concentration of Tris buffer, C, that will maintain the pH within these limits. Thus, C is unknown. At the start:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{Tris}^0]_0}{[\mathrm{Tris}^+]_0} \qquad 7.9 = 8.1 + \log\frac{[\mathrm{Tris}^0]_0}{[\mathrm{Tris}^+]_0}$$

$$\frac{[\mathrm{Tris}^+]_0}{[\mathrm{Tris}^0]_0} = \text{antilog } 0.2$$

$$\frac{[\mathrm{Tris}^+]_0}{[\mathrm{Tris}^0]_0} = \frac{1.585}{1} \qquad \text{or} \qquad [\mathrm{Tris}^+]_0 = \frac{1.585}{2.585}[C] = 0.613\,[C]$$

and

$$[\mathrm{Tris}^0]_0 = \frac{1}{2.585}[C] = 0.387\,[C]$$

At the end:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{Tris}^0]_f}{[\mathrm{Tris}^+]_f} \qquad 8.4 = 8.1 + \log\frac{[\mathrm{Tris}^0]_f}{[\mathrm{Tris}^+]_f}$$

$$\frac{[\mathrm{Tris}^0]_f}{[\mathrm{Tris}^+]_f} = \text{antilog } 0.3$$

$$\frac{[\mathrm{Tris}^0]_f}{[\mathrm{Tris}^+]_f} = \frac{2}{1} \qquad \text{or} \qquad [\mathrm{Tris}^0]_f = \frac{2}{3}[C] = 0.667\,[C]$$

$$\text{and} \qquad [\mathrm{Tris}^+]_f = \frac{1}{3}[C] = 0.333\,[C]$$

$$[\mathrm{Tris}^+]_f = [\mathrm{Tris}^+]_0 - 0.05$$

$$\therefore \quad 0.333[C] = 0.613[C] - 0.05$$

$$0.05 = 0.28\,[C] \qquad [C] = \frac{0.05}{0.28}$$

$$\boxed{[C] = 0.1786\ M}$$

Thus, at the start, the buffer contains:

$$[\mathrm{Tris}^+] = (0.613)(0.1786) = \boxed{0.1095\ M}$$

$$[\mathrm{Tris}^0] = (0.387)(0.1786) = \boxed{0.0691\ M}$$

At the end of the reaction, the buffer contains:

$$[\text{Tris}^+] = (0.333)(0.1786) = \boxed{\mathbf{0.0595}\ M}$$

$$[\text{Tris}^0] = (0.667)(0.1786) = \boxed{\mathbf{0.1191}\ M}$$

POLYPROTIC ACIDS

A polyprotic acid ionizes in successive steps:

$$\begin{tikzcd} H_2A \arrow[r, shift left, "K_{a_1}"] & H^+ + HA^- \arrow[l, shift left] \arrow[d, shift left, "K_{a_2}"] \\ & H^+ + A^{2-} \arrow[u, shift left] \end{tikzcd}$$

$$K_{a_1} = \frac{[H^+][HA^-]}{[H_2A]}$$

$$K_{a_2} = \frac{[H^+][A^{2-}]}{[HA^-]}$$

Note that HA^- is the conjugate base of H_2A, but the conjugate acid of A^{2-}. For most common weak diprotic acids, K_{a_1} is at least one order of magnitude greater than K_{a_2}. Consequently, the pH of a solution of H_2A is established almost exclusively by the first ionization.

Titration and buffer calculations for weak diprotic and triprotic acids are done exactly as shown earlier for weak monoprotic acids. The only new consideration is which K_a or pK_a value to use. Very simply, we use the appropriate constant that describes the equilibrium between the species we are dealing with. For example, Figure 1-4 shows the titration of a weak diprotic acid with OH^- ($pK_{a_1} = 4$, $pK_{a_2} = 7$). The pH at any point along the titration curve is given by:

$$\text{pH} = pK_{a_1} + \log \frac{[HA^-]}{[H_2A]} \quad \text{and} \quad \text{pH} = pK_{a_2} + \log \frac{[A^{2-}]}{[HA^-]}$$

Thus, if we know the exact ratio of either conjugate base-conjugate acid pair, we can calculate the pH. Alternately, if we know the pH, we can calculate the ratios of $[HA^-]/[H_2A]$ and $[A^{2-}]/[HA^-]$, hence, the ratio of all three species.

AMPHOTERIC SALTS—INTERMEDIATE IONS OF POLYPROTIC ACIDS

An intermediate ion of a polyprotic acid when dissolved in water undergoes both ionization as an acid (reaction 1) and ionization as a base or hydrolysis (reaction 2).

1. $HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+ \qquad K_{eq_1} = K_{a_2}$
2. $HA^- + H_2O \rightleftharpoons H_2A + OH^- \qquad K_{eq_2} = K_{h_1} = K_{b_2} = \dfrac{K_w}{K_{a_1}}$

If reaction 1 proceeds further to the right (that is, has a greater K_{eq}) than reaction 2, the solution is acidic. If reaction 2 proceeds further to the right

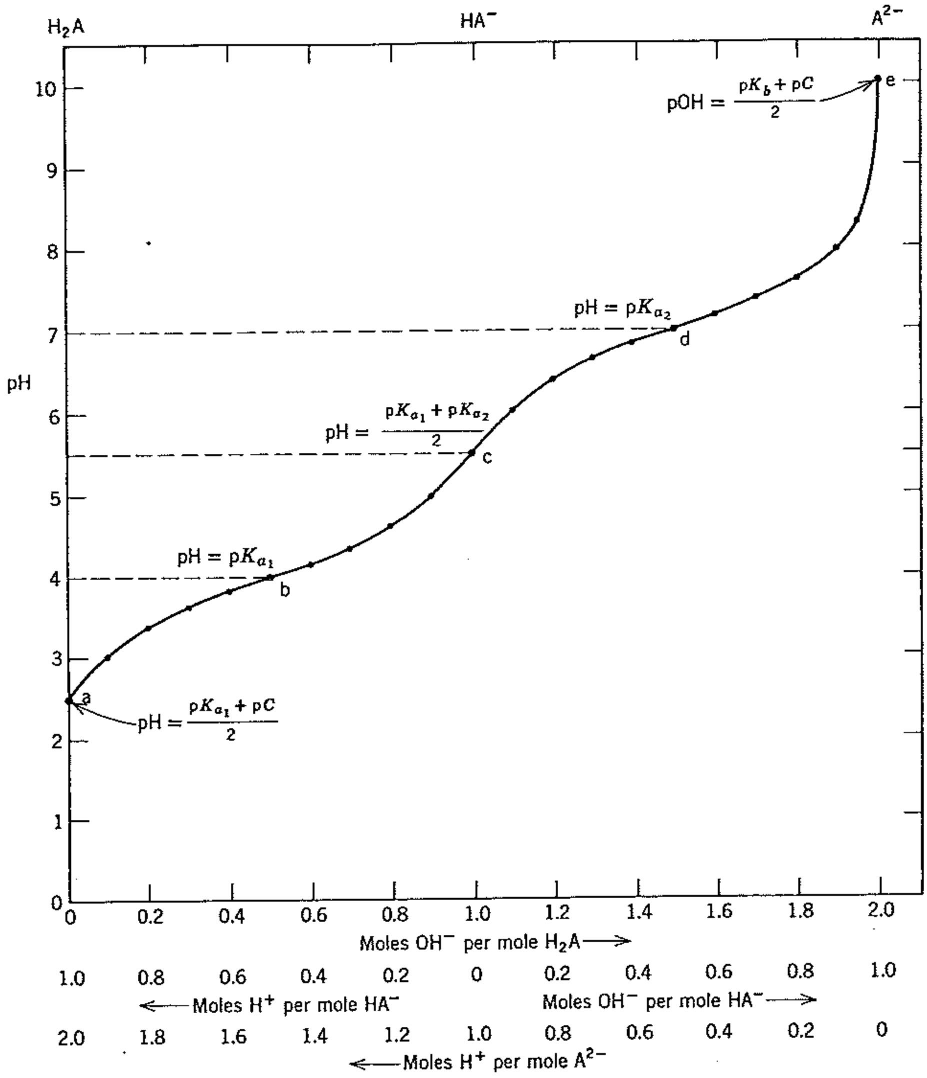


Figure 1-4 Titration of a weak diprotic acid, H_2A, with a strong base (e.g., KOH). $pK_{a_1} = 4.0$; $pK_{a_2} = 7.0$; $[H_2A]$ at the start $= 0.1\ M$.

than reaction 1, the solution is basic. However, the acidity or alkalinity is not as great as we might expect judging from the relative values of K_{eq_1} and K_{eq_2} because of a further compensating reaction that takes place. If reaction 1 goes further to the right than reaction 2, then some of the excess H_3O^+ produced reacts with unreacted HA^- according to reaction 3.

3. $$HA^- + H_3O^+ \rightleftharpoons H_2A + H_2O \qquad K_{eq_3} = \frac{1}{K_{a_1}}$$

If, however, reaction 2 proceeds further than reaction 1, some of the excess OH^- produced reacts with HA^- according to reaction 4.

4. $$HA^- + OH^- \rightleftharpoons A^{2-} + H_2O \qquad K_{eq_4} = \frac{1}{K_{h_2}} = \frac{1}{K_{b_1}} = \frac{K_{a_2}}{K_w}$$

Thus, the two major reactions taking place in the solution are either 1 plus 3 or 2 plus 4. The sum of either pair of reactions is identical and is called a "disproportionation" reaction 5. The equilibrium constant for a disproportionation reaction always is the ratio of the K_a for the next acid dissociation to the K_a for the preceding acid dissociation (K_{a_2}/K_{a_1}), as shown below.

1. $HA^- + H_2O \rightleftharpoons A^{2-} + H_3O^+ \qquad K_{eq_1} = K_{a_2}$

3. $HA^- + H_3O^+ \rightleftharpoons H_2A + H_2O \qquad K_{eq_3} = \dfrac{1}{K_{a_1}}$

Sum: 5. $2HA^- \rightleftharpoons A^{2-} + H_2A \qquad K_{eq_5} = K_{eq_1} \times K_{eq_3} = K_{dis}$

$$K_{dis} = \frac{K_{a_2}}{K_{a_1}}$$

or:

2. $HA^- + H_2O \rightleftharpoons H_2A + OH^- \qquad K_{eq_2} = \dfrac{K_w}{K_{a_1}}$

4. $HA^- + OH^- \rightleftharpoons A^{2-} + H_2O \qquad K_{eq_4} = \dfrac{K_{a_2}}{K_w}$

Sum: 5. $2HA^- \rightleftharpoons A^{2-} + H_2A \qquad K_{eq_5} = K_{eq_2} \times K_{eq_4} = K_{dis}$

$$K_{dis} = \frac{K_w}{K_{a_1}} \times \frac{K_{a_2}}{K_w}$$

$$K_{dis} = \frac{K_{a_2}}{K_{a_1}}$$

We can arrive at the same disproportionation reaction by assuming that 1 molecule of HA^- releases a proton and another molecule accepts the proton.

$$HA^- \rightleftharpoons H^+ + A^{2-} \qquad K_{eq} = K_{a_2}$$

$$HA^- + H^+ \rightleftharpoons H_2A \qquad K_{eq} = \frac{1}{K_{a_1}}$$

Sum: 5. $2HA^- \rightleftharpoons H_2A + A^{2-} \qquad K_{eq} = \dfrac{K_{a_2}}{K_{a_1}} = K_{dis}$

The disproportionation reaction tends to equalize the concentrations of the two ionic forms on either side of the intermediate ion. When writing reaction 5, we assume that the component reactions proceed to the same extent (we cancel H_2O and OH^- or H_2O and H_3O^+). Actually, reaction 1 or reaction 2 proceeds slightly further than reaction 3 or 4; that is why the solution is acidic or basic. However, the actual *amounts* of OH^- or H_3O^+ produced (by reaction 1 or 2) and utilized (by reaction 3 or 4) are much greater than the *difference between* the amounts produced and utilized. Consequently, we can safely use reaction 5 as a basis for calculating the concentrations of all ionic forms (H_2A, HA^-, and A^{2-}) in the solution.

The H^+ ion concentration and subsequently the pH of the solution may then be calculated from any K_{eq} expression containing the above components:

$$K_{a_1} = \frac{[H^+][HA^-]}{[H_2A]} \qquad K_{a_2} = \frac{[H^+][A^{2-}]}{[HA^-]}$$

$$K_{b_2} = \frac{[H_2A][OH^-]}{[HA^-]} = \frac{K_w}{K_{a_1}} \qquad K_{b_1} = \frac{[HA^-][OH^-]}{[A^{2-}]} = \frac{K_w}{K_{a_2}}$$

We can also derive equations from which the H^+ ion concentration and the pH may be determined directly from the K_{a_2} and K_{a_1} values.

$$K_{\text{dis}} = \frac{[H_2A][A^{2-}]}{[HA^-]^2} = \frac{K_{a_2}}{K_{a_1}}$$

$$[H_2A] = [A^{2-}]$$

$$\therefore \frac{[H_2A]^2}{[HA^-]^2} = \frac{K_{a_2}}{K_{a_1}} \quad \text{or} \quad \frac{[H_2A]}{[HA^-]} = \frac{\sqrt{K_{a_2}}}{\sqrt{K_{a_1}}}$$

Substituting the $[H_2A]/[HA^-]$ ratio into the K_{a_1} expression:

$$K_{a_1} = \frac{[H^+][HA^-]}{[H_2A]} \qquad [H^+] = \frac{K_{a_1}[H_2A]}{[HA^-]} = \frac{K_{a_1}\sqrt{K_{a_2}}}{\sqrt{K_{a_1}}}$$

$$\frac{K_{a_1}}{\sqrt{K_{a_1}}} = \sqrt{K_{a_1}} \qquad \therefore \quad [H^+] = \sqrt{K_{a_1}}\sqrt{K_{a_2}}$$

$$\boxed{[H^+] = \sqrt{K_{a_1}K_{a_2}}} \qquad (36)$$

$$\log [H^+] = \tfrac{1}{2}(\log K_{a_1} + \log K_{a_2})$$
$$-\log [H^+] = -\tfrac{1}{2}(\log K_{a_1} + \log K_{a_2})$$
$$-\log [H^+] = \frac{-\log K_{a_1} - \log K_{a_2}}{2}$$

$$\boxed{\mathrm{pH} = \frac{\mathrm{p}K_{a_1} + \mathrm{p}K_{a_2}}{2}} \qquad (37)$$

Intermediate ions are the predominant species at intermediate equivalence points. Therefore, we can predict that the pH at an intermediate equivalence point during the titration of a polyprotic acid (or amino acid) is the average of the $\mathrm{p}K_a$ values on either side of the equivalence point. For amino acids the pH is designated p*I* (isoelectric point) if the intermediate ion in question is the one that carries no *net* charge. At the p*I* the major ionic species present is AA^0. However, because of the disproportionation reaction, small (and essentially equal) amounts of AA^{-1} and AA^{+1} are also present. The pH is designated pH_m if the major ionic species present carries the maximum number of charges, regardless of sign. By the same reasoning we can show that the pH of a solution of a salt of a weak acid and a weak base is the average of the two $\mathrm{p}K_a$ values. For example, the pH of a solution of NH_4OAc is given by:

$$\mathrm{pH} = \frac{\mathrm{p}K_{a_{NH_4^+}} + \mathrm{p}K_{a_{HOAc}}}{2}$$

· Problem 1-36

Describe the preparation of 10 liters of 0.045 *M* potassium phosphate buffer, pH 7.5.

Solution

The pH of this buffer is a little above the pK_{a_2} of H_3PO_4 as shown in the titration curve in Figure 1-5. Consequently, the two major ionic species present are $H_2PO_4^-$ (conjugate acid) and HPO_4^{2-} (conjugate base) with the HPO_4^{2-} predominating.

The buffer can be prepared in any one of several ways: (1) by mixing KH_2PO_4 and K_2HPO_4 in the proper proportions, (2) by starting with H_3PO_4 and converting it to KH_2PO_4 plus K_2HPO_4 by adding the proper amount of KOH, (3) by starting with KH_2PO_4 and converting a portion of it to K_2HPO_4 by adding KOH, (4) by starting with K_2HPO_4 and converting a portion of it to KH_2PO_4 by adding a strong acid such as HCl, (5) by starting with K_3PO_4 and converting it to KH_2PO_4 plus K_2HPO_4 by adding HCl, and (6) by mixing K_3PO_4 and KH_2PO_4 in the proper proportions. Regardless of which method is used, the first step involves calculating the proportion and amounts of the two ionic species in the buffer.

The buffer contains a total of 10 liters × 0.045 *M* = 0.45 mole of phosphate.

$$pH = pK_{a_2} + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$7.5 = 7.2 + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \qquad 0.3 = \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = \text{antilog of } 0.3 = 2 = \frac{2}{1} \text{ ratio}$$

$\therefore$ $\frac{2}{3} \times 0.45$ mole = 0.30 mole of HPO_4^{2-} is needed and $\frac{1}{3} \times 0.45$ mole = 0.15 mole of $H_2PO_4^-$ is needed.

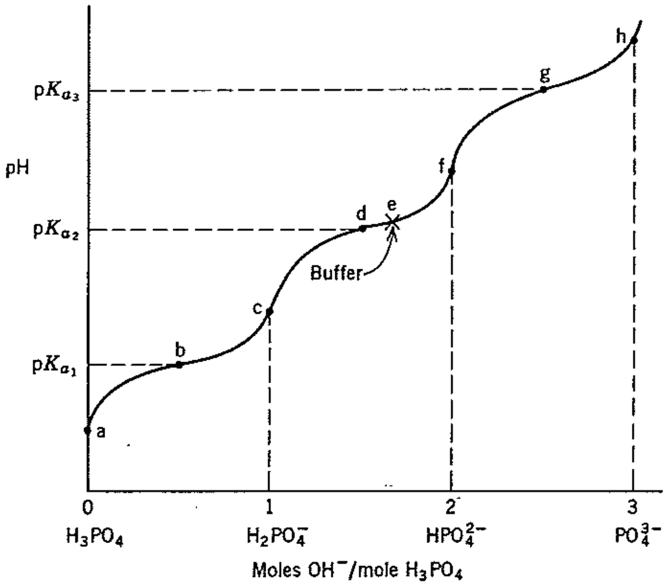


Figure 1-5 Titration curve of H_3PO_4.

1. *From KH_2PO_4 and K_2HPO_4*—Weigh out 0.30 mole of K_2HPO_4 (52.8 g) and 0.15 mole of KH_2PO_4 (20.4 g) and dissolve in sufficient water to make 10 liters final volume. Or, if stock solutions of the two phosphates are available, measure out the appropriate volumes of each and dilute to 10 liters. In practice, we might prepare 0.045 M K_2HPO_4 and 0.045 M KH_2PO_4 and simply mix the two until the pH (as measured with a pH meter) is 7.5. Since both stock solutions are 0.045 M, the total phosphate concentration will remain 0.045 M regardless of what volumes of each are added.
2. *From H_3PO_4 and KOH*—Start with 0.45 mole of H_3PO_4 (position a in Figure 1-5) and add sufficient KOH to titrate *completely* 1 hydrogen (to position c) and $\frac{2}{3}$ of the second hydrogen (to position e).

$$H_3PO_4 \xrightarrow{OH^-} H_2PO_4^- \xrightarrow{OH^-} HPO_4^{2-}$$

For example, suppose we have available only stock concentrated (15 M) H_3PO_4 and a standard solution of 1.5 M KOH. We need 0.45 mole of H_3PO_4.

$$\text{liters} \times M = \text{number of moles}$$
$$\text{liters} \times 15 = 0.45 \text{ mole}$$
$$\text{liters} = \frac{0.45}{15} = 0.03 \text{ liter}$$

∴ Take 30 ml of H_3PO_4. Add 0.45 mole of KOH to convert *all* the H_3PO_4 to $H_2PO_4^-$; then add another $\frac{2}{3} \times 0.45 = 0.30$ mole of KOH to convert 0.3 mole of $H_2PO_4^-$ to HPO_4^{2-}. In other words, a total of 0.75 mole of KOH is required.

Since we have available 1.5 M KOH, we can calculate how much of this solution to add.

$$\text{liters} \times M = \text{number of moles}$$
$$\text{liters} = \frac{\text{number of moles}}{M} = \frac{0.75}{1.5} = 0.500$$

∴ Add 500 ml of KOH to the 30 ml of concentrated H_3PO_4; then add sufficient water to bring the final volume to 10 liters.

3. *From KH_2PO_4 and KOH*—We can start with KH_2PO_4 (position c) and add sufficient KOH to convert $\frac{2}{3}$ of the $H_2PO_4^-$ to HPO_4^{2-} (position e).

$$H_2PO_4^- \xrightarrow{OH^-} HPO_4^{2-}$$

For example, suppose we have available only solid KH_2PO_4 and KOH. We need 0.45 mole of KH_2PO_4.

$$\frac{wt_g}{MW} = \text{number of moles}$$
$$wt_g = (0.45)(136) = 61.2 \text{ g}$$

Dissolve the KH_2PO_4 in some water; then add 0.30 mole of KOH (solid or dissolved in some water).

$$wt_g = (0.30)(56) = 16.8 \text{ g of KOH}$$

Next, add sufficient water to bring the volume to 10 liters.

4. *From K_2HPO_4 and HCl*—The HPO_4^{2-} (position f) may be converted to $H_2PO_4^-$ by adding HCl.

$$HPO_4^{2-} \xrightarrow{H^+} H_2PO_4^-$$

Because we want to end up with an $HPO_4^{2-}/H_2PO_4^-$ of $\frac{2}{1}$, we want to convert only $\frac{1}{3}$ of the HPO_4^{2-} to $H_2PO_4^-$ (to reach position e). Suppose we have available solid K_2HPO_4 and a 2 M solution of HCl. Weigh out 0.45 moles of K_2HPO_4.

$$\text{wt}_g = \text{number of moles} \times \text{MW}$$

$$\text{wt}_g = (0.45)(174) = 78.3\text{ g}$$

Dissolve the KH_2PO_4 in some water; then add $\frac{1}{3} \times 0.45 = 0.15$ mole of HCl.

$$\text{liters} \times M = \text{number of moles}$$

$$\text{liters} = \frac{\text{number of moles}}{M} = \frac{0.15}{2} = 0.075\text{ liter}$$

∴ Add 75 ml of 2 M HCl. Then add sufficient water to bring the volume to 10 liters.

5. *From K_3PO_4 and HCl*—Start with 0.45 mole of K_3PO_4 (position h) and add sufficient HCl to convert all the PO_4^{3-} to HPO_4^{2-} (position f). Then add additional HCl to convert $\frac{1}{3}$ of the HPO_4^{2-} to $H_2PO_4^-$ (position e).

$$PO_4^{3-} \xrightarrow{H^+} HPO_4^{2-} \xrightarrow{H^+} H_2PO_4^-$$

We need 0.45 mole of K_3PO_4.

$$\text{wt}_g = \text{number of moles} \times \text{MW}$$

$$\text{wt}_g = (0.45)(212) = 95.4\text{ g}$$

Dissolve the K_3PO_4 in water. Add 0.45 mole of HCl to convert all the PO_4^{3-} to HPO_4^{2-}. Then add another $\frac{1}{3} \times 0.45 = 0.15$ mole of HCl to convert 0.15 mole of HPO_4^{2-} to $H_2PO_4^-$. The final solution then contains 0.15 mole of $H_2PO_4^-$ and 0.30 mole of HPO_4^{2-}. Now add sufficient water to make 10 liters.

6. *From KH_2PO_4 and K_3PO_4*—The KH_2PO_4 and K_3PO_4 react to form K_2HPO_4. The $H_2PO_4^-$ acts as an acid and the PO_4^{3-} acts as a base.

$$H_2PO_4^- + PO_4^{3-} \rightleftharpoons 2HPO_4^{2-}$$

The reaction is the reverse of the disproportionation reaction. Note that each mole of $H_2PO_4^-$ and PO_4^{3-} yields 2 moles of HPO_4^{2-}. Thus, to produce 0.30 mole of HPO_4^{2-}, 0.15 mole of $H_2PO_4^-$ and 0.15 mole of PO_4^{3-} are required. But, in addition to the 0.30 mole of HPO_4^{2-}, the final solution contains 0.15 mole of $H_2PO_4^-$. Therefore, dissolve 0.30 mole of KH_2PO_4 and 0.15 mole of K_3PO_4 in water. Of the original 0.30 mole of KH_2PO_4, 0.15 mole reacts with the PO_4^{3-} to produce 0.30 mole of HPO_4^{2-}, leaving 0.15 mole as $H_2PO_4^-$. Then add sufficient water to make 10 liters.

• Problem 1-37

Calculate the concentration of all ionic species of succinate present in a solution (buffer) of 0.1 M succinate, pH 4.59.

Solution

We can see from the titration curve sketched in Figure 1-6 that the major ionic species present at pH 4.59 are H_2succinate and Hsuccinate$^-$ with the latter predominating. However, because pK_{a_2} is close to pK_{a_1}, an appreciable amount of succinate^{2-} is also present.

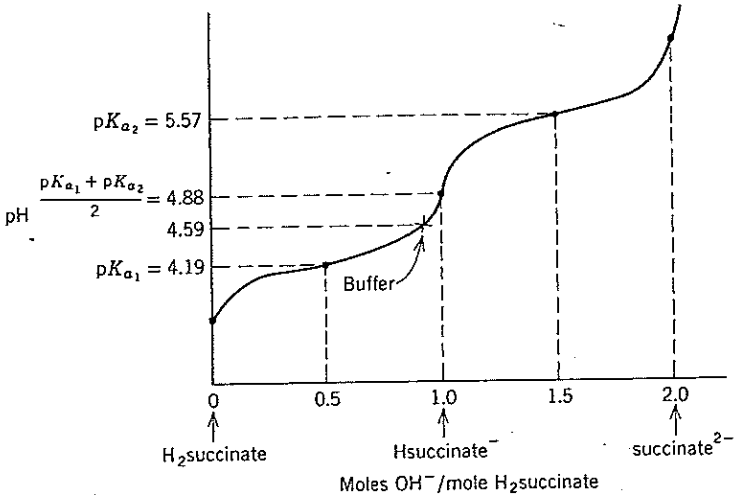


Figure 1-6 Titration curve of succinic acid.

First calculate the ratio of Hsuccinate$^-$/H_2succinate using the Henderson-Hasselbalch equation.

$$\text{pH} = pK_{a_1} + \log \frac{[\text{Hsuccinate}^-]}{[\text{H}_2\text{succinate}]} \qquad 4.59 = 4.19 + \log \frac{[\text{Hsuccinate}^-]}{[\text{H}_2\text{succinate}]}$$

$$0.40 = \log \frac{[\text{Hsuccinate}^-]}{[\text{H}_2\text{succinate}]} \qquad \frac{[\text{Hsuccinate}^-]}{[\text{H}_2\text{succinate}]} = \text{antilog of } 0.40 = 2.51$$

$\therefore$ The Hsuccinate$^-$/H_2succinate ratio is 2.51.

Next calculate the Hsuccinate$^-$/succinate^{2-} ratio at pH 4.59.

$$\text{pH} = pK_{a_2} + \log \frac{[\text{succinate}^{2-}]}{[\text{Hsuccinate}^-]} \qquad 4.59 = 5.57 + \log \frac{[\text{succinate}^{2-}]}{[\text{Hsuccinate}^-]}$$

$$-0.98 = \log \frac{[\text{succinate}^{2-}]}{[\text{Hsuccinate}^-]} \quad \text{or} \quad +0.98 = \log \frac{[\text{Hsuccinate}^-]}{[\text{succinate}^{2-}]}$$

$$\frac{[\text{Hsuccinate}^-]}{[\text{succinate}^{2-}]} = \text{antilog of } 0.98 = 9.55$$

$\therefore$ The Hsuccinate$^-$/succinate^{2-} ratio is 9.55:1.

The three ionic species are in the following proportions:

H_2succinate		Hsuccinate$^-$		succinate^{2-}
1	:	2.51		
		9.55	:	1

The two ratios must be expressed relative to a common component such as Hsuccinate$^-$. So, if 1 part succinate^{2-} is present for every 9.55 parts of Hsuccinate$^-$, calculate how much succinate^{2-} is present for every 2.51 parts of Hsuccinate$^-$.

$$\frac{1}{9.55} = \frac{y}{2.51} \qquad 9.55y = 2.51$$

$$y = \frac{2.51}{9.55} = 0.263$$

That is, the ratio of the three ionic species is:

H_2succinate		Hsuccinate$^-$		succinate^{2-}	total
1	:	2.51	:	0.263	3.773 parts

The *total* succinate concentration is 0.1 M.

$$\frac{1}{3.773}\times 0.1\ M = \boxed{\mathbf{0.0265\ \mathit{M}\ H_2succinate}}$$

$$\frac{2.51}{3.773}\times 0.1\ M = \boxed{\mathbf{0.0665\ \mathit{M}\ Hsuccinate^-}}$$

$$\frac{0.263}{3.773}\times 0.1\ M = \boxed{\mathbf{0.00697\ \mathit{M}\ succinate^{2-}}}$$

· Problem 1-38 ·

(a) What is the pH of a 0.1 M solution of monosodium succinate? (b) What are the concentrations of un-ionized succinic acid, Hsuccinate$^-$ and succinate^{2-} in the solution ($pK_{a_1} = 4.19$ and $pK_{a_2} = 5.57$)?

Solution

Monosodium succinate (Hsuccinate$^-$) is an intermediate ion of a polyprotic acid. The pH of a 0.1 M solution and the concentrations of all three ionic forms of succinic acid may be calculated as shown.

(a)
$$\text{pH} = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{4.19 + 5.57}{2} = \frac{9.76}{2}$$

$$\boxed{\mathbf{pH = 4.88}}$$

(b) The concentrations of all species present can be calculated in two ways. First, considering the disproportionation reaction:

$$2\text{Hsuccinate}^- \rightarrow \text{H}_2\text{succinate} + \text{succinate}^{2-}$$

$$K_{\text{dis}} = \frac{[\text{H}_2\text{succinate}][\text{succinate}^{2-}]}{[\text{Hsuccinate}^-]^2} = \frac{K_{a_2}}{K_{a_1}} = \frac{2.69\times 10^{-6}}{6.46\times 10^{-5}} = 4.16\times 10^{-2}$$

Let

$$y = M \text{ of Hsuccinate}^- \text{ that disappears}$$

$$\therefore\ \frac{y}{2} = M \text{ of H}_2\text{succinate produced}$$

and

$$\frac{y}{2} = M \text{ of succinate}^{2-} \text{ produced}$$

$$\frac{(y/2)(y/2)}{(0.1-y)^2} = 4.16\times 10^{-2} \qquad \sqrt{\frac{y^2}{4(0.1-y)^2}} = \sqrt{4.16\times 10^{-2}}$$

$$\frac{y}{2(0.1-y)} = 2.04\times 10^{-1} \qquad \frac{y}{(0.2-2y)} = 0.204$$

$$y = 0.0408 - 0.408y \qquad 1.408y = 0.0408$$

$$y = \frac{0.0408}{1.408} = 0.0290 \qquad \frac{y}{2} = 0.0145$$

$$\boxed{\begin{aligned} \mathbf{H_2succinate} &= \mathbf{0.0145}\ M \\ \mathbf{succinate^{2-}} &= \mathbf{0.0145}\ M \\ \mathbf{Hsuccinate^{-}} &= \mathbf{0.100 - 0.029 = 0.071}\ M \end{aligned}}$$

Alternatively, the concentrations can be calculated using the Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_{a_1} + \log\frac{[\text{Hsuccinate}^-]}{[\text{H}_2\text{succinate}]} \qquad 4.88 = 4.19 + \log\frac{[\text{Hsuccinate}^-]}{[\text{H}_2\text{succinate}]}$$

$$0.69 = \log\frac{[\text{Hsuccinate}^-]}{[\text{H}_2\text{succinate}]} \qquad \frac{[\text{Hsuccinate}^-]}{[\text{H}_2\text{succinate}]} = \text{antilog of } 0.69 = 4.9$$

∴ The ratio of $\text{Hsuccinate}^-/\text{H}_2\text{succinate}$ is 4.9 : 1.
Next calculate the ratio of $\text{Hsuccinate}^-/\text{succinate}^{2-}$.

$$\mathrm{pH} = \mathrm{p}K_{a_2} + \log\frac{[\text{succinate}^{2-}]}{[\text{Hsuccinate}^-]} \qquad 4.88 = 5.57 + \log\frac{[\text{succinate}^{2-}]}{[\text{Hsuccinate}^-]}$$

$$-0.69 = \log\frac{[\text{succinate}^{2-}]}{[\text{Hsuccinate}^-]} \quad \text{or} \quad +0.69 = \log\frac{[\text{Hsuccinate}^-]}{[\text{succinate}^{2-}]}$$

$$\frac{[\text{Hsuccinate}^-]}{[\text{succinate}^{2-}]} = \text{antilog of } 0.69 = 4.9$$

∴ The ratio of $\text{Hsuccinate}^-/\text{succinate}^{2-}$ is also 4.9 : 1. The concentrations of all three ionic species are in the ratio of 1 : 4.9 : 1.

$$\underset{1}{\text{H}_2\text{succinate}} \rightleftharpoons \underset{4.9}{\text{Hsuccinate}^-} \rightleftharpoons \underset{1}{\text{succinate}^{2-}}$$

The *total* concentration of succinate is 0.1 M.

$$\frac{1}{6.9} \times 0.1\ M = \text{H}_2\text{succinate concentration}$$

$$\frac{4.9}{6.9} \times 0.1\ M = \text{Hsuccinate}^- \text{ concentration}$$

$$\frac{1}{6.9} \times 0.1\ M = \text{succinate}^{2-} \text{ concentration}$$

$$\boxed{\begin{aligned} \therefore\ \mathbf{[H_2succinate]} &= \mathbf{0.0145}\ M \\ \mathbf{[Hsuccinate^{-}]} &= \mathbf{0.0710}\ M \\ \mathbf{[succinate^{2-}]} &= \mathbf{0.0145}\ M \end{aligned}}$$

DILUTIONS OF BUFFERS

· **Problem 1-39**

According to the Henderson-Hasselbalch equation, the pH of a buffer depends only on the *ratio* of conjugate base activity to conjugate acid activity. Explain then why the pH of a buffer changes when it is diluted.

Solution

The pH of a buffer changes with dilution for several reasons:

1. *Changes in Activity Coefficients*—The activity coefficients of different ions are not the same at any given concentration and do not change in an identical manner with a given change in concentration. For example, we can see from Appendix V that $\gamma_{HPO_4^{2-}}$ is 0.445 in a 0.1 *M* solution and 0.903 in a 0.001 *M* solution. The activity coefficient of its conjugate acid ($\gamma_{H_2PO_4^-}$) is 0.744 in a 0.1 *M* solution and 0.928 in a 0.001 *M* solution. In general, dilution results in an increase in γ; γ approaches unity at infinite dilution. The greater the charge on the ion, the greater is the change in its activity coefficient for a given change in concentration. Consider a "0.2 *M* phosphate buffer" containing equal molar amounts of HPO_4^{2-} and $H_2PO_4^-$ (0.1 *M* of each ionic species). The exact pH of the solution can be calculated taking into account the activity coefficients of the two ions. We can also calculate the pH of the solution after it is diluted 100-fold, taking into account the change in activity coefficients.

$$\mathrm{pH} = \mathrm{p}K_{a_2} + \log \frac{a_{HPO_4^{2-}}}{a_{H_2PO_4^-}} = \mathrm{p}K_{a_2} + \log \frac{\gamma_{HPO_4^{2-}}[HPO_4^{2-}]}{\gamma_{H_2PO_4^-}[H_2PO_4^-]}$$

<u>0.2 *M* Buffer</u>

$$\mathrm{pH} = 7.2 + \log \frac{(0.445)(0.1)}{(0.744)(0.1)}$$
$$= 7.2 + \log 0.598$$
$$= 7.2 - 0.22$$
$$\boxed{\mathbf{pH = 6.98}}$$

<u>0.002 *M* Buffer</u>

$$\mathrm{pH} = 7.2 + \log \frac{(0.903)(0.001)}{(0.928)(0.001)}$$
$$= 7.2 + \log 0.973$$
$$= 7.2 - 0.01$$
$$\boxed{\mathbf{pH = 7.19}}$$

In general, the log a_{A^-}/a_{HA} term of "acidic" buffers increases upon dilution, resulting in an increase in pH. In "basic" buffers, the log $a_{R\text{-}NH_2}/a_{R\text{-}NH_3^+}$ term decreases upon dilution, resulting in a decrease in pH.

2. *Changes in the Degree of Dissociation of HA*—As shown earlier, the degree of dissociation of a weak acid increases as the solution is diluted. In a solution of a weak acid alone (no added conjugate base), the acid is 10% dissociated when $[HA]_{orig} = 100\,K_a$ and 50% dissociated when $[HA]_{orig} = 2\,K_a$. Thus, the log A^-/HA term increases as the solution is diluted. In a buffer solution (weak acid plus added conjugate base), the A^- tends to suppress the dissociation of HA. Consequently, in a buffer solution containing $[HA] = 2\,K_a$, the HA is somewhat less than 50% dissociated.

For example, consider a 0.02 *M* succinate buffer, prepared by dissolving 0.01 mole of succinic acid and 0.01 mole of monosodium succinate in sufficient water to make 1 liter final volume. The monosodium succinate ionizes completely and the succinic acid ionizes partially. Let

$$y = M \text{ of succinic acid that dissociates}$$

$$\therefore \quad y = M \text{ of } H^+ \text{ produced upon dissociation}$$

and

$$y = M \text{ of } HA^- \text{ produced upon dissociation of the acid}$$

$$\therefore \quad [HA^-] = 0.01 + y \qquad [H_2A] = 0.01 - y \qquad \text{and} \qquad [H^+] = y$$

$$K_a = \frac{[H^+][HA^-]}{[H_2A]} = \frac{(y)(0.01 + y)}{(0.01 - y)} = 6.46 \times 10^{-5}$$

Because the concentrations of H_2A and HA^- are more than 100 times the K_{a_1} value, y is small compared to 0.01 and may be neglected.

$$\therefore \quad [H^+] = K_{a_1} \qquad pH = pK_{a_1} = 4.19$$

Now let us dilute the above buffer 100 times.

$$[HA^-] = 10^{-4} + y \qquad [H_2A] = 10^{-4} - y \qquad \text{and} \qquad [H^+] = y$$

Now the concentration of buffer components is of the same order of magnitude as the K_a value. Thus, H_2A is more than 10% dissociated and y is not small compared to 10^{-4}. Consequently, we must solve for y exactly.

$$K_a = \frac{(y)(10^{-4} + y)}{(10^{-4} - y)} = 6.46 \times 10^{-5}$$

$$6.46 \times 10^{-9} - 6.46 \times 10^{-5}y = 10^{-4}y + y^2$$

$$y^2 + 10 \times 10^{-5}y + 6.46 \times 10^{-5}y - 6.46 \times 10^{-9} = 0$$

$$y^2 + 16.46 \times 10^{-5}y - 6.46 \times 10^{-9} = 0$$

$$y = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where $a = 1 \qquad b = 16.46 \times 10^{-5} \qquad c = 6.46 \times 10^{-9}$.

$$y = \frac{-16.46 \times 10^{-5} \pm \sqrt{(16.46 \times 10^{-5})^2 - 4(-6.46 \times 10^{-9})}}{2}$$

$$y = \frac{-16.46 \times 10^{-5} \pm \sqrt{271 \times 10^{-10} + 258 \times 10^{-10}}}{2}$$

$$y = \frac{-16.46 \times 10^{-5} \pm \sqrt{529 \times 10^{-10}}}{2}$$

$$y = \frac{-16.46 \times 10^{-5} \pm 23.0 \times 10^{-5}}{2} = \frac{6.54 \times 10^{-5}}{2}$$

$$y = 3.27 \times 10^{-5}$$

$$[H^+] = 3.27 \times 10^{-5}\,M \qquad \therefore \quad pH = 4.49$$

$$[H_2A] = (10 \times 10^{-5}) - (3.27 \times 10^{-5}) = 6.73 \times 10^{-5}\,M$$

$$[HA^-] = (10 \times 10^{-5}) + (3.27 \times 10^{-5}) = 13.27 \times 10^{-5}\,M$$

Note that the $[HA^-]/[H_2A]$ ratio that is essentially 1 in the $10^{-2}\,M$ buffer changes to about 2 when the buffer is diluted 100-fold.

3. Finally, as the buffer is diluted extensively, its contribution toward the H^+ or OH^- ion concentration of the solution approaches that of water and the pH approaches 7.

· Problem 1-40

Suppose that you prepare a buffer by dissolving 0.10 mole per liter of a weak acid, HA, and 0.10 mole per liter of its sodium salt, A^-. Assume that $pK_a = 3$. (a) What is the pH of the buffer? (b) How much does the buffer have to be diluted for the pH to increase by 1 unit? Neglect changes in activity coefficients.

Solution

(a) Let $y = M$ of HA that dissociates

$$\therefore \quad [HA] = 0.10 - y \qquad [A^-] = 0.10 + y \qquad \text{and} \qquad [H^+] = y$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(y)(0.10 + y)}{(0.10 - y)} = 10^{-3}$$

Because the concentrations of HA and A^- are much larger than K_a, y is small and may be neglected in the HA and A^- terms.

$$K_a = \frac{(y)(0.10)}{(0.10)} = 10^{-3}$$

$$y = 10^{-3} = [H^+]$$

$$\boxed{\mathbf{pH = 3}}$$

(b) If the pH increases by 1 unit upon dilution (to pH 4.0), then $[H^+] = 10^{-4}\,M = y$. Calculate the new "original" concentrations of HA and A^- that we must start with (or dilute the original buffer to) so that when the addition and subtraction of y are made (when the HA dissociates) the ratio of A^-/HA is 10:1.

Let C = new "original" M of HA and A^-.

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad 10^{-3} = \frac{(10^{-4})(C + 10^{-4})}{(C - 10^{-4})}$$

$$10^{-3}\,C - 10^{-7} = 10^{-4}\,C + 10^{-8}$$

$$0.9 \times 10^{-3}\,C = 1.1 \times 10^{-7}$$

$$C = \frac{1.1 \times 10^{-7}}{0.9 \times 10^{-3}} = 1.22 \times 10^{-4}$$

In other words, if we start by dissolving 1.22×10^{-4} moles per liter each of HA and A^-, $1 \times 10^{-4}\,M$ HA dissociates producing $2.22 \times 10^{-4}\,M$ A^- and leaving $0.22 \times 10^{-4}\,M$ HA.

Check:

$$10^{-3} = \frac{(10^{-4})(2.22 \times 10^{-4})}{(0.22 \times 10^{-4})} = (10^{-4})(10)$$

We will obtain exactly the same result by diluting the 0.2 M buffer to the above new concentrations.

$$\left.\begin{matrix}0.10\,M\ \text{HA}\\ +\\ 0.10\,M\ \text{A}^-\end{matrix}\right\}\xrightarrow{\text{dilution}\ldots}\begin{matrix}1.22\times 10^{-4}\,M\ \text{HA}\\ +\\ 1.22\times 10^{-4}\,M\ \text{A}^-\end{matrix}$$

$$\Big\downarrow\ \text{\ldots results in further dissociation of HA}$$

$$\begin{matrix}0.22\times 10^{-4}\,M\ \text{HA}\\ +\\ 2.22\times 10^{-4}\,M\ \text{A}^-\end{matrix}$$

∴ The original buffer must be diluted 820-fold.
$\frac{1}{820}\times 0.10\,M = 1.22\times 10^{-4}\,M$

GENERAL RULE

As a general rule for solving buffer problems, we can assume that the concentrations of conjugate acid and conjugate base present in solution are the same as the concentrations of each originally added to the solution (or produced by partial titration of one or the other). This general rule does not hold when the buffer is extremely dilute (when the concentrations of buffer components are in the region of the K_a value). In such dilute buffers, the changes (y) are large compared to the original concentrations.

CORRECTIONS FOR TOTAL IONIC STRENGTH

Ions (in addition to those of the buffer components) influence the ionic strength and affect the activity coefficients of the buffer components. Thus, even in a very dilute solution containing equimolar concentrations of, for example, HPO_4^{2-} and $H_2PO_4^-$, the pH will not equal pK_a if a relatively high concentration of NaCl is present. Instead of correcting the activity coefficients of the buffer components for the total ionic strength, it is simpler to define a new, *apparent* or *effective* pK_a that relates the pH (i.e., $-\log a_{H^+}$) to the actual concentrations of buffer components at a given total ionic strength. The apparent pK_a is designated pK'_a.

$$\boxed{K'_a = \frac{a_{H^+}[A^-]}{[HA]}} \quad \text{and} \quad \boxed{pH = pK'_a + \log\frac{[A^-]}{[HA]}} \tag{38}$$

The effect of total ionic strength on K_a or pK_a can be quantitatively predicted from the Debye-Hückel equation. Thus, at any total ionic strength, the effective pK_a is given by:

$$\boxed{pK'_a = pK_a + \Delta pK_a} \tag{39}$$

The values for ΔpK_a at three different total ionic strengths are given in Appendix VI.

· Problem 1-41

What is the pH of a 0.05 M KCl solution containing 0.01 M K_2HPO_4 and 0.01 M KH_2PO_4?

Solution

The pH is *not* 7.2 even though $[HPO_4^{2-}] = [H_2PO_4^-]$. If we correct for the activity coefficients of HPO_4^{2-} and $H_2PO_4^-$, we still will not obtain the correct pH. We must correct for the total ionic strength, part of which results from the KCl. First calculate the ionic strength. The solution contains: 0.01 M HPO_4^{2-} + 0.01 M $H_2PO_4^-$ + 0.05 M Cl^- + 0.08 M K^+ (one K^+ for every $H_2PO_4^-$ and Cl^-; two K^+ for every HPO_4^{2-}).

$$\frac{\Gamma}{2} = \frac{[HPO_4^{2-}](2)^2 + [H_2PO_4^-](1)^2 + [Cl^-](1)^2 + [K^+](1)^2}{2}$$

$$= \frac{(0.01)(2)^2 + (0.01)(1) + (0.05)(1) + (0.08)(1)}{2}$$

$$= \frac{0.18}{2} = 0.09$$

From Appendix VI, we see that at ~ 0.10 ionic strength, ΔpK_a for a conjugate acid with a charge of -1 is -0.32.

$$pK_a' = pK_a + \Delta pK_a \qquad pK_a' = 7.2 + (-0.32)$$

$$pK_a' = 6.88$$

Since $[HPO_4^{2-}] = [H_2PO_4^-]$, $pH = pK_a'$.

$$\boxed{pH = 6.88}$$

BUFFERS OF CONSTANT IONIC STRENGTH

In order to determine the effect of pH on a reaction, we must make certain that all the buffers used are of the same ionic strength (or else establish that changing ionic strength has no effect). Facts not often appreciated are (a) a buffer of any given composition has a different ionic strength at different pH values, and (b) two buffers of different composition may have different ionic strengths at the same pH. The simplest way to deal with a series of buffers of varying ionic strengths is to determine which buffer has the greatest ionic strength and then make all the others up to that maximum by adding a neutral, noninhibitory salt, such as KCl.

· Problem 1-42

(a) Which buffer has the greater ionic strength: a 0.05 M Tris buffer, pH 7.5, or a 0.05 M phosphate buffer, pH 7.5? (b) How can the ionic strengths be equalized?

Solution

(a) The Tris buffer contains Tris^0, Tris$^+$, and a counter ion, for example, Cl$^-$. (The buffer might have been made by titrating Tris^0 with HCl.) Tris^0 is uncharged and, thus, has no effect on ionic strength. The concentrations of H$^+$ and OH$^-$ are exceedingly low and, thus, can also be neglected. If we kept track of the amount of HCl added to attain pH 7.5, we would automatically know the concentration of Tris$^+$. If not, we can calculate [Tris$^+$]:

$$\text{pH} = \text{p}K_a + \log\frac{[\text{Tris}^0]}{[\text{Tris}^+]} \qquad 7.5 = 8.1 + \log\frac{[\text{Tris}^0]}{[\text{Tris}^+]}$$

$$-0.6 = \log\frac{[\text{Tris}^0]}{[\text{Tris}^+]} \qquad [\text{Tris}^+] = \frac{4}{5}\times 0.05\ M = 0.04\ M$$

$$\therefore\quad [\text{Cl}^-] = 0.04\ M$$

A more accurate calculation would include γ_{Tris^+} (about 0.9 for monopositive ions in the region of 0.05 M).

The phosphate buffer contains $H_2PO_4^-$, HPO_4^{2-} and, for example, K$^+$. The pH is in the region of pK_{a_2}. Therefore, there is *approximately* 0.025 M of each phosphate species present. (If we prepared the buffer ourselves, we would know the exact amounts of HPO_4^{2-} and $H_2PO_4^-$ present.) The activity coefficients of HPO_4^{2-} and $H_2PO_4^-$ in the region of 0.025 M are 0.64 and 0.88, respectively (estimated from a semi-log plot of the values given in Appendix V).

$$\text{pH} = \text{p}K_{a_2} + \log\frac{\gamma_{HPO_4^{2-}}[HPO_4^{2-}]}{\gamma_{H_2PO_4^-}[H_2PO_4^-]} \qquad 7.5 = 7.2 + \log\frac{0.64[HPO_4^{2-}]}{0.88[H_2PO_4^-]}$$

$$0.3 = \log\frac{0.64[HPO_4^{2-}]}{0.88[H_2PO_4^-]} \qquad \therefore\quad \frac{0.64[HPO_4^{2-}]}{0.88[H_2PO_4^-]} = \frac{2}{1}$$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{(2)(0.88)}{(1)(0.64)} = \frac{2.75}{1}$$

$$\therefore\quad [HPO_4^{2-}] = \frac{2.75}{3.75}\times 0.05 = 0.037\ M$$

$$[H_2PO_4^-] = \frac{1}{3.75}\times 0.05 = 0.013\ M$$

The phosphate buffer contains: 0.037 M HPO_4^{2-}, 0.013 M $H_2PO_4^-$, and $(0.037)(2) + (0.013)(1) = 0.087\ M$ K$^+$.

The ionic strengths of the two buffers are:

Tris: $$\frac{\Gamma}{2} = \frac{[\text{Tris}^+](1)^2 + [\text{Cl}^-](1)^2}{2} = \frac{0.04 + 0.04}{2}$$

$$\boxed{\frac{\Gamma}{2} = 0.04}$$

Phosphate:
$$\frac{\Gamma}{2} = \frac{[HPO_4^{2-}](2)^2 + [H_2PO_4^-](1)^2 + [K^+](1)^2}{2}$$
$$= \frac{(0.037)(4) + (0.013)(1) + (0.087)(1)}{2} = \frac{0.248}{2}$$

$$\boxed{\frac{\Gamma}{2} = 0.124}$$

Thus, the 0.05 *M* phosphate buffer has about three times the ionic strength of the 0.05 *M* Tris buffer at pH 7.5.

(b) The Tris buffer can be made up to 0.124 ionic strength by adding $0.124 - 0.04 = 0.084$ *M* KCl. (The pH may change slightly when the ionic strength is adjusted from 0.04 to 0.124.)

E. AMINO ACIDS AND PEPTIDES

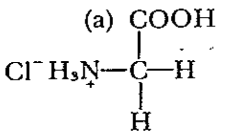
The common amino acids are simply weak polyprotic acids. Calculations of pH, buffer preparation, and capacity, and so on, are done exactly as shown in the preceding sections. Neutral amino acids (e.g., glycine, alanine, threonine) are treated as diprotic acids (Table 1-1). Acidic amino acids (e.g., aspartic acid, glutamic acid) and basic amino acids (e.g., lysine, histidine, arginine) are treated as triprotic acids, exactly as shown earlier for phosphoric acid.

· **Problem 1-43**

"Glycine" can be obtained in three forms: (a) glycine hydrochloride, (b) isoelectric glycine (sometimes called glycine, free base), and (c) sodium glycinate. Draw the structures of these three forms.

Solution

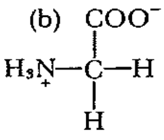
(a)



$$\mathrm{Cl^-\,H_3\overset{+}{N}-\underset{H}{\overset{COOH}{C}}-H}$$

glycine hydrochloride
(AA^{+1})

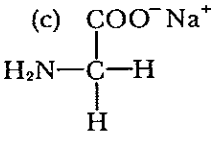
(b)



$$\mathrm{H_3\overset{+}{N}-\underset{H}{\overset{COO^-}{C}}-H}$$

isoelectric glycine
(AA^0)

(c)



$$\mathrm{H_2N-\underset{H}{\overset{COO^-Na^+}{C}}-H}$$

sodium glycinate
(AA^{-1})

· **Problem 1-44**

Calculate the pH of a 0.1 *M* solution of (a) glycine hydrochloride, (b) isoelectric glycine, and (c) sodium glycinate.

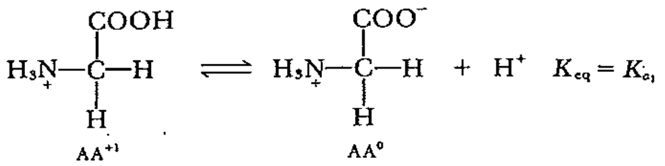
Solution

(a) Glycine hydrochloride is essentially a diprotic acid. Because the carboxyl group is so much stronger an acid ($K_{a_1} = 4.57 \times 10^{-3}$, $pK_{a_1} = 2.34$) than

Table 1-1 Predominant Species and pH at Key Points Along the Titration Curve of Weak Diprotic Acids

Start	pK_{a_1} *(halfway to 1st equiv. point)*	*First Equivalence Point*	pK_{a_2} *(halfway to 2nd equiv. point)*	*Second Equivalence Point*
H_2A	50% H_2A 50% HA^-	HA^-	50% HA^- 50% A^{2-}	A^{2-}
H_2CO_3 (CO_2)	50% $H_2CO_3 + CO_2$ 50% HCO_3^-	HCO_3^-	50% HCO_3^- 50% CO_3^{2-}	CO_3^{2-}
$HOOC\text{-}(CH_2)_2\text{-}COOH$	50% $HOOC\text{-}(CH_2)_2\text{-}COOH$ 50% $^-OOC\text{-}(CH_2)_2\text{-}COOH$	$^-OOC\text{-}(CH_2)\text{-}COOH$	50% $^-OOC\text{-}(CH_2)\text{-}COOH$ 50% $^-OOC\text{-}(CH_2)\text{-}COO^-$	$^-OOC\text{-}(CH_2)_2\text{-}COO^-$
$H_3N^+\text{-}CHR\text{-}COOH$	50% $H_3N^+\text{-}CHR\text{-}COOH$ 50% $H_3N^+\text{-}CHR\text{-}COO^-$	$H_3N^+\text{-}CHR\text{-}COO^-$ ($pH = pI$)	50% $H_3N^+\text{-}CHR\text{-}COO^-$ 50% $H_2N\text{-}CHR\text{-}COO^-$	$H_2N\text{-}CHR\text{-}COO^-$
$H_3N^+\text{-}R\text{-}NH_3^+$	50% $H_3N^+\text{-}R\text{-}NH_3^+$ 50% $H_3N^+\text{-}R\text{-}NH_2$	$H_3N^+\text{-}R\text{-}NH_2$	50% $H_3N^+\text{-}R\text{-}NH_2$ 50% $H_2N\text{-}R\text{-}NH_2$	$H_2N\text{-}R\text{-}NH_2$
$pH \simeq \frac{pK_{a_1} + p[Conc]}{2}$	$pH = pK_{a_1}$	$pH = \frac{pK_{a_1} + pK_{a_2}}{2}$	$pH = pK_{a_2}$	$pOH \simeq \frac{pK_{b_2} + p[Conc]}{2}$ $pH = 14 - pOH$

the charged amino group ($pK_{a_2} = 9.6$), the pH of the solution is established almost exclusively by the extent to which the carboxyl ionizes.



$$\underset{AA^{+1}}{\mathrm{H_3\underset{+}{N}-\overset{\overset{COOH}{|}}{\underset{\underset{H}{|}}{C}}-H}} \rightleftharpoons \underset{AA^{0}}{\mathrm{H_3\underset{+}{N}-\overset{\overset{COO^-}{|}}{\underset{\underset{H}{|}}{C}}-H}} + H^+ \quad K_{eq} = K_{a_1}$$

$$K_{a_1} = \frac{[AA^0][H^+]}{[AA^{+1}]}$$

Let

$$y = M \text{ of } AA^{+1} \text{ that ionizes}$$
$$\therefore \quad y = M \text{ of } H^+ \text{ produced}$$

and

$$y = M \text{ of } AA^0 \text{ produced}$$

and

$$0.1 - y = M \text{ of } AA^{+1} \text{ remaining at equilibrium}$$

$$K_{a_1} = \frac{(y)(y)}{(0.1 - y)} = 4.57 \times 10^{-3}$$

Because of the proximity of the amino and carboxyl groups, the carboxyl group is a stronger acid than that of acetic acid. The y in the denominator cannot be ignored.

$$4.57 \times 10^{-4} - 4.57 \times 10^{-3}y = y^2$$
$$y^2 + 4.57 \times 10^{-3}y - 4.57 \times 10^{-4} = 0$$

$$y = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where $a = 1$ $\quad b = 4.57 \times 10^{-3}$ $\quad c = -4.57 \times 10^{-4}$.
Solving for y, we obtain:

$$\boxed{[H^+] = 1.92 \times 10^{-2}\,M} \qquad \boxed{pH = 1.72}$$

Thus, glycine hydrochloride is 19.2% ionized in a 0.1 M solution.

(b) Isoelectric glycine is an intermediate ion of a polyprotic acid.

The pH of a solution of an intermediate ion is essentially independent of the concentration of the ion. The pH may be calculated from the pK_a values on either side of the ion; that is, from the pK_a of the next acid group to ionize and the pK_a of the previous acid group ionized.

$$pH = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{2.34 + 9.6}{2} = \frac{11.94}{2}$$

$$\boxed{pH = 5.97}$$

At this point, it would be convenient to review *why* the pH is the average of pK_{a_2} and pK_{a_1}. The pI is defined as that pH where the predominant ionic form is AA^0, and any small concentration of AA^+ present is balanced by an equal concentration of AA^-. We know that:

$$K_{a_1} = \frac{[AA^0][H^+]}{[AA^+]} \quad \text{and} \quad K_{a_2} = \frac{[AA^-][H^+]}{[AA^0]}$$

$$\therefore \quad [AA^0] = \frac{K_{a_1}[AA^+]}{[H^+]} \quad \text{and} \quad [H^+] = \frac{K_{a_2}[AA^0]}{[AA^-]}$$

Substituting for $[AA^0]$:

$$[H^+] = \frac{K_{a_2}K_{a_1}[AA^+]}{[AA^-][H^+]} \quad \text{or} \quad [H^+]^2 = \frac{K_{a_2}K_{a_1}[AA^+]}{[AA^-]}$$

But: $[AA^+] = [AA^-]$

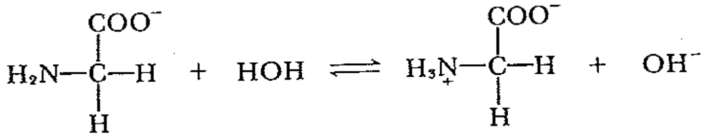
$$\therefore \quad \boxed{[H^+] = \sqrt{K_{a_2}K_{a_1}}} \quad \text{and} \quad \boxed{pH = \frac{pK_{a_2} + pK_{a_1}}{2}} \tag{40}$$

(c) Sodium glycinate is a diprotic base. Both the un-ionized amino group and the carboxylate ion can accept a proton from water. However, because the amino group is a much stronger base than the carboxylate ion, the pH of the solution depends almost entirely on the extent to which the amino group ionizes. We can check the relative base strengths by calculating K_b for each group. For the amino group,

$$K_{b_1} = \frac{K_w}{K_{a_2}} = \frac{10^{-14}}{10^{-9.6}} = 10^{-4.4} = 3.98 \times 10^{-5}$$

For the carboxylate ion,

$$K_{b_2} = \frac{K_w}{K_{a_1}} = \frac{10^{-14}}{10^{-2.34}} = 10^{-11.66} = 2.19 \times 10^{-12}$$



$$H_2N\text{—}\overset{\displaystyle COO^-}{\underset{\displaystyle H}{C}}\text{—}H + HOH \rightleftharpoons H_3\overset{+}{N}\text{—}\overset{\displaystyle COO^-}{\underset{\displaystyle H}{C}}\text{—}H + OH^-$$

AA^{-1} $\qquad$ AA^0

$$K_{b_1} = \frac{[OH^-][AA^0]}{[AA^{-1}]} = \frac{(y)(y)}{(0.1 - y)}$$

Because the concentration of sodium glycinate is large compared to K_{b_1}, we can neglect the y in the denominator.

$$3.98 \times 10^{-5} = \frac{y^2}{0.1} \qquad y^2 = 3.98 \times 10^{-6}$$

$$y = \sqrt{3.98 \times 10^{-6}} = 1.995 \times 10^{-3}$$

$$[OH^-] = 1.995 \times 10^{-3}\,M \simeq 2 \times 10^{-3}\,M$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12}$$

$$\mathrm{pH} = \log\frac{1}{[\mathrm{H}^+]} = \log\frac{1}{5\times10^{-12}} = \log 2\times10^{11}$$

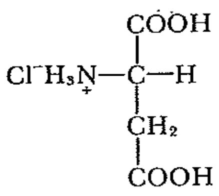
$$\boxed{\mathbf{pH = 11.3}}$$

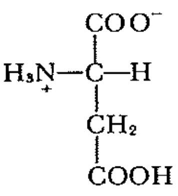
• Problem 1-45

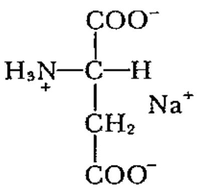
(a) Draw the structures of the various forms of "aspartic acid" that may be obtained. (b)–(e) Show how each form ionizes in water.

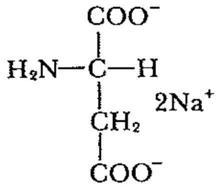
Solution

(a) "Aspartic acid" may be obtained in four forms: aspartic hydrochloride (AA^{+1}), isoelectric aspartic acid (AA^0), monosodium aspartate (AA^{-1}), and disodium aspartate (AA^{-2}). The structures are shown below.

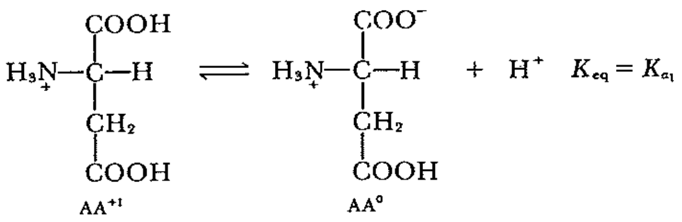

aspartic hydrochloride (AA^{+1})


isoelectric aspartic acid (AA^0)


monosodium aspartate (AA^{-1})


disodium aspartate (AA^{-2})

(b) Aspartic hydrochloride ionizes as a typical polyprotic acid. The pK_a values for the three acidic groups are 2.1 (α-COOH), 3.86 (β-COOH), and 9.82 (α-NH_3^+). Because the α-COOH is so much stronger an acid than the other two groups, the pH of an aspartic hydrochloride solution depends almost exclusively on the concentration of aspartic hydrochloride and the extent to which the α-COOH ionizes.



The pH calculations may be made exactly as described in the preceding problem for glycine hydrochloride.

$$K_{a_1} = \frac{[AA^0][H^+]}{[AA^{+1}]}$$

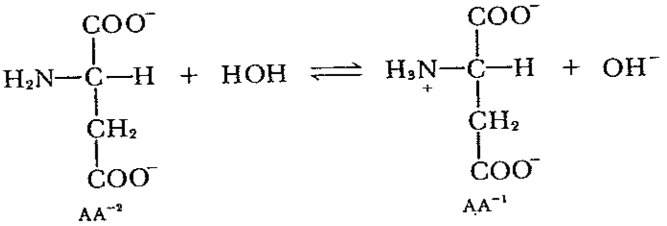
(c) Disodium aspartate ionizes as a typical polyprotic base. The pK_b values for the three basic groups can be calculated from their respective pK_a values as shown in Table 1-2.

$$pK_b = 14 - pK_a$$

Table 1-2

Conjugate Acid	pK_a	*Conjugate Base*	pK_b
α-COOH	2.1 (pK_{a_1})	α-COO^-	11.9 (pK_{b_3})
β-COOH	3.86 (pK_{a_2})	β-COO^-	10.14 (pK_{b_2})
α-NH_3^+	9.82 (pK_{a_3})	α-NH_2	4.18 (pK_{b_1})

Note that the pK_a values of the conjugate acids are numbered in decreasing order of acid strength. The pK_b values are numbered in decreasing order of base strength. Therefore, the α-NH_3^+ group is the weakest acid and its pK_a value is designated pK_{a_3}. The conjugate base of the α-NH_3^+ group is the α-NH_2 group which is the strongest of the basic groups. Hence, its pK_b value is designated pK_{b_1}. Because pK_{b_2} is almost 6 pH units less than pK_{b_1} (K_{b_2} is almost 10^6 times less than K_{b_1}), the pH of a disodium aspartate solution is established almost exclusively by the concentration of the salt and the extent of ionization of the α-NH_2 group.

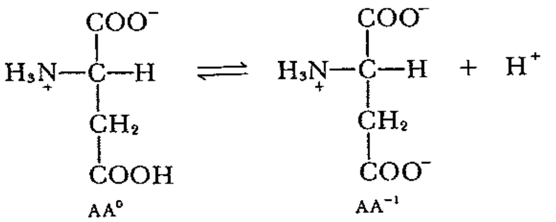


$$K_{eq} = K_{b_1} = \frac{K_w}{K_{a_3}}$$

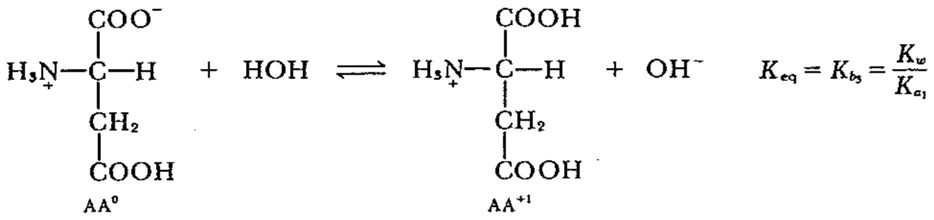
Calculations of pH are done exactly as described in the previous problem for sodium glycinate.

$$K_{b_1} = \frac{[AA^{-1}][OH^-]}{[AA^{-2}]}$$

(d) The two remaining forms of aspartic acid are intermediate ions of polyprotic acids. For example, consider isoelectric aspartic acid. The compound ionizes both as an acid and a base.



$$K_{eq} = K_{a_2}$$

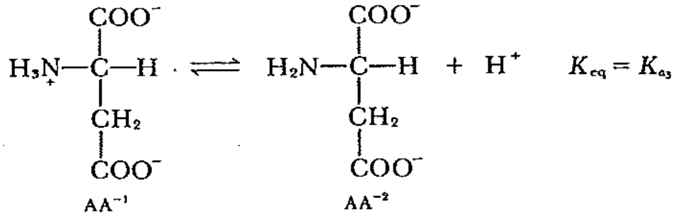


$$\underset{\mathrm{AA^0}}{\mathrm{H_3\overset{+}{N}{-}CH(CH_2COOH){-}COO^-}} + \mathrm{HOH} \rightleftharpoons \underset{\mathrm{AA^{+1}}}{\mathrm{H_3\overset{+}{N}{-}CH(CH_2COOH){-}COOH}} + \mathrm{OH^-} \qquad K_{eq} = K_{b_3} = \frac{K_w}{K_{a_1}}$$

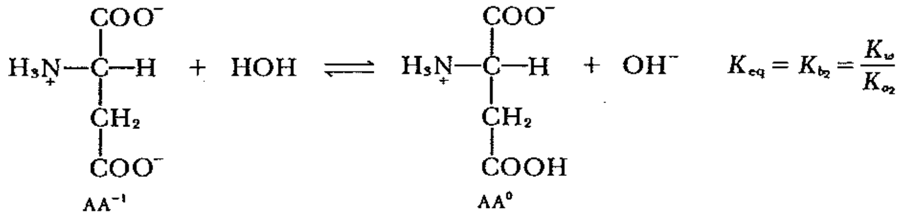
The pH of solutions of isoelectric aspartic acid may be calculated from the pK_{a_1} and pK_{a_2} values (the pK_a values on either side of isoelectric aspartic acid in its titration curve).

$$\mathrm{pH} = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{2.1 + 3.86}{2} = \frac{5.96}{2} = 2.98$$

(e) The remaining form, monosodium aspartate, is also an intermediate ion of a polyprotic acid. Its ionizations as an acid and as a base are shown below.



$$\underset{\mathrm{AA^{-1}}}{\mathrm{H_3\overset{+}{N}{-}CH(CH_2COO^-){-}COO^-}} \rightleftharpoons \underset{\mathrm{AA^{-2}}}{\mathrm{H_2N{-}CH(CH_2COO^-){-}COO^-}} + \mathrm{H^+} \qquad K_{eq} = K_{a_3}$$



$$\underset{\mathrm{AA^{-1}}}{\mathrm{H_3\overset{+}{N}{-}CH(CH_2COO^-){-}COO^-}} + \mathrm{HOH} \rightleftharpoons \underset{\mathrm{AA^0}}{\mathrm{H_3\overset{+}{N}{-}CH(CH_2COOH){-}COO^-}} + \mathrm{OH^-} \qquad K_{eq} = K_{b_2} = \frac{K_w}{K_{a_2}}$$

The group shown ionizing as an acid (the α-NH_3^+) is the only remaining acidic group. The group shown ionizing as a base (the β-COO^- group) is the stronger of the two basic groups present. The ionization of the α-COO^- group as a base contributes little toward establishing the pH of the solution because it is so much weaker a base than is the β-COO^- group. The pH of solutions of monosodium aspartate may be calculated from the pK_{a_2} and pK_{a_3} values.

$$\mathrm{pH} = \frac{pK_{a_2} + pK_{a_3}}{2} = \frac{3.86 + 9.82}{2} = \frac{13.68}{2} = 6.84$$

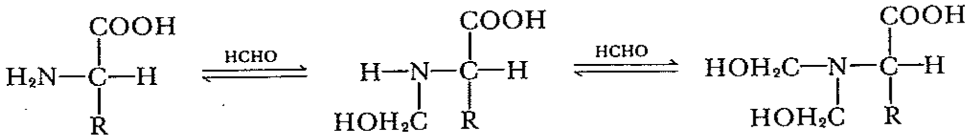
• Problem 1-46

Sketch the pH curves for the titration of 100 ml of 0.1 M alanine hydrochloride with KOH in the (a) absence and (b) presence of excess formaldehyde.

Solution

(a) The titration curve resembles that of a typical diprotic acid with two buffering plateaus in the regions of the pK_a values. It takes 1 mole of OH^- per mole of amino acid to go from the starting point to the first end (equivalence) point and 0.5 mole of OH^- per mole of amino acid to get to the midway (the pK_{a_1}) position. To go from the first endpoint to the second end (equivalence) point, another mole of KOH per mole of amino acid is required; 1.5 moles of KOH per mole of amino acid hydrochloride bring the pH to the point midway between the first and second equivalence points (to the pK_{a_2} value).

(b) Formaldehyde reacts with amino groups to form methylol derivatives.



$$H_2N-\underset{R}{\overset{COOH}{C}}-H \xrightleftharpoons{HCHO} H-\underset{HOH_2C}{N}-\underset{R}{\overset{COOH}{C}}-H \xrightleftharpoons{HCHO} HOH_2C-\underset{HOH_2C}{N}-\underset{R}{\overset{COOH}{C}}-H$$

The methylol derivatives are stronger acids (weaker bases) than are the original unsubstituted amino groups. In other words, the pK_{a_2} value for the substituted amino acid is lower than the pK_{a_2} value for the original amino acid. The titration curves are sketched in Figure 1-7. Note that formaldehyde has no effect on the amounts of KOH required to titrate the amino acid to pK_{a_1}, pK_{a_2} (or pK'_{a_2}), and the equivalence points. Also note that only the pK_{a_2} value is shifted; formaldehyde has no effect on the α-COOH group.

· **Problem 1-47**

Calculate the isoelectric point (pI) and the pH at which the maximum total number of charges are present (pH_m) for (a) glycine, (b) aspartic acid, and (c) lysine.

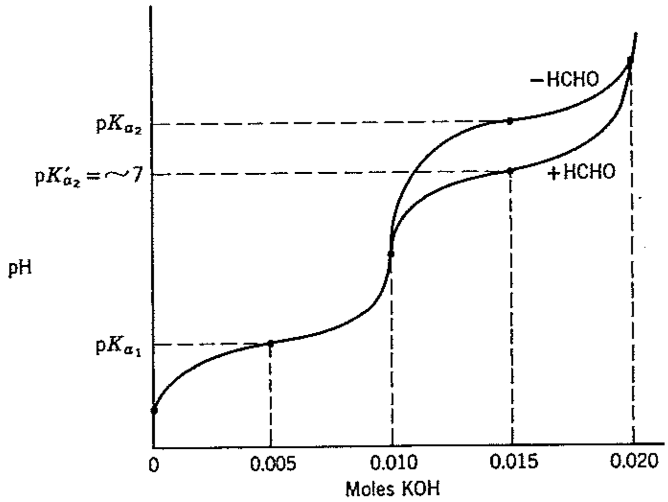


Figure 1-7 Titration curve of 0.01 moles of alanine hydrochloride in the presence and in the absence of formaldehyde.

Solution

The isoelectric point, pI, is the pH at which the amino acid or peptide carries no net charge; that is, the predominant ionic form is the isoelectric species, AA^0, and (because the isoelectric form ionizes both as an acid and as a base) there are equal amounts of the ionic forms AA^{+1} and AA^{-1}. (The ionization of AA^0 to form AA^{+1} and AA^{-1} is a disproportionation reaction, as described earlier.) The pI may also be thought of as the pH of a solution of the isoelectric form of the amino acid.

The pI of amino acids is the pH at one equivalence point along the titration curve, specifically the equivalence point at which all the AA^{+1} is converted to AA^0. The pH at this point is, as usual, the average of the pK_a value to follow and the pK_a value just passed. Similarly, pH_m is the pH at one equivalence point and may be similarly calculated. To determine pI and pH_m simply sketch the titration curve and indicate the predominant ionic species present at each key point. Or, prepare a table showing the ionic form of each titratable group at key points. For simplicity, assume that you are starting with the maximally protonated amino acid or peptide.

(a) *Glycine.* As shown in Table 1-3, glycine exists as the "zwitterion" or isoelectric form at the first equivalence point. At this point, glycine also bears the greatest total number of charges. Therefore:

$$pI = pH_m = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{2.34 + 9.6}{2} = \frac{11.94}{2} = 5.97$$

(b) *Aspartic acid.* We can see from Table 1-3 and Figure 1-8 that aspartic acid carries no net charge at the first equivalence point.

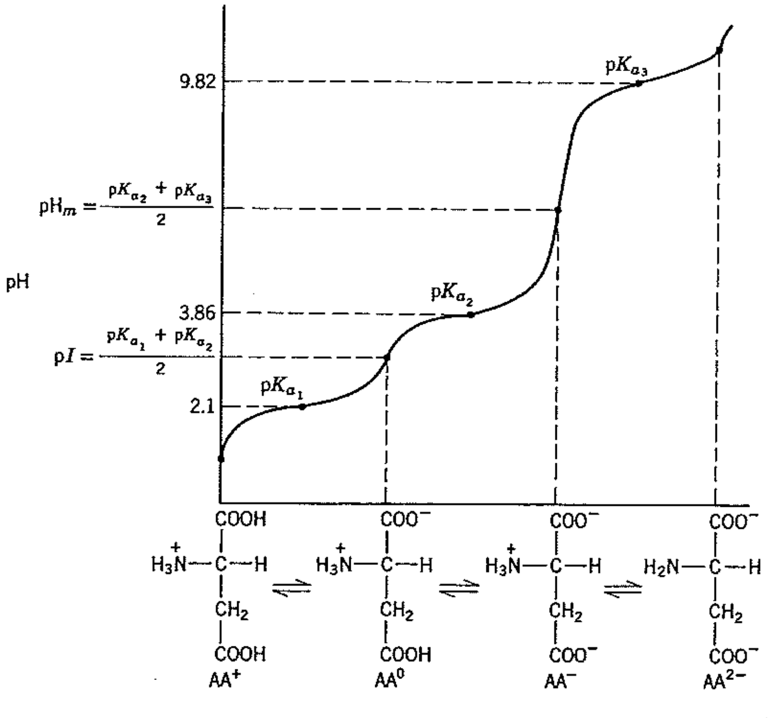


Figure 1-8 Titration curve of aspartic acid. For clarity, the vertical axis is not drawn to scale.

Table 1-3 Aspartic Acid

Ionizable Group	*Predominant Ionic Form at Different Positions along the Titration Curve*						
	Start	pK_{a_1}	*First Equivalence*	pK_{a_2}	*Second Equivalence*	pK_{a_3}	*Third Equivalence*
α-carboxyl	COOH	COOH($\frac{1}{2}$) COO^-($\frac{1}{2}$)	COO^-	COO^-	COO^-	COO^-	COO^-
β-carboxyl	COOH	COOH	COOH	COOH($\frac{1}{2}$) COO^-($\frac{1}{2}$)	COO^-	COO^-	COO^-
α-amino	NH_3^+	NH_3^+	NH_3^+	NH_3^+	NH_3^+	NH_3^+($\frac{1}{2}$) NH_2($\frac{1}{2}$)	NH_2
Net charge	+1	$+\frac{1}{2}$	0	$-\frac{1}{2}$	−1	$-1\frac{1}{2}$	−2

Table 1-4 Lysine

	Predominant Ionic Form at Different Positions along the Titration Curve						
Ionizable Group	*Start*	pK_{a_1}	*First Equivalence*	pK_{a_2}	*Second Equivalence*	pK_{a_3}	*Third Equivalence*
α-carboxyl	COOH	$COOH(\frac{1}{2})$ $COO^-(\frac{1}{2})$	COO^-	COO^-	COO^-	COO^-	COO^-
α-amino	NH_3^+	NH_3^+	NH_3^+	$NH_3^+(\frac{1}{2})$ $NH_2(\frac{1}{2})$	NH_2	NH_2	NH_2
ε-amino	NH_3^+	NH_3^+	NH_3^+	NH_3^+	NH_3^+	$NH_3^+(\frac{1}{2})$ $NH_2(\frac{1}{2})$	NH_2
Net charge	+2	$+1\frac{1}{2}$	+1	$+\frac{1}{2}$	0	$-\frac{1}{2}$	−1

$$pI = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{2.09 + 3.86}{2} = \frac{5.95}{2} = 2.98$$

We can also see that aspartic acid carries the maximum total number of charges at the second equivalence point.

$$pH_m = \frac{pK_{a_2} + pK_{a_3}}{2} = \frac{3.86 + 9.82}{2} = \frac{13.68}{2} = 6.84$$

When constructing Table 1-3, we assumed that at the first equivalence point the α-carboxyl is completely ionized and that the β-carboxyl is completely un-ionized. These assumptions, of course, are not entirely true; the actual degree to which the α- and β-carboxyls are ionized can be calculated using the Henderson-Hasselbalch equation. If we carry out the calculation, we find that the proportion of α-carboxyl that is still in the COOH form exactly equals the proportion of β-carboxyl in the COO^- form. (At pH 2.98, we are just as far above the pK_{a_1} for the α-carboxyl as we are below the pK_{a_2} for the β-carboxyl.) Thus, to determine the net charge on the molecule, we are justified in tallying only the predominant ionic forms at each key point along the titration curve.

(c) *Lysine.* We see from Table 1-4 and Figure 1-9 that lysine carries no net charge at the second equivalence point.

$$pI = \frac{pK_{a_2} + pK_{a_3}}{2} = \frac{8.95 + 10.53}{2} = \frac{19.48}{2} = 9.74$$

We also see that lysine carries the maximum total number of charges at the first equivalence point (all ionizable groups charged).

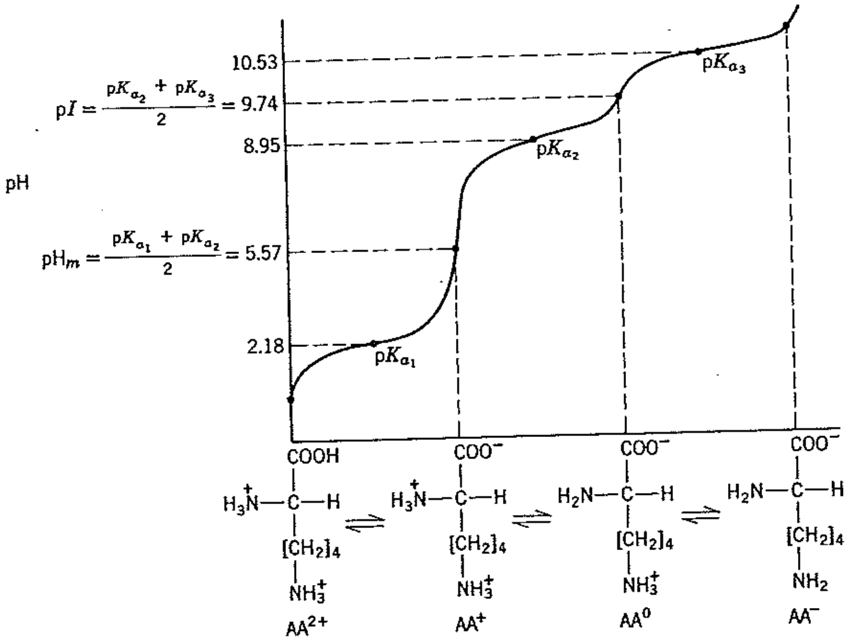


Figure 1-9 Titration curve of lysine. For clarity, the vertical axis is not drawn to scale.

$$pH_m = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{2.18 + 8.95}{2} = \frac{11.13}{2} = 5.57$$

We assumed that at the second equivalence point the α-amino group is completely uncharged and the ϵ-amino group is completely ionized. These assumptions are valid for calculating the net charge on lysine for the same reasons described earlier concerning aspartic acid.

· Problem 1-48

An enzyme catalyzing the decarboxylation of lysine accepts only the isoelectric form as a substrate. What is the actual concentration of isoelectric lysine in a 10^{-3} *M* solution of lysine in a buffer at pH 7.60?

Solution

At pH 7.60, the predominant ionic forms of lysine are AA^+ and AA^0 (Fig. 1-9). The equilibrium between these two species is described by K_{a_2}.

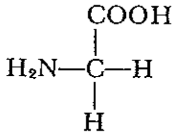
$$pH = pK_{a_2} + \log\frac{[AA^0]}{[AA^+]} \qquad 7.60 = 8.95 + \log\frac{[AA^0]}{[AA^+]}$$

$$1.35 = \log\frac{[AA^+]}{[AA^0]} \qquad \frac{[AA^+]}{[AA^0]} = \frac{22.4}{1}$$

$$\therefore \quad [AA^0] = \frac{1}{23.4} \times 10^{-3} \qquad \boxed{[AA^0] = 4.27 \times 10^{-5}\,M}$$

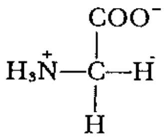
· Problem 1-49

It is generally assumed that the completely uncharged form of a neutral amino acid shown below does not exist in solution. Instead, the major species of, for example, glycine at pH values around p*I* is the isoelectric form.



$$H_2N-\overset{COOH}{\underset{H}{C}}-H$$

Uncharged form



$$H_3\overset{+}{N}-\overset{COO^-}{\underset{H}{C}}-H$$

Isoelectric form

Assuming $pK_{a_1} \simeq 2.5$ and $pK_{a_2} \simeq 9.5$, estimate the fraction of the total glycine present as the "rare" uncharged form at pH 5.5.

Solution

From the Henderson-Hasselbalch equation, we find that the ratio of R-COOH/R-COO$^-$ at pH 5.5 is about 10^{-3}. (The solution is 3 pH units above pK_{a_1}.) The ratio of $R\text{-}NH_2/R\text{-}NH_3^+$ is about 10^{-4}. (The solution is 4 pH units below pK_{a_2}.) Therefore, the combination, which gives the ratio of $H_2N\text{-}R\text{-}COOH/H_3N^+\text{-}R\text{-}COO^-$, is $10^{-3} \times 10^{-4} = 10^{-7}$.

∴ **one ten-millionth of the total glycine is present as the completely uncharged species**

Additional problems on the charge properties of amino acids, peptides, and proteins will be found in Chapter 2.

· Problem 1-50

Calculate the ionic strength of a 0.05 M glycine buffer, pH 9.6.

Solution

The pH = pK_{a_2}; therefore $[AA^0] = [AA^-]$. Of the glycine species present only the net charged AA^- contributes to the ionic strength. If the buffer was prepared by titrating isoelectric glycine (AA^0) with NaOH, the solution contains 0.025 M AA^0, 0.025 M AA^-, and 0.025 M Na^+. The ionic strength of a 1:1 salt is identical to the molarity of either ion.

$$\therefore \quad \boxed{\frac{\Gamma}{2} = 0.025}$$

If the buffer was prepared by titrating 0.05 moles of glycine hydrochloride (AA^+) with NaOH, then at pH 9.6 the buffer would contain 0.050 M Cl^-, 0.075 M Na^+, 0.025 M AA^-, and 0.025 M AA^0, of which the first three would contribute to the ionic strength:

$$\frac{\Gamma}{2} = \frac{(0.050) + (0.075) + (0.025)}{2} = \boxed{0.075}$$

Thus, if a low ionic strength is an important consideration, the first method of preparing the buffer is preferred.

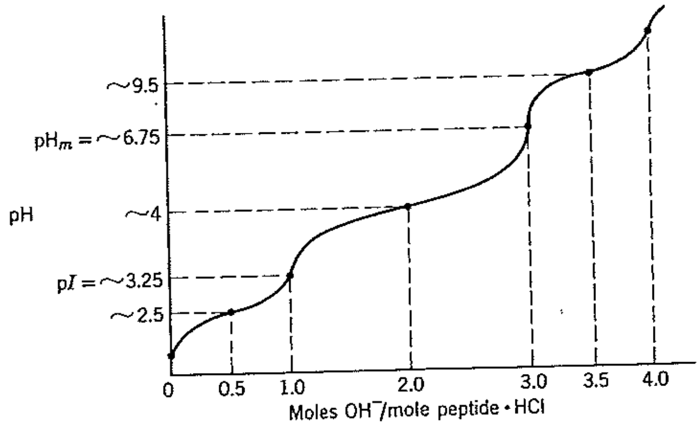


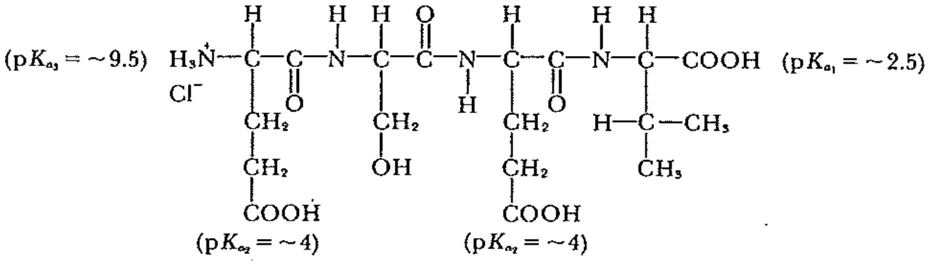
Figure 1-10 Titration curve of glutamylserylglutamylvaline hydrochloride. For clarity, the vertical axis is not drawn to scale.

· **Problem 1-51**

Sketch the pH curve for the titration of 1 mole of glutamylserylglutamylvaline hydrochloride.

Solution

Titration and buffer calculations involving peptides are done exactly as shown earlier for polyprotic acids. We must remember that the amino acid carboxyl groups used in forming the peptide bond are no longer available for titration. The structure of the fully protonated glutamylserylglutamylvaline is shown below. It is assumed that the α-COOH group retains a pK_a of ~2.5

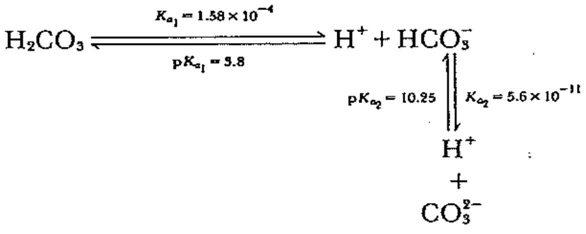


and that both γ-COOH groups have identical pK_a values of ~4.0. In reality, the α-COOH group would probably be a much weaker acid once the α-amino group of valine is tied up in a peptide bond. The theoretical titration curve is shown in Figure 1-10. In practice, two distinct buffering plateaus at pK_{a_1} and pK_{a_2} would not be as obvious as shown.

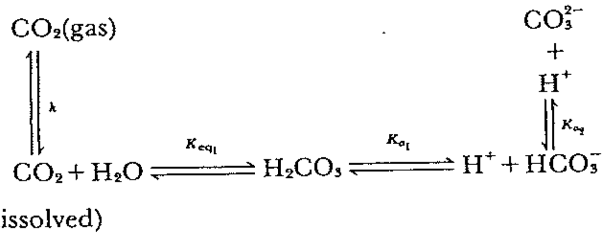
F. BLOOD BUFFERS

THE HCO_3^-/CO_2 SYSTEM

The HCO_3^-/CO_2 system is one of the two major blood buffers. Carbonic acid ionizes as a typical weak diprotic acid:



However, most of the conjugate acid dissolved in blood and cytoplasm is present as CO_2, not H_2CO_3. The dissolved CO_2 is in equilibrium with CO_2 in the gas phase. A more complete presentation of the CO_2 buffer system is shown below.



The equilibrium between CO_2 (gas) and CO_2 (dissolved) is given by:

$$\boxed{[CO_2]_{\text{dissolved}} = k\,(P_{CO_2})} \qquad (41)$$

That is, the concentration of dissolved CO_2 is directly proportional to the partial pressure of CO_2 in the gas phase. At 37°C and an ionic strength of 0.15, $k = 3.01 \times 10^{-5}$ when P_{CO_2} is expressed in terms of mm Hg. The equilibrium constant for the reaction: dissolved $CO_2 + H_2O \rightleftharpoons H_2CO_3$ is about 5×10^{-3}:

$$K_{eq_1} = \frac{[H_2CO_3]}{[CO_2]_{\text{dis.}}} = 5 \times 10^{-3}$$

Thus, the overall equilibrium constant between dissolved CO_2 and $H^+ + HCO_3^-$ is given by:

$$K_a' = \frac{[H^+][HCO_3^-]}{[CO_2]} = K_{eq_1} \times K_{a_1}$$
$$= (5 \times 10^{-3})(1.58 \times 10^{-4}) = 7.9 \times 10^{-7}$$

and $\qquad pK_a' = 6.1.$

The relationship can also be written as:

$$K_a' = \frac{[H^+][HCO_3^-]}{(3.01 \times 10^{-5})P_{CO_2}} = 7.9 \times 10^{-7}$$

At any pH:

$$pH = 6.1 + \log\frac{[HCO_3^-]}{[CO_2]} \quad \text{and} \quad pH = 6.1 + \log\frac{[HCO_3^-]}{(3.01 \times 10^{-5})P_{CO_2}}$$

For all practical purposes, a bicarbonate buffer can be considered to be composed of HCO_3^- (conjugate base) and dissolved CO_2 (conjugate acid).

The pH of blood is maintained at about 7.4. If the pK_a' of CO_2 is 6.1, how can the HCO_3^-/CO_2 help buffer blood at pH 7.4? Everything we have learned so far suggests that a buffer is effective only in the region of its pK_a. The key here is that *in vivo* the HCO_3^-/CO_2 buffer is an *open system* in which the concentration of dissolved CO_2 is maintained constant. Any excess CO_2 produced by the reaction $H^+ + HCO_3^- \rightarrow H_2O + CO_2$ is expelled by the lungs. In contrast, the usual laboratory buffer is a *closed system*. The concentration of conjugate acid increases when H^+ reacts with the conjugate base. The effectiveness of the open system is illustrated below.

· Problem 1-52

Blood plasma contains a total carbonate pool (essentially $HCO_3^- + CO_2$) of 2.52×10^{-2} *M*. (a) What is the HCO_3^-/CO_2 ratio and the concentration of each buffer component present at pH 7.4? (b) What would the pH be if $10^{-2}\ M\ H^+$ is added under conditions where the increased $[CO_2]$ cannot be released? (c) What would the pH be if $10^{-2}\ M\ H^+$ is added and the excess CO_2 eliminated (thereby maintaining the original $[CO_2]$)?

Solution

(a)

$$pH = pK_a' + \log\frac{[HCO_3^-]}{[CO_2]} \qquad 7.4 = 6.1 + \log\frac{[HCO_3^-]}{[CO_2]}$$

$$1.3 = \log\frac{[HCO_3^-]}{[CO_2]} \qquad \therefore \qquad \boxed{\frac{[HCO_3^-]}{[CO_2]} = \frac{20}{1}}$$

$$[HCO_3^-] = \frac{20}{21} \times 2.52 \times 10^{-2} = \boxed{2.40 \times 10^{-2}\ M}$$

$$[CO_2] = \boxed{1.2 \times 10^{-3}\ M}$$

(b) If $0.01\ M\ H^+$ is added:

$$[HCO_3^-]_{\text{final}} = 0.024 - 0.010 = 0.014\ M$$

$$[CO_2]_{\text{final}} = 0.0012 + 0.010 = 0.0112\ M$$

$$pH = 6.1 + \log\frac{0.014}{0.0112} = 6.1 + \log 1.25$$

$$= 6.1 + 0.097 \qquad \boxed{pH = 6.2}$$

Clearly, in a closed system, the HCO_3^-/CO_2 mixture has very little buffer capacity at pH 7.4.

(c) In an open system:

$$0.024\ M\ HCO_3^- + 0.01\ M\ H^+ + 0.0012\ M\ CO_2$$

$$\downarrow$$

$$0.014\ M\ HCO_3^- + 0.0112\ M\ CO_2$$

$$\downarrow \longrightarrow 0.01\ M\ CO_2 \text{ exhaled}$$

$$0.014\ M\ HCO_3^- + 0.0012\ M\ CO_2$$

$$pH = 6.1 + \log\frac{0.014}{0.0012} = 6.1 + \log 11.667$$

$$= 6.1 + \log 1.07 \qquad \boxed{pH = 7.16}$$

In an open system, the pH decreases only 0.24 pH unit. At first glance, it would seem that in an open system, the HCO_3^- reserve would be rapidly depleted. However, *in vivo*, HCO_3^- is constantly replenished by the oxidative metabolic pathways, as described in the following section.

· **Problem 1-53**

The pH of a sample of arterial blood is 7.42. Upon acidification of 10 ml of the blood, 5.91 ml of CO_2 (corrected for standard temperature and pressure) are produced. Calculate (a) the total concentration of dissolved CO_2 in the blood $[CO_2 + HCO_3^-]$, (b) the concentrations of dissolved CO_2 and HCO_3^-, and (c) the partial pressure of the dissolved CO_2 in terms of mm Hg.

Solution

(a) First calculate the number of moles of CO_2 represented by 5.91 ml at S.T.P. One mole of a "perfect" gas occupies 22.4 liters at S.T.P. The experimental value for CO_2 is 22.26 liters.

$$\therefore \quad \frac{5.91 \times 10^{-3}\text{ liters}}{22.26\text{ liters/mole}} = 0.265 \times 10^{-3}\text{ moles}$$

This amount of CO_2 came from 10 ml of blood.

$$\therefore \quad \text{concentration of ``total CO}_2\text{''} = \frac{26.5 \times 10^{-5}\text{ moles}}{10 \times 10^{-3}\text{ liters}} = \boxed{2.65 \times 10^{-2}\,M}$$

(b)

$$\text{pH} = \text{p}K_{a_1} + \log\frac{[HCO_3^-]}{[CO_2]}$$

$$7.42 = 6.1 + \log\frac{[HCO_3^-]}{[CO_2]} \qquad 1.32 = \log\frac{[HCO_3^-]}{[CO_2]}$$

$$\frac{[HCO_3^-]}{[CO_2]} = \text{antilog of } 1.32 = \frac{20.89}{1}$$

$$[HCO_3^-] = \frac{20.89}{21.89} \times 2.65 \times 10^{-2}\,M = \boxed{2.53 \times 10^{-2}\,M}$$

$$[CO_2] = \frac{1}{21.89} \times 2.65 \times 10^{-2}\,M = \boxed{1.21 \times 10^{-3}\,M}$$

(c)

$$[CO_2]_{\text{dissolved}} = kP_{CO_2}$$

$$P_{CO_2} = \frac{[CO_2]}{k} = \frac{1.21 \times 10^{-3}}{3.01 \times 10^{-5}} = \boxed{40.22\text{ mm Hg}}$$

HEMOGLOBIN

Aside from its well-known function as an oxygen carrier, hemoglobin plays an important role as a blood buffer. In order to understand the interrelationship between oxygen uptake and release, and the buffering action of hemoglobin, we must consider the interaction of several simultaneous equilibria. A greatly simplified version* of the equilibria is developed below.

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* The simplified version considers only the binding of a single molecule of O_2 to a hemoglobin monomer. In this way, O_2 binding to HHgb or Hgb can be described by a single oxygen

At any time, hemoglobin is present as a mixture of deoxygenated and oxygenated forms. The proportion of each depends on the concentration (partial pressure) of O_2.

$$\text{"deoxyhemoglobin"} + O_2 \rightleftharpoons \text{"oxyhemoglobin"}$$

Hemoglobin contains many ionizable groups. One in particular is a histidine residue that has a pK_a around neutrality. Thus, at any time, hemoglobin is also present as a mixture of protonated and unprotonated forms. The proportion of each depends on the pH of the blood.

$$\begin{array}{c}\text{"H Hemoglobin"}\\ \upharpoonleft\!\downharpoonright\\ \text{"Hemoglobin"}\\ +\\ H^+\end{array}$$

In order to combine the two simultaneous equilibria, we must recognize that "deoxyhemoglobin" represents a mixture of protonated deoxyhemoglobin (conjugate acid) plus nonprotonated deoxyhemoglobin (conjugate base). Similarly, "oxyhemoglobin" represents a mixture of H oxyhemoglobin (conjugate acid) and oxyhemoglobin (conjugate base). To state it in another way: the conjugate acid of hemoglobin exists in oxygenated and deoxygenated forms. So does the conjugate base of hemoglobin. Thus, there are really four species of hemoglobin present at any time. The proportion of each depends on the concentration of O_2 and the pH. The combined equilibria are shown in Figure 1-11.

Hemoglobin in the red blood cells arrives in the lungs mainly as a mixture of deoxy forms, HHgb + Hgb. The proportion of each is governed by the pH and the pK_a of deoxyhemoglobin. Since the pH is about 7.4, and pK_a is about 7.7, approximately two thirds of the total deoxyhemoglobin is present as the conjugate acid form. In the lungs, hemoglobin picks up oxygen. The horizontal equilibrium shifts to the right (reaction 1). $HHgbO_2$ is a stronger acid than HHgb. (A conformational change in the molecule upon oxygenation decreases the pK_a of the histidine group in the region of the heme to about 6.2.) As a result, the vertical equilibrium shifts downward (reaction 2) and H^+ is released. The increased $[H^+]$ forces the $H^+ + HCO_3^-$ equilibrium to the right (reaction 3). This results in the removal of H^+ and the release of CO_2 to the atmosphere. The oxygenated hemoglobin (mostly as the conjugate base $HgbO_2$ at pH 7.4) is transported to the tissues where the low O_2 partial pressure causes the horizontal equilibrium to shift to the left. O_2 is given off (reaction 4). Hgb is a stronger base than $HgbO_2$ (which follows, if $HHgbO_2$ is a stronger acid than HHgb). Thus, after O_2 is released, the vertical equilibrium shifts upward. As a result, H^+ ions (produced from the oxidation of food—reaction 6) are taken up by Hgb (reaction 7). Stated differently (but equivalently): in the tissues, the higher

---

dissociation constant. The "percent saturation versus $[O_2]$" curve for this model would be a hyperbola. Hemoglobin is actually a tetramer which displays "cooperative" binding of four molecules of O_2. The O_2 binding curve is sigmoidal (Chapter 4). The simplified scheme used in the present discussion is incorrect, but it conveys the essential features of the interaction between O_2, H^+, and CO_2.

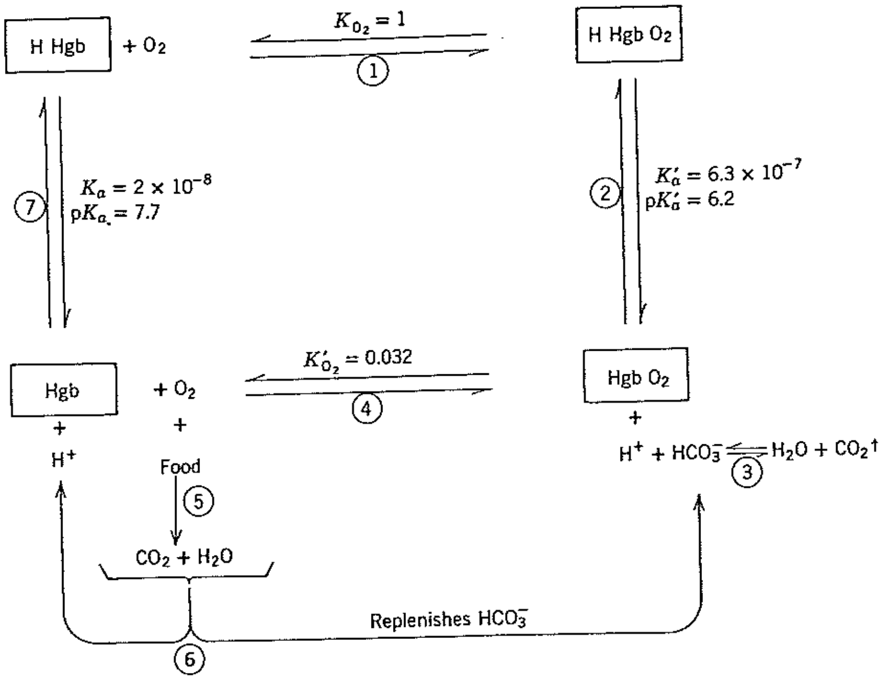
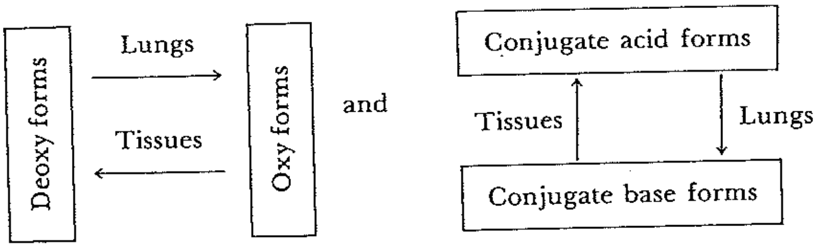
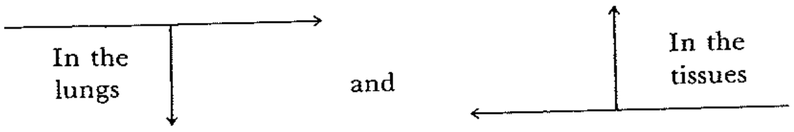


Figure 1-11 A simplified model for the oxygen/H$^+$ equilibria of hemoglobin. K_{O_2} is arbitrarily taken as unity. All constants are dissociation constants. pK_a is taken as 7.7, but values of 7.71 to 8.18 have been reported. pK'_a is taken as 6.2, but values of 6.17 to 6.68 have been reported.

[H$^+$] forces the vertical equilibrium upward. The conjugate acid of hemoglobin has a lower O_2 affinity (higher O_2 dissociation constant) than the conjugate base of hemoglobin. Consequently, O_2 is released (i.e., the horizontal equilibrium shifts to the left). Of course, both the H$^+$ and O_2 shifts occur simultaneously. The sequence of events can be summarized as shown below.



or, the overall equilibrium shifts as follows:



As an overall result, the oxidation of food yields CO_2, H$^+$, and HCO_3^- yet the concentrations of all three (hence, the pH of the tissues and blood) remain essentially constant.

· Problem 1-54

Consult Figure 1-11. If $K_a = 2 \times 10^{-8}$; $K'_a = 6.3 \times 10^{-7}$, and $K_{O_2} = 1$, why must K'_{O_2} equal 0.032?

Solution

The overall equilibrium constant between any two points is the same regardless of the path taken. Thus, K_{eq} for the sequence $HHgbO_2 \rightleftharpoons O_2 + HHgb \rightleftharpoons H^+ + Hgb$ equals K_{eq} for the sequence $HHgbO_2 \rightleftharpoons H^+ + HgbO_2 \rightleftharpoons O_2 + Hgb$. The overall K_{eq} of a sequence of reactions is the product of the K_{eq}'s of each step.

$$\therefore \quad K_{O_2} \times K_a = K'_a \times K'_{O_2}$$

$$K'_{O_2} = \frac{K_{O_2} \times K_a}{K'_a} = \frac{(1)(2 \times 10^{-8})}{(6.3 \times 10^{-7})}$$

$$\boxed{K'_{O_2} = 0.032}$$

Thus, $HgbO_2$ has a lower oxygen dissociation constant (higher O_2 binding constant) than $HHgbO_2$.

· Problem 1-55

How many moles of H^+ can be taken up by hemoglobin at pH 7.4 as a consequence of the release of one mole of O_2? Assume $pK_a = 7.7$ and $pK'_a = 6.2$.

Solution

Using the Hendersen-Hasselbalch equation, we can calculate that, at pH 7.4, $15.85/16.85 = 0.941$ of the total oxyhemoglobin is in the $HgbO_2$ form, and $1/16.84 = 0.059$ is in the $HHgbO_2$ form. Similarly, we can calculate that, at pH 7.4, one third $= 0.333$ of the total deoxyhemoglobin is in the Hgb form and two thirds $= 0.667$ is in the HHgb form. Thus after the release of one mole of O_2, the conjugate base/conjugate acid ratio must decrease to maintain equilibrium. That is, the conjugate base/conjugate acid equilibrium ratio of 15.85 : 1 for oxyhemoglobin is much higher than the corresponding equilibrium ratio of 0.5 : 1 for deoxyhemoglobin. Therefore, when oxyhemoglobin is converted to deoxyhemoglobin, the amount of the conjugate base must decrease (by picking up an H^+ to become the conjugate acid). Specifically, the release of one mole of O_2 forces the uptake of $(0.667 - 0.059)$ or $(0.941 - 0.333) = 0.608$ moles of H^+. Under physiological conditions, slightly more than 0.6 moles of H^+ are formed (from CO_2 entering the blood) for every mole of O_2 released. This extra H^+ is partially absorbed by the noncarbonate blood buffers (phosphate and plasma proteins). As a result, the pH of venous blood is actually 7.38 in normal resting individuals, compared to pH 7.41 for arterial blood.

· Problem 1-56

The oxygen binding curve for hemoglobin is shown in Figure 1-12. In the presence of CO_2, the partial pressure of O_2 required for any given fraction of

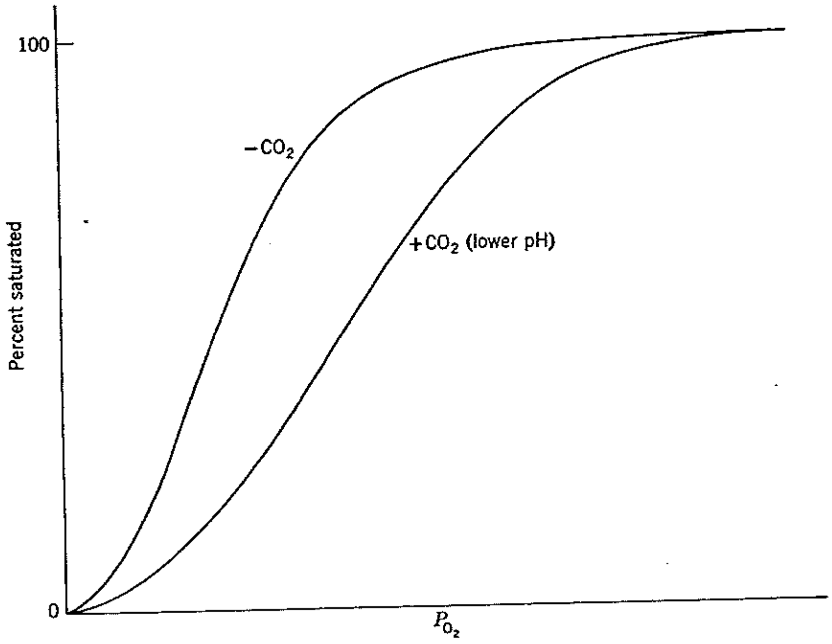


Figure 1-12 Oxygen binding by hemoglobin in the absence and in the presence of CO_2.

saturation is increased. Suggest an explanation for this "Bohr effect," as it is known.

Solution

As shown in Figure 1-11, $HHgbO_2$ has a greater oxygen dissociation constant than $HgbO_2$ or, in other words, HHgb has a lower O_2 affinity than does Hgb. In effect, CO_2 shifts the equilibrium between the conjugate acid and conjugate base forms of hemoglobin. *In vivo*, CO_2 rapidly diffuses into the red blood cells, and reacts with water to produce $H^+ + HCO_3^-$. (In fact, the red blood cells contain an enzyme called carbonic anhydrase that accelerates the reaction $CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$.) The decreased pH shifts the vertical equilibria of Figure 1-11 upward. Thus, hemoglobin is forced to a form with a lower O_2 affinity and O_2 is given off. In other words, at any given P_{O_2}, less O_2 is bound to hemoglobin in the presence of CO_2 because CO_2 causes the pH to decrease. As a result, a higher P_{O_2} is required to attain any given percent saturation.

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PRACTICE PROBLEMS

Consult Appendices IV and VII for K_a and pK_a values. Answers to the Practice Problems are given on pages 421–423.

Concentrations of Solutions

1. A solution contains 15 g of $CaCl_2$ in a total volume of 190 ml. Express the concentration of this solution in terms of (a) g/liter, (b) % (w/v), (c) mg %, (d) *M*, and (e) osmolarity. (f) What is the ionic strength of the solution?

2. A solution was prepared by dissolving 8.0 g of solid ammonium sulfate (MW = 132.14, specific volume = 0.565 ml/g) in 35 ml (i.e., 35 g) of water. (a) What is the final volume of the solution? Express the concentration of ammonium sulfate in terms of (b) % (w/w), (c) % (w/v), (d) *m*, (e) *M*, (f) osmolarity, and (g) mole fraction ammonium sulfate. (h) What is the ionic strength of the solution?

3. Starting with 150 ml of a 40% saturated ammonium sulfate solution at 0°C calculate (a) the weight of solid ammonium sulfate that must be added to bring the solution to 60% saturation, and (b) the volume of saturated solution that must be added to attain 60% saturation. The specific volume of ammonium sulfate is 0.565 ml/g.

4. What is the molarity of pure ethanol—that is, how many moles are present in 1 liter of pure ethanol? The density of ethanol is 0.789 g/ml. The MW of ethanol is 46.07.

Strong Acids and Bases—pH

5. Calculate the pH, pOH, and number of H^+ and OH^- ions per liter in each of the following solutions: (a) 0.01 *M* HCl, (b) 10^{-4} *M* HNO_3, (c) 0.0025 *M* H_2SO_4, (d) 3.7×10^{-5} *M* KOH, (e) 5×10^{-8} *M* HCl, (f) 2.9×10^{-3} *M* NaOH, (g) 1 *M* HCl, (h) 10 *M* HNO_3, and (i) 3×10^{-5} *N* H_2SO_4.

6. Calculate the H^+ ion concentration (*M*), the OH^- ion concentration, and the number of H^+ and OH^- ions per liter in solutions having pH values of (a) 2.73, (b) 5.29, (c) 6.78, (d) 8.65, (e) 9.52, (f) 11.41, and (g) 0.

7. Calculate the (a) $[H^+]$, (b) $[OH^-]$, (c) pH, and (d) pOH of the final solution obtained after 100 ml of 0.2 *M* NaOH are added to 150 ml of 0.4 *M* H_2SO_4.

8. Calculate the pH and pOH of a solution obtained by adding 0.2 g of solid KOH to 1.5 liters of 0.002 *M* HCl.

9. The pH of a 0.10 *M* HCl solution was found to be 1.15. Calculate the (a) a_{H^+} and (b) γ_{H^+} in this solution.

10. The activity coefficient of the hydroxyl ion (γ_{OH^-}) is 0.72 in a 0.1 *M* solution of KOH. Calculate the pH and pOH of this solution.

11. Concentrated H_2SO_4 is 96% H_2SO_4 by weight and has a density of 1.84 g/ml. Calculate the volume of concentrated acid required to make (a) 750 ml of 1 *N* H_2SO_4, (b) 600 ml of 1 *M* H_2SO_4, (c) 1000 g of a dilute H_2SO_4 solution containing 12% H_2SO_4 by weight, (d) an H_2SO_4 solution containing 6.5 equivalents per liter, and (e) a dilute H_2SO_4 solution of pH 3.8.

12. Concentrated HCl is 37.5% HCl by weight and has a density of 1.19. (a) Calculate the molarity of the concentrated acid. (b) Describe the preparation of 500 ml of 0.2 *M* HCl. (c) Describe the preparation of 350 ml of 0.5 *N* HCl. (d) Describe the preparation of an HCl solution containing 25% HCl by weight. (e) Describe the preparation of a dilute HCl solution having a pH of 4.7.

13. Calculate the weight of solid NaOH required to prepare (a) 5 liters of a 2 *M* solution, (b) 2 liters of a solution of pH 11.5, and (c) 500 ml of 62% w/w solution. The density of 62% NaOH solution is 1.15 g/ml.

14. How many milliliters of 0.12 *M* H_2SO_4 are required to neutralize exactly *half* of the OH^- ions present in 540 ml of 0.18 *N* NaOH?

15. How many grams of solid Na_2CO_3 are required to neutralize exactly 2 liters of an HCl solution of pH 2.0?

16. How many milliliters of 0.15 *M* KOH are required to neutralize exactly 180 g of pure H_2SO_4?

Weak Acids and Bases—Buffers

When solving the problems below, assume that $\gamma = 1$ for all substances unless otherwise indicated.

17. The weak acid, HA, is 2.4% dissociated in a 0.22 *M* solution. Calculate (a) the K_a, (b) the pH of the solution, (c) the amount of 0.1 *N* KOH required to neutralize 550 ml of the weak acid solution, and (d) the number of H^+ ions in 550 ml of the weak acid solution.

18. The pH of a 0.27 *M* solution of a weak acid, HA, is 4.3. (a) What is the H^+ ion concentration in the solution? (b) What is the degree of ionization of the acid? (c) What is the K_a?

19. The K_a of a weak acid, HA, is 3×10^{-4}. Calculate (a) the OH^- ion concentration in the solution and (b) the degree of dissociation of the acid in a 0.15 *M* solution.

20. At what concentration of weak acid, HA (in terms of its K_a), will the acid be 25% dissociated?

21. (a) Calculate the pH of a 0.05 *M* solution of ethanolamine, $K_b = 2.8 \times 10^{-5}$. (b) What is the degree of ionization of the amine?

22. Calculate the pK_a and pK_b of weak acids with K_a values of (a) 6.23×10^{-4}, (b) 2.9×10^{-5}, (c) 3.4×10^{-5}, and (d) 7.2×10^{-6}.

23. Calculate the pK_b and pK_a of weak bases with K_b values of (a) 2.1×10^{-5}, (b) 3.1×10^{-6}, (c) 7.8×10^{-5}, and (d) 9.2×10^{-4}.

24. Calculate the pH of a 0.2 *M* solution of an amine that has a pK_a of 9.5.

25. What is the pH of a 0.20 *M* solution of (a) H_3PO_4, (b) KH_2PO_4, (c) K_2HPO_4, (d) K_3PO_4, (e) potassium acetate, (f) NH_4Br, (g) sodium phenolate, (h) trisodium citrate, (i) disodium citrate, and (j) ethanolamine hydrochloride?

26. How many milliliters of 0.1 *M* KOH are required to titrate completely 270 ml of 0.4 *M* propionic acid?

27. How many milliliters of 0.2 *M* KOH are required to titrate completely 650 ml of 0.05 *M* citric acid?

28. What are the final hydrogen ion concentration and pH of a solution obtained by mixing 100 ml of 0.2 *M* KOH with 150 ml of 0.1 *M* HOAc? pK_a of HOAc = 4.77.

29. What are the final hydrogen ion concentration and pH of a solution obtained b mixing 200 ml of 0.4 *M* aqueous NH_3 wit 300 ml of 0.2 *M* HCl? ($K_b = 1.8 \times 10^{-5}$)

30. What are the final hydrogen ion con centration and pH of a solution obtained b mixing 250 ml of 0.1 *M* citric acid with 300 m of 0.1 *M* KOH? pK_a's are 3.06, 4.74, and 5.4

31. What are the final hydrogen ion con centration and pH of a solution obtained b mixing 400 ml of 0.2 *M* NaOH with 150 ml o 0.1 *M* H_3PO_4? pK_a's are 2.12, 7.21, and 12.32.

32. What are the concentrations of N and NH_4Cl in a 0.15 *M* "ammonia" buffer, p 9.6 ($K_b = 1.8 \times 10^{-5}$)?

33. (a) What is the pH of a solution co taining 0.01 *M* HPO_4^{2-} and 0.01 *M* PO_4^{3-} (a sume $\gamma = 1$)? (b) Calculate the actual pH using the activity coefficients listed in Appe dix V. (c) What is pK'_{a_3} at a total ion strength of 0.1? (Consult Appendix VI.)

34. What is the pH of a solution contai ing 0.3 *M* Tris(hydroxymethyl)amin methane (free base) and 0.2 *M* Tris hyd chloride? $pK_a = 8.1$.

35. What is the pH of a solution conta ing 0.2 g/liter Na_2CO_3 and 0.2 g/liter NaHC ($pK_{a_2} = 10.25$)

36. What is the pH of a solution prepa by dissolving 5.35 g of NH_4Cl in a liter of 0.2 NH_3? (K_b of NH_3 is 1.8×10^{-5})

37. Describe the preparation of 2 liters 0.25 *M* formate buffer, pH 4.5, starting fr 1 *M* formic acid and solid sodium form (HCOONa). pK_a of HCOOH is 3.75.

38. Describe the preparation of 40 liter 0.02 *M* phosphate buffer, pH 6.9, start from (a) a 2 *M* H_3PO_4 solution and a KOH solution, (b) a 0.8 *M* H_3PO_4 solution solid NaOH, (c) a commercial concentra H_3PO_4 solution and 1 *M* KOH, (d) 1 *M* s tions of KH_2PO_4 and Na_2HPO_4, (e) s KH_2PO_4 and K_2HPO_4, (f) solid K_2HPO_4 1.5 *M* HCl, (g) 1.2 *M* K_2HPO_4 and 2 *M* H (h) solid KH_2PO_4 and 2 *M* KOH, (i) 1. KH_2PO_4 and 1 *M* NaOH, and (j) solid Na and 1 *M* HCl.

39. What volume of glacial acetic acid (density 1.06 g/ml) and what weight of solid potassium acetate are required to prepare 5 liters of 0.2 *M* acetate buffer, pH 5.0?

40. An enzyme-catalyzed reaction was carried out in a solution buffered with 0.03 *M* phosphate, pH 7.2. As a result of the reaction, 0.004 mole/liter of acid was formed. (a) What was the pH at the end of the reaction? (b) What would the pH be if no buffer were present? (c) Write the chemical equation showing how the phosphate buffer resisted a large change in pH.

41. An enzyme-catalyzed reaction was carried out in a solution containing 0.2 *M* Tris buffer. The pH of the reaction mixture at the start was 7.8. As a result of the reaction, 0.033 mole/liter of H^+ was consumed. (a) What was the ratio of $Tris^0$ (free base) to $Tris^+$ Cl^- at the start of the reaction? (b) What was the $Tris^0/Tris^+$ ratio at the end of the reaction? (c) What was the final pH of the reaction mixture? (d) What would the final pH be if no buffer were present? (e) Write the chemical equations showing how the Tris buffer maintained a near constant pH during the reaction. The pK_a of Tris is 8.1.

42. When a sulfate ester is hydrolyzed, an H^+ ion is produced:

$$R\text{-}O\text{-}SO_3^- + H_2O \longrightarrow ROH + SO_4^{2-} + H^+$$

The above reaction was carried out in 1.0 ml of 0.02 *M* Tris buffer, pH 8.10, containing 0.01 *M* $R\text{-}O\text{-}SO_3^-$ and an enzyme called a sulfatase that catalyzes the reaction. At the end of 10 minutes, the pH of the reaction mixture decreased to 7.97. How many μmoles of $R\text{-}O\text{-}SO_3^-$ were hydrolyzed during the 10 minute incubation period?

43. Calculate the (a) instantaneous and (b) practical buffer capacity in the acid and alkaline directions of a 0.01 *M* phosphate buffer, pH 6.8.

44. The pK_a values of malic acid are 3.40 and 5.05. (a) What is the pH of a solution of 0.05 *M* monosodium malate? (b) What is the pH at the first equivalence point when malic acid is titrated with KOH? (c) What are the ratios and concentrations of all malate species in a 0.05 *M* solution at pH 4.70?

Amino Acids and Peptides

45. Calculate the pH of a 1 *mM* solution of (a) alanine hydrochloride, (b) isoelectric alanine, and (c) the sodium salt of alanine.

46. Calculate the volume of 0.1 *M* KOH required to titrate completely (a) 450 ml of 0.25 *M* alanine hydrochloride, (b) 200 ml of 0.10 *M* isoelectric serine, (c) 400 ml of 0.15 *M* monosodium glutamate, and (d) 400 ml of 0.15 *M* isoelectric glutamic acid.

47. Calculate the volume of 0.2 *M* HCl required to titrate completely (a) 200 ml of 0.25 *M* isoelectric leucine, (b) 375 ml of 0.25 *M* isoelectric glutamic acid, (c) 490 ml of 0.25 *M* isoelectric lysine, and (d) 125 ml of 0.25 *M* sodium salt of lysine.

48. Calculate the pH of a solution obtained by adding 20 ml of 0.20 *M* KOH to 480 ml of 0.02 *M* isoelectric glycine.

49. What is the major ionic species present at pH 7.5 in 0.15 *M* solutions of (a) leucine, (b) aspartic acid, and (c) lysine.

50. Describe the preparation of 1 liter of 0.2 *M* histidine buffer, pH 6.5, starting from solid histidine hydrochloride monohydrate (MW = 209.6) and 1 *M* KOH. pK_{a_2} of histidine = 6.0. (His. HCl is AA^+).

Blood Buffers

51. What is the concentration of dissolved CO_2 in equilibrium with an atmosphere containing a partial pressure of CO_2 of 40 mm Hg?

52. What are the ratios of $CO_2/HCO_3^-/CO_3^{2-}$ in blood plasma at pH 7.4? ($pK_{a_1} = 6.1$, $pK_{a_2} = 10.25$)

53. Blood plasma at pH 7.4 contains 2.4×10^{-2} *M* HCO_3^- and 1.2×10^{-3} *M* CO_2. Calculate the pH after the addition of 3.2×10^{-3} *M* H^+. Assume that the concentration of dissolved CO_2 is maintained constant at 1.2×10^{-3} *M* by the release of excess CO_2.

54. Consider the hemoglobin reaction scheme shown in Figure 1-11. If $K_a = 6.6 \times 10^{-9}$, $K_a' = 2.4 \times 10^{-7}$, and $K_{O_2} = 1$, what must K_{O_2}' be?

55. The pK_a's of $HHgbO_2$ and HHgb from an aquatic mammal are 6.62 and 8.18, respectively. Calculate the number of moles of H^+ taken up by the hemoglobin per mole of O_2 released at pH 7.4.

WHAT'S AHEAD

8.1 LEWIS SYMBOLS AND THE OCTET RULE

We begin with descriptions of the three main types of chemical bonds: *ionic, covalent,* and *metallic*. In evaluating bonding, *Lewis symbols* provide a useful shorthand for keeping track of valence electrons.

8.2 IONIC BONDING

We observe that in ionic substances the atoms are held together by the electrostatic attractions between ions of opposite charge. We discuss the energetics of forming ionic substances and describe the *lattice energy* of these substances.

8.3 COVALENT BONDING

We examine the bonding in molecular substances in which atoms bond by sharing one or more electron pairs. In general, the electrons are shared in such a way that each atom attains an *octet* of electrons.

8.4 BOND POLARITY AND ELECTRONEGATIVITY

We define *electronegativity* as the ability of an atom in a compound to attract electrons to itself. In general, electron pairs are shared unequally between atoms with different electronegativities, leading to *polar covalent bonds*.

8

CHEMICAL BONDING AS ART. The *Atomium* is a 110-m-high steel sculpture commissioned for the 1958 World's Fair in Brussels. The nine spheres represent atoms, and the connecting rods evoke the chemical bonds holding them together. One sphere sits in the center of a cube formed by the other eight, a common arrangement of the atoms in metallic elements, such as iron.

8.5 DRAWING LEWIS STRUCTURES

We see that *Lewis structures* are a simple yet powerful way of predicting covalent bonding patterns in molecules. In addition to the octet rule, we see that the concept of *formal charge* can be used to identify the dominant Lewis structure.

8.6 RESONANCE STRUCTURES

We observe that in some cases more than one equivalent Lewis structure can be drawn for a molecule or polyatomic ion. The bonding description in such cases is a blend of two or more *resonance structures*.

8.7 EXCEPTIONS TO THE OCTET RULE

We recognize that the octet rule is more of a guideline than an absolute rule. Exceptions to the rule include molecules with an odd number of electrons, molecules where large differences in electronegativity prevent an atom from completing its octet, and molecules where an element from period 3 or below in the periodic table attains more than an octet of electrons.

8.8 STRENGTHS OF COVALENT BONDS

We observe that bond strengths vary with the number of shared electron pairs as well as other factors. We use *average bond enthalpy* values to estimate the enthalpies of reactions in cases where thermodynamic data are unavailable.

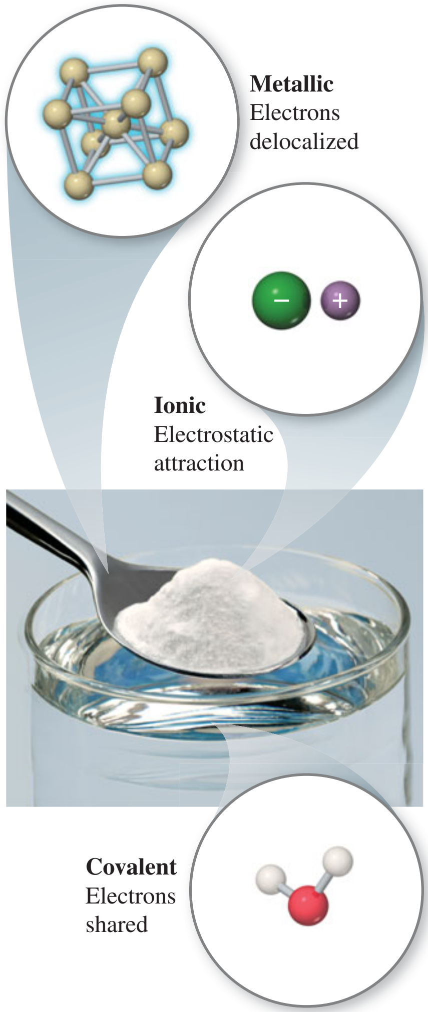
BASIC CONCEPTS OF CHEMICAL BONDING

WHENEVER TWO ATOMS OR IONS are strongly held together, we say there is a **chemical bond** between them. There are three general types of chemical bonds: *ionic, covalent, and metallic* (▶ **FIGURE 8.1**). We can get a glimpse of these three types of bonds by thinking about the simple act of using a stainless-steel spoon to add table salt to a glass of water. Table salt is sodium chloride, NaCl, which consists of sodium ions, Na^+, and chloride ions, Cl^-. The structure is held together by **ionic bonds**, which are due to the attractions between oppositely charged ions. The water consists mainly of H_2O molecules. The hydrogen and oxygen atoms are bonded to one another through **covalent bonds**, in which molecules are formed by the sharing of electrons between atoms. The spoon consists mainly of iron metal, in which Fe atoms are connected to one another via **metallic bonds**, which are formed by electrons that are relatively free to move through the metal. These different substances—NaCl, H_2O, and Fe metal—behave as they do because of the ways in which their constituent atoms are connected to one another.

What determines the type of bonding in any substance? How do the characteristics of these bonds give rise to different physical and chemical properties? The keys to answering the first question are found in the electronic structure of the atoms involved, discussed in Chapters 6 and 7. In this chapter and the next, we examine the relationship between the electronic structure of atoms and the ionic and covalent chemical bonds they form. We will discuss metallic bonding in greater detail in Chapter 12.

GO FIGURE

Which of these three bond types do you expect to see in $CO_2(g)$?



▲ **FIGURE 8.1 Ionic, covalent, and metallic bonds.** Different types of interactions between atoms lead to different types of chemical bonds.

8.1 LEWIS SYMBOLS AND THE OCTET RULE

The electrons involved in chemical bonding are the *valence electrons*, which, for most atoms, are those in the outermost occupied shell. (Section 6.8) The American chemist G. N. Lewis (1875–1946) suggested a simple way of showing the valence electrons in an atom and tracking them during bond formation, using what are now known as either *Lewis electron-dot symbols* or simply Lewis symbols.

The **Lewis symbol** for an element consists of the element's chemical symbol plus a dot for each valence electron. Sulfur, for example, has the electron configuration $[\mathrm{Ne}]3s^2 3p^4$ and therefore six valence electrons. Its Lewis symbol is

$$\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}\cdot$$

The dots are placed on the four sides of the symbol—top, bottom, left, and right—and each side can accommodate up to two electrons. All four sides are equivalent, which means that the choice of on which sides to place two electrons rather than one electron is arbitrary. In general, we spread out the dots as much as possible. In the Lewis symbol for S, for instance, we prefer the dot arrangement shown rather the arrangement having two electrons on three of the sides and none on the fourth.

The electron configurations and Lewis symbols for the main-group elements of periods 2 and 3 are shown in ▼ TABLE 8.1. Notice that the number of valence electrons in any representative element is the same as the element's group number. For example, the Lewis symbols for oxygen and sulfur, members of group 6A, both show six dots.

GIVE IT SOME THOUGHT

Are all these Lewis symbols for Cl correct?

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot \qquad :\overset{\cdot\cdot}{\underset{\cdot}{\mathrm{Cl}}}: \qquad :\overset{\cdot}{\underset{\cdot}{\mathrm{Cl}}}\cdot$$

The Octet Rule

Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table. The noble gases have very stable electron arrangements, as evidenced by their high ionization energies, low affinity for additional electrons, and general lack of chemical reactivity. (Section 7.8) Because all the noble gases except He have eight valence electrons, many atoms undergoing reactions end up with eight valence electrons. This observation has led to a guideline known as the **octet rule:** *Atoms tend to gain, lose, or share electrons until they are surrounded by eight valence electrons.*

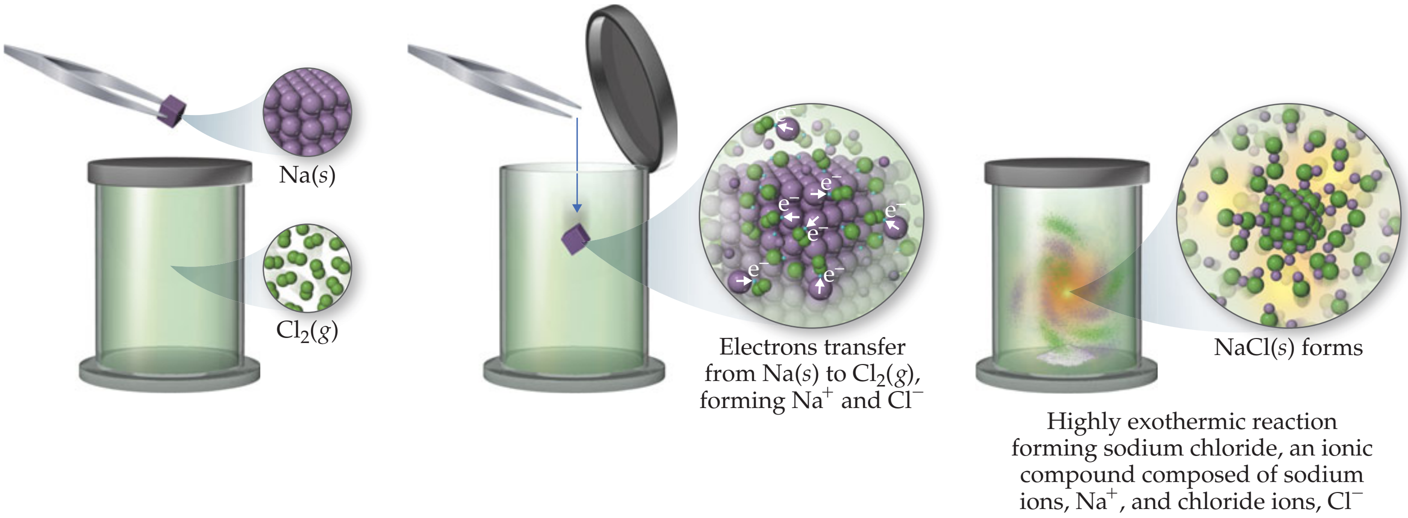
An octet of electrons consists of full *s* and *p* subshells in an atom. In a Lewis symbol, an octet is shown as four pairs of valence electrons arranged around the element symbol, as in the Lewis symbols for Ne and Ar in Table 8.1. There are exceptions to the octet rule, but it provides a useful framework for introducing many important concepts of bonding.

TABLE 8.1 • Lewis Symbols

Group	Element	Electron Configuration	Lewis Symbol	Element	Electron Configuration	Lewis Symbol
1A	Li	$[\mathrm{He}]2s^1$	$\mathrm{Li}\cdot$	Na	$[\mathrm{Ne}]3s^1$	$\mathrm{Na}\cdot$
2A	Be	$[\mathrm{He}]2s^2$	$\cdot\mathrm{Be}\cdot$	Mg	$[\mathrm{Ne}]3s^2$	$\cdot\mathrm{Mg}\cdot$
3A	B	$[\mathrm{He}]2s^2 2p^1$	$\cdot\overset{\cdot}{\mathrm{B}}\cdot$	Al	$[\mathrm{Ne}]3s^2 3p^1$	$\cdot\overset{\cdot}{\mathrm{Al}}\cdot$
4A	C	$[\mathrm{He}]2s^2 2p^2$	$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{C}}}\cdot$	Si	$[\mathrm{Ne}]3s^2 3p^2$	$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{Si}}}\cdot$
5A	N	$[\mathrm{He}]2s^2 2p^3$	$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{N}}}:$	P	$[\mathrm{Ne}]3s^2 3p^3$	$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{P}}}:$
6A	O	$[\mathrm{He}]2s^2 2p^4$	$:\overset{\cdot}{\underset{\cdot}{\mathrm{O}}}:$	S	$[\mathrm{Ne}]3s^2 3p^4$	$:\overset{\cdot}{\underset{\cdot}{\mathrm{S}}}:$
7A	F	$[\mathrm{He}]2s^2 2p^5$	$\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:$	Cl	$[\mathrm{Ne}]3s^2 3p^5$	$\cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$
8A	Ne	$[\mathrm{He}]2s^2 2p^6$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Ne}}}:$	Ar	$[\mathrm{Ne}]3s^2 3p^6$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Ar}}}:$

GO FIGURE

Do you expect a similar reaction between potassium metal and elemental bromine?



▲ **FIGURE 8.2 Reaction of sodium metal with chlorine gas to form the ionic compound sodium chloride.**

8.2 IONIC BONDING

Ionic substances generally result from the interaction of metals on the left side of the periodic table with nonmetals on the right side (excluding the noble gases, group 8A). For example, when sodium metal, Na(*s*), is brought into contact with chlorine gas, $Cl_2(g)$, a violent reaction ensues (▲ **FIGURE 8.2**). The product of this very exothermic reaction is sodium chloride, NaCl(*s*):

$$\mathrm{Na}(s) + \tfrac{1}{2}\,\mathrm{Cl_2}(g) \longrightarrow \mathrm{NaCl}(s) \qquad \Delta H_f^\circ = -410.9\ \mathrm{kJ} \qquad [8.1]$$

Sodium chloride is composed of Na^+ and Cl^- ions arranged in a three-dimensional array (▶ **FIGURE 8.3**).

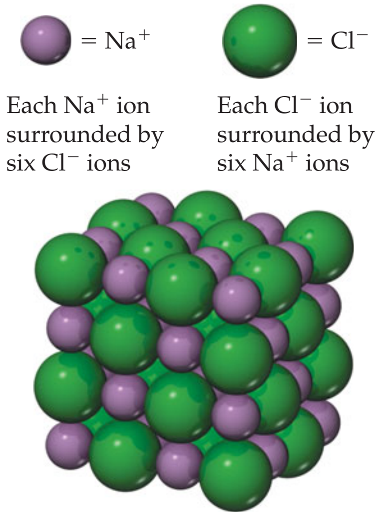
The formation of Na^+ from Na and Cl^- from Cl_2 indicates that an electron has been lost by a sodium atom and gained by a chlorine atom—we can envision an *electron transfer* from the Na atom to the Cl atom. Two of the atomic properties discussed in Chapter 7 give us an indication of how readily electron transfer occurs: ionization energy, which indicates how easily an electron can be removed from an atom, and electron affinity, which measures how much an atom wants to gain an electron. ∞ (Sections 7.4 and 7.5) Electron transfer to form oppositely charged ions occurs when one atom readily gives up an electron (low ionization energy) and another atom readily gains an electron (high electron affinity). Thus, NaCl is a typical ionic compound because it consists of a metal of low ionization energy and a nonmetal of high electron affinity. Using Lewis electron-dot symbols (and showing a chlorine atom rather than the Cl_2 molecule), we can represent this reaction as

$$\mathrm{Na}\cdot + \cdot\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}\!: \longrightarrow \mathrm{Na}^+ + [:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:]^- \qquad [8.2]$$

The arrow indicates the transfer of an electron from the Na atom to the Cl atom. Each ion has an octet of electrons, the Na^+ octet being the $2s^22p^6$ electrons that lie below the single 3*s* valence electron of the Na atom. We have put a bracket around the chloride ion to emphasize that all eight electrons are located on it.

GO FIGURE

If no color key were provided, is there a way for you to guess whether the green spheres represent Na^+ or Cl^-? If so, what information would you use?



▲ **FIGURE 8.3 The crystal structure of sodium chloride.**

GIVE IT SOME THOUGHT

Describe the electron transfers that occur in the formation of calcium fluoride from elemental calcium and elemental fluorine.

Ionic substances possess several characteristic properties. They are usually brittle substances with high melting points. They are usually crystalline. Furthermore, ionic crystals often can be cleaved; that is, they break apart along smooth, flat surfaces. These characteristics result from electrostatic forces that maintain the ions in a rigid, well-defined, three-dimensional arrangement such as that shown in Figure 8.3.

Energetics of Ionic Bond Formation

The formation of sodium chloride from sodium and chlorine is *very* exothermic, as indicated by the large negative enthalpy of formation value given in Equation 8.1, $\Delta H_f^\circ = -410.9$ kJ. Appendix C shows that the heat of formation of other ionic substances is also quite negative. What factors make the formation of ionic compounds so exothermic?

In Equation 8.2 we represented the formation of NaCl as the transfer of an electron from Na to Cl. Recall from Section 7.4 that the loss of electrons from an atom is always an endothermic process. Removing an electron from Na(g) to form $Na^+(g)$, for instance, requires 496 kJ/mol. Recall from Section 7.5 that when a nonmetal gains an electron, the process is generally exothermic, as seen from the negative electron affinities of the elements. Adding an electron to Cl(g), for example, releases 349 kJ/mol. From the magnitudes of these energies, we can see that the transfer of an electron from a Na atom to a Cl atom would not be exothermic—the overall process would be an endothermic process that requires $496 - 349 = 147$ kJ/mol. This endothermic process corresponds to the formation of sodium and chloride ions that are infinitely far apart—in other words, the positive energy change assumes that the ions do not interact with each other, which is quite different from the situation in ionic solids.

GIVE IT SOME THOUGHT

Consider the trends in ionization energies of the alkali metals and electron affinities of the halogens shown in Figures 7.9 and 7.11. For which pair is electron transfer from the alkali metal atom to the halogen atom most likely to be an exothermic process?

The principal reason ionic compounds are stable is the attraction between ions of opposite charge. This attraction draws the ions together, releasing energy and causing the ions to form a solid array, or lattice, such as that shown in Figure 8.3. A measure of how much stabilization results from arranging oppositely charged ions in an ionic solid is given by the **lattice energy**, which is *the energy required to completely separate one mole of a solid ionic compound into its gaseous ions.*

To envision this process for NaCl, imagine that the structure in Figure 8.3 expands from within, so that the distances between the ions increase until the ions are very far apart. This process requires 788 kJ/mol, which is the value of the lattice energy:

$$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g) \qquad \Delta H_{\text{lattice}} = +788 \text{ kJ/mol} \qquad [8.3]$$

Notice that this process is highly endothermic. The reverse process—the coming together of $Na^+(g)$ and $Cl^-(g)$ to form NaCl(s)—is therefore highly exothermic ($\Delta H = -788$ kJ/mol).

▶ **TABLE 8.2** lists the lattice energies for a number of ionic compounds. The large positive values indicate that the ions are strongly attracted to one another in ionic solids. The energy released by the attraction between ions of unlike charge more than makes up for the endothermic nature of ionization energies, making the formation of ionic compounds an exothermic process. The strong attractions also cause most ionic materials to be hard and brittle with high melting points—for example, NaCl melts at 801 °C.

TABLE 8.2 • Lattice Energies for Some Ionic Compounds

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	$MgCl_2$	2326
LiCl	834	$SrCl_2$	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KCl	701		
KBr	671		
CsCl	657		
CsI	600		

The magnitude of the lattice energy of an ionic solid depends on the charges of the ions, their sizes, and their arrangement in the solid. We saw in Section 5.1 that the potential energy of two interacting charged particles is given by

$$E_{el} = \frac{\kappa Q_1 Q_2}{d} \qquad [8.4]$$

In this equation Q_1 and Q_2 are the charges on the particles, d is the distance between their centers, and κ is a constant, 8.99×10^9 J-m/C^2. Equation 8.4 indicates that the attractive interaction between two oppositely charged ions increases as the magnitudes of their charges increase and as the distance between their centers decreases. Thus, *for a given arrangement of ions, the lattice energy increases as the charges on the ions increase and as their radii decrease*. The magnitude of lattice energies depends predominantly on the ionic charges because ionic radii vary over only a limited range.

SAMPLE EXERCISE 8.1 Magnitudes of Lattice Energies

Without consulting Table 8.2, arrange the ionic compounds NaF, CsI, and CaO in order of increasing lattice energy.

SOLUTION

Analyze From the formulas for three ionic compounds, we must determine their relative lattice energies.

Plan We need to determine the charges and relative sizes of the ions in the compounds. We then use Equation 8.4 qualitatively to determine the relative energies, knowing that (a) the larger the ionic charges, the greater the energy and (b) the farther apart the ions are, the lower the energy.

Solve NaF consists of Na^+ and F^- ions, CsI of Cs^+ and I^- ions, and CaO of Ca^{2+} and O^{2-} ions. Because the product Q_1Q_2 appears in the numerator of Equation 8.4, the lattice energy increases dramatically when the charges increase. Thus, we expect the lattice energy of CaO, which has 2+ and 2− ions, to be the greatest of the three.

The ionic charges are the same in NaF and CsI. As a result, the difference in their lattice energies depends on the difference in the distance between ions in the lattice. Because ionic size increases as we go down a group in the periodic table (Section 7.3), we know that Cs^+ is larger than Na^+ and I^- is larger than F^-. Therefore, the distance between Na^+ and F^- ions in NaF is less than the distance between the Cs^+ and I^- ions in CsI. As a result, the lattice energy of NaF should be greater than that of CsI. In order of increasing energy, therefore, we have CsI $<$ NaF $<$ CaO.

Check Table 8.2 confirms our predicted order is correct.

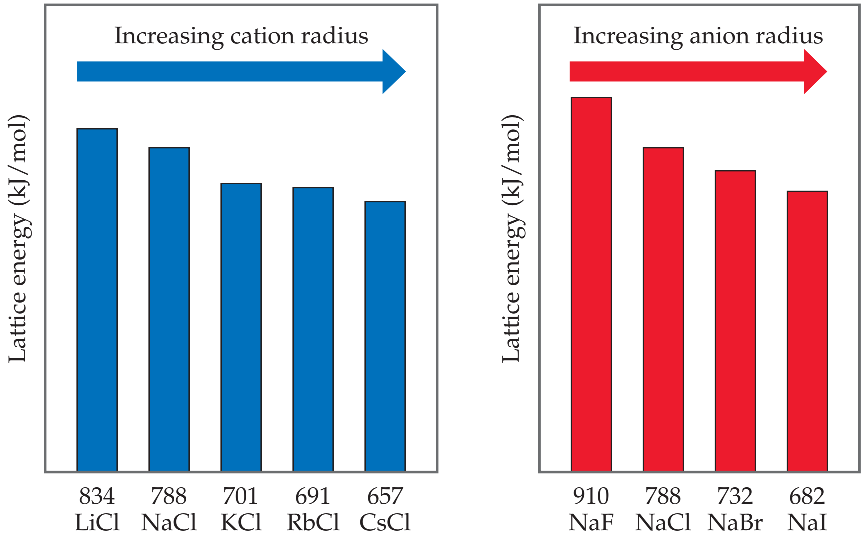
PRACTICE EXERCISE

Which substance do you expect to have the greatest lattice energy, MgF_2, CaF_2, or ZrO_2?

Answer: ZrO_2

GO FIGURE

Using this figure, can you place an upper and lower limit on the lattice energy of KF?



► **FIGURE 8.4 Periodic trends in lattice energy as a function of cation or anion radius.**

Because lattice energy decreases as distance between ions increases, lattice energies follow trends that parallel those in ionic radius shown in Figure 7.6. In particular, because ionic radius increases as we go down a group of the periodic table, we find that, for a given type of ionic compound, lattice energy decreases as we go down a group. ▲ **FIGURE 8.4** illustrates this trend for the alkali chlorides MCl (M = Li, Na, K, Rb, Cs) and the sodium halides NaX (X = F, Cl, Br, I).

Electron Configurations of Ions of the *s*- and *p*-Block Elements

The energetics of ionic bond formation helps explain why many ions tend to have noble-gas electron configurations. For example, sodium readily loses one electron to form Na^+, which has the same electron configuration as Ne:

$$\text{Na} \quad 1s^22s^22p^63s^1 = [\text{Ne}]3s^1$$
$$\text{Na}^+ \quad 1s^22s^22p^6 = [\text{Ne}]$$

Even though lattice energy increases with increasing ionic charge, we never find ionic compounds that contain Na^{2+} ions. The second electron removed would have to come from an inner shell of the sodium atom, and removing electrons from an inner shell requires a very large amount of energy. ∞ (Section 7.4) The increase in lattice energy is not enough to compensate for the energy needed to remove an inner-shell electron. Thus, sodium and the other group 1A metals are found in ionic substances only as 1+ ions.

Similarly, adding electrons to nonmetals is either exothermic or only slightly endothermic as long as the electrons are added to the valence shell. Thus, a Cl atom easily adds an electron to form Cl^-, which has the same electron configuration as Ar:

$$\text{Cl} \quad 1s^22s^22p^63s^23p^5 = [\text{Ne}]3s^23p^5$$
$$\text{Cl}^- \quad 1s^22s^22p^63s^23p^6 = [\text{Ne}]3s^23p^6 = [\text{Ar}]$$

To form a Cl^{2-} ion, the second electron would have to be added to the next higher shell of the Cl atom, an addition that is energetically very unfavorable. Therefore, we never observe Cl^{2-} ions in ionic compounds. We thus expect ionic compounds of the representative metals from groups 1A, 2A, and 3A to contain 1+, 2+, and 3+ cations, respectively, and usually expect ionic compounds of the representative nonmetals of groups 5A, 6A, and 7A to contain 3−, 2−, and 1− anions, respectively.

A CLOSER LOOK

CALCULATION OF LATTICE ENERGIES: THE BORN–HABER CYCLE

Lattice energies cannot be determined directly by experiment. They can, however, be calculated by envisioning the formation of an ionic compound as occurring in a series of well-defined steps. We can then use Hess's law (Section 5.6) to combine the steps in a way that gives the lattice energy for the compound. By so doing, we construct a **Born–Haber cycle**, a thermochemical cycle named after the German scientists Max Born (1882–1970) and Fritz Haber (1868–1934), who introduced it to analyze the factors contributing to the stability of ionic compounds.

In the Born–Haber cycle for NaCl, we consider the formation of NaCl(*s*) from Na(*s*) and Cl_2(*g*) by two routes, as shown in ▶ **FIGURE 8.5**. The enthalpy change for the direct route (red arrow) is the heat of formation of NaCl(*s*):

$$\mathrm{Na}(s) + \tfrac{1}{2}\,\mathrm{Cl_2}(g) \longrightarrow \mathrm{NaCl}(s) \qquad \Delta H_f^\circ[\mathrm{NaCl}(s)] = -411\ \mathrm{kJ} \qquad [8.5]$$

The indirect route has five steps (green arrows in Figure 8.5). First, we generate Na(*g*) atoms by vaporizing Na(*s*). Then we form Cl(*g*) atoms by breaking the bonds in Cl_2 molecules. The enthalpy changes are (Appendix C):

$$\mathrm{Na}(s) \longrightarrow \mathrm{Na}(g) \qquad \Delta H_f^\circ[\mathrm{Na}(g)] = 108\ \mathrm{kJ} \qquad [8.6]$$

$$\tfrac{1}{2}\,\mathrm{Cl_2}(g) \longrightarrow \mathrm{Cl}(g) \qquad \Delta H_f^\circ[\mathrm{Cl}(g)] = 122\ \mathrm{kJ} \qquad [8.7]$$

Note that both processes are endothermic.

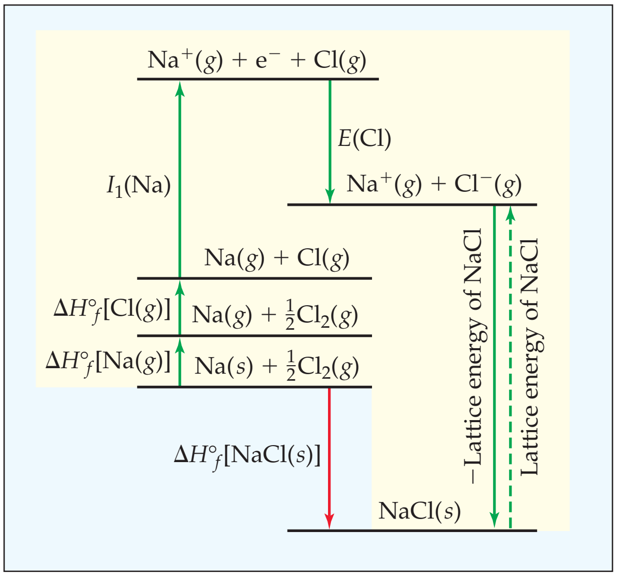
In the next two steps we remove the electron from Na(*g*) to form Na^+(*g*) and then add the electron to Cl(*g*) to form Cl^-(*g*). The enthalpy changes for these processes equal the first ionization energy of Na, I_1(Na), and the electron affinity of Cl, denoted *E*(Cl), respectively: (Sections 7.4, 7.5)

$$\mathrm{Na}(g) \longrightarrow \mathrm{Na}^+(g) + \mathrm{e}^- \qquad \Delta H = I_1(\mathrm{Na}) = 496\ \mathrm{kJ} \qquad [8.8]$$

$$\mathrm{Cl}(g) + \mathrm{e}^- \longrightarrow \mathrm{Cl}^-(g) \qquad \Delta H = E(\mathrm{Cl}) = -349\ \mathrm{kJ} \qquad [8.9]$$

Finally, we combine the Na^+(*g*) and Cl^-(*g*) to form NaCl(*s*). Because forming solid NaCl is the reverse of breaking the solid into its gaseous ions, the enthalpy change for solid formation is the negative of the lattice energy, the quantity we want to determine:

$$\mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \longrightarrow \mathrm{NaCl}(s) \qquad \Delta H = -\Delta H_{\mathrm{lattice}} = ? \qquad [8.10]$$



▲ **FIGURE 8.5 Born–Haber cycle for formation of NaCl.** This Hess's law representation shows the energetic relationships in the formation of the ionic solid from its elements.

The result of the five-step pathway is formation of NaCl(*s*) from Na(*s*) and $\frac{1}{2}$ Cl_2(*g*). Thus, from Hess's law we know that the sum of the enthalpy changes for the five steps equals the enthalpy change for the direct reaction (Equation 8.5):

$$\Delta H_f^\circ[\mathrm{NaCl}(s)] = \Delta H_f^\circ[\mathrm{Na}(g)] + \Delta H_f^\circ[\mathrm{Cl}(g)] + I_1(\mathrm{Na}) + E(\mathrm{Cl}) - \Delta H_{\mathrm{lattice}}$$

$$-411\ \mathrm{kJ} = 108\ \mathrm{kJ} + 122\ \mathrm{kJ} + 496\ \mathrm{kJ} - 349\ \mathrm{kJ} - \Delta H_{\mathrm{lattice}}$$

Solving for $\Delta H_{\mathrm{lattice}}$:

$$\Delta H_{\mathrm{lattice}} = 108\ \mathrm{kJ} + 122\ \mathrm{kJ} + 496\ \mathrm{kJ} - 349\ \mathrm{kJ} + 411\ \mathrm{kJ} = 788\ \mathrm{kJ}$$

Thus, the lattice energy of NaCl is 788 kJ/mol.

RELATED EXERCISES: 8.28, 8.29, 8.30, 8.83, 8.102, 8.103

SAMPLE EXERCISE 8.2 Charges on Ions

Predict the ion generally formed by **(a)** Sr, **(b)** S, **(c)** Al.

SOLUTION

Analyze We must decide how many electrons are most likely to be gained or lost by atoms of Sr, S, and Al.

Plan In each case we can use the element's position in the periodic table to predict whether the element forms a cation or an anion. We can then use its electron configuration to determine the most likely ion formed.

Solve **(a)** Strontium is a metal in group 2A and therefore forms a cation. Its electron configuration is [Kr]$5s^2$, and so we expect that the two valence electrons can be lost easily to give an Sr^{2+} ion. **(b)** Sulfur is a nonmetal in group 6A and will thus tend to be found as an anion. Its electron configuration ([Ne]$3s^23p^4$) is two electrons short of a noble-gas configuration. Thus, we expect that sulfur will form S^{2-} ions. **(c)** Aluminum is a metal in group 3A. We therefore expect it to form Al^{3+} ions.

Check The ionic charges we predict here are confirmed in Tables 2.4 and 2.5.

PRACTICE EXERCISE

Predict the charges on the ions formed when magnesium reacts with nitrogen.

Answer: Mg^{2+} and N^{3-}

Transition-Metal Ions

Because ionization energies increase rapidly for each successive electron removed, the lattice energies of ionic compounds are generally large enough to compensate for the loss of up to only three electrons from atoms. Thus, we find cations with charges of 1+, 2+, or 3+ in ionic compounds. Most transition metals, however, have more than three electrons beyond a noble-gas core. Silver, for example, has a $[Kr]4d^{10}5s^1$ electron configuration. Metals of group 1B (Cu, Ag, Au) often occur as 1+ ions (as in CuBr and AgCl). In forming Ag^+, the 5*s* electron is lost, leaving a completely filled 4*d* subshell. As in this example, transition metals generally do not form ions that have a noble-gas configuration. The octet rule, although useful, is clearly limited in scope.

Recall from Section 7.4 that when a positive ion forms from an atom, electrons are always lost first from the subshell having the largest value of *n*. Thus, *in forming ions, transition metals lose the valence-shell* s *electrons first, then as many* d *electrons as required to reach the charge of the ion*. For instance, in forming Fe^{2+} from Fe, which has the electron configuration $[Ar]3d^64s^2$, the two 4*s* electrons are lost, leading to an $[Ar]3d^6$ configuration. Removal of an additional electron gives Fe^{3+}, whose electron configuration is $[Ar]3d^5$.

GIVE IT SOME THOUGHT

Which element forms a 3+ ion that has the electron configuration $[Kr]4d^6$?

8.3 COVALENT BONDING

The vast majority of chemical substances do not have the characteristics of ionic materials. Most of the substances with which we come into daily contact—such as water—tend to be gases, liquids, or solids with low melting points. Many, such as gasoline, vaporize readily. Many are pliable in their solid forms—for example, plastic bags and paraffin.

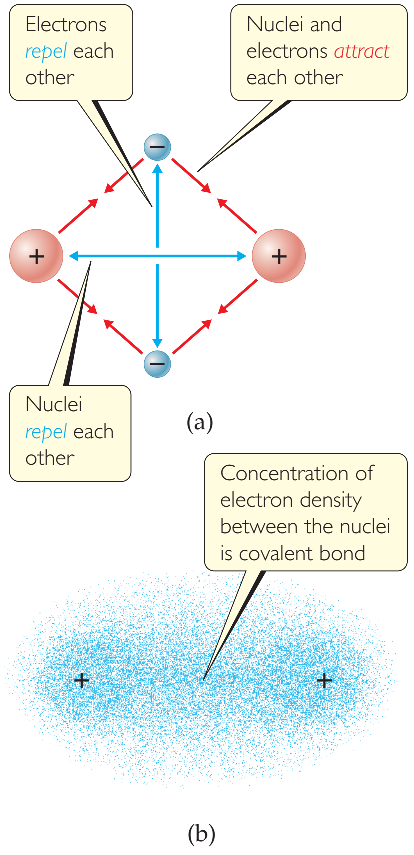
For the very large class of substances that do not behave like ionic substances, we need a different model for the bonding between atoms. G. N. Lewis reasoned that atoms might acquire a noble-gas electron configuration by sharing electrons with other atoms. A chemical bond formed by sharing a pair of electrons is a *covalent bond*.

The hydrogen molecule, H_2, provides the simplest example of a covalent bond. When two hydrogen atoms are close to each other, the two positively charged nuclei repel each other, the two negatively charged electrons repel each other, and the nuclei and electrons attract each other, as shown in ◀ **FIGURE 8.6**(a). Because the molecule is stable, we know that the attractive forces must overcome the repulsive ones. Let's take a closer look at the attractive forces that hold this molecule together.

By using quantum mechanical methods analogous to those used for atoms in Section 6.5, we can calculate the distribution of electron density in molecules. Such a calculation for H_2 shows that the attractions between the nuclei and the electrons cause electron density to concentrate between the nuclei, as shown in Figure 8.6(b). As a result, the overall electrostatic interactions are attractive. Thus, the atoms in H_2 are held together principally because the two positive nuclei are attracted to the concentration of negative charge between them. In essence, the shared pair of electrons in any covalent bond acts as a kind of "glue" to bind atoms together.

GO FIGURE

What would happen to the magnitudes of the attractions and repulsions represented in (a) if the nuclei were farther apart?



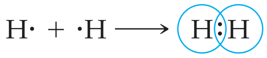
▲ **FIGURE 8.6 The covalent bond in H_2.** (a) The attractions and repulsions among electrons and nuclei in the hydrogen molecule. (b) Electron distribution in the H_2 molecule.

GIVE IT SOME THOUGHT

Ionizing an H_2 molecule to H_2^+ changes the strength of the bond. Based on the description of covalent bonding given previously, do you expect the H—H bond in H_2^+ to be weaker or stronger than the H—H bond in H_2?

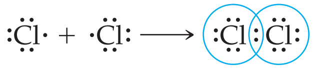
Lewis Structures

The formation of covalent bonds can be represented with Lewis symbols. The formation of the H_2 molecule from two H atoms, for example, can be represented as



In forming the covalent bond, each hydrogen atom acquires a second electron, achieving the stable, two-electron, noble-gas electron configuration of helium.

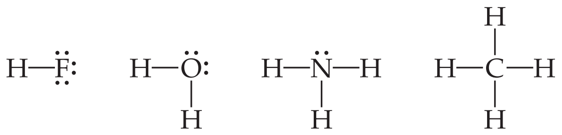
Formation of a covalent bond between two Cl atoms to give a Cl_2 molecule can be represented in a similar way:



By sharing the bonding electron pair, each chlorine atom has eight electrons (an octet) in its valence shell, thus achieving the noble-gas electron configuration of argon.

The structures shown here for H_2 and Cl_2 are called either **Lewis structures** or *Lewis electron-dot structures*. In writing Lewis structures, we usually show each shared electron pair as a line and any unshared electron pairs as dots. Written this way, the Lewis structures for H_2 and Cl_2 are

For nonmetals, the number of valence electrons in a neutral atom is the same as the group number. Therefore, one might predict that 7A elements, such as F, would form one covalent bond to achieve an octet; 6A elements, such as O, would form two covalent bonds; 5A elements, such as N, would form three; and 4A elements, such as C, would form four. These predictions are borne out in many compounds, as in, for example, the compounds with hydrogen of the nonmetals of the second row of the periodic table:



SAMPLE EXERCISE 8.3 Lewis Structure of a Compound

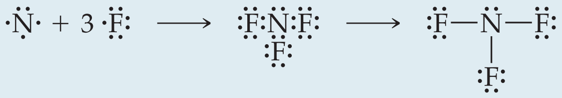
Given the Lewis symbols for nitrogen and fluorine in Table 8.1, predict the formula of the stable binary compound (a compound composed of two elements) formed when nitrogen reacts with fluorine and draw its Lewis structure.

SOLUTION

Analyze The Lewis symbols for nitrogen and fluorine reveal that nitrogen has five valence electrons and fluorine has seven.

Plan We need to find a combination of the two elements that results in an octet of electrons around each atom. Nitrogen requires three additional electrons to complete its octet, and fluorine requires one. Sharing a pair of electrons between one N atom and one F atom will result in an octet of electrons for fluorine but not for nitrogen. We therefore need to figure out a way to get two more electrons for the N atom.

Solve Nitrogen must share a pair of electrons with three fluorine atoms to complete its octet. Thus, the binary compound these two elements form must be NF_3:



Check The Lewis structure in the center shows that each atom is surrounded by an octet of electrons. Once you are accustomed to thinking of each line in a Lewis structure as representing *two* electrons, you can just as easily use the structure on the right to check for octets.

PRACTICE EXERCISE

Compare the Lewis symbol for neon with the Lewis structure for methane, CH_4. In what important way are the electron arrangements about neon and carbon alike? In what important way are they different?

Answer: Both atoms have an octet of electrons. However, the electrons about neon are unshared electron pairs, whereas those about carbon are shared with four hydrogen atoms.

Multiple Bonds

A shared electron pair constitutes a single covalent bond, generally referred to simply as a **single bond**. In many molecules, atoms attain complete octets by sharing more than one pair of electrons. When two electron pairs are shared, two lines are drawn in the Lewis structure, representing a **double bond**. In carbon dioxide, for example, bonding occurs between carbon, with four valence electrons, and oxygen, with six:

$$:\dot{\underset{\cdot}{O}}: + \cdot\dot{\underset{\cdot}{C}}\cdot + :\dot{\underset{\cdot}{O}}: \longrightarrow \ddot{\underset{\cdot\cdot}{O}}::C::\ddot{\underset{\cdot\cdot}{O}} \qquad (\text{or } \ddot{\underset{\cdot\cdot}{O}}=C=\ddot{\underset{\cdot\cdot}{O}})$$

As the diagram shows, each oxygen atom acquires an octet by sharing two electron pairs with carbon. Carbon acquires an octet by sharing two electron pairs with each of the two oxygen atoms; each double bond involves four electrons.

A **triple bond** corresponds to the sharing of three pairs of electrons, such as in the N_2 molecule:

$$:\dot{\underset{\cdot}{N}}\cdot + \cdot\dot{\underset{\cdot}{N}}: \longrightarrow :N:::N: \qquad (\text{or } :N\equiv N:)$$

Because each nitrogen atom has five valence electrons, three electron pairs must be shared to achieve the octet configuration.

The properties of N_2 are in complete accord with its Lewis structure. Nitrogen is a diatomic gas with exceptionally low reactivity that results from the very stable nitrogen–nitrogen bond. The nitrogen atoms are separated by only 1.10 Å. The short separation distance between the two N atoms is a result of the triple bond between the atoms. From studies of the structures of many different substances in which nitrogen atoms share one or two electron pairs, we have learned that the average distance between bonded nitrogen atoms varies with the number of shared electron pairs:

$N-N$	$N=N$	$N\equiv N$
1.47 Å	1.24 Å	1.10 Å

As a general rule, the length of the bond between two atoms decreases as the number of shared electron pairs increases.

GIVE IT SOME THOUGHT

The C—O bond length in carbon monoxide, CO, is 1.13 Å, whereas the C—O bond length in CO_2 is 1.24 Å. Without drawing a Lewis structure, do you think that CO contains a single, double, or triple bond?

8.4 BOND POLARITY AND ELECTRONEGATIVITY

When two identical atoms bond, as in Cl_2 or H_2, the electron pairs must be shared equally. When two atoms from opposites sides of the periodic table bond, such as NaCl, there is relatively little sharing of electrons, which means that NaCl is best described as composed of Na^+ and Cl^- ions. The 3*s* electron of the Na atom is, in effect, transferred completely to chlorine. The bonds that are found in most substances fall somewhere between these extremes.

Bond polarity is a measure of how equally or unequally the electrons in any covalent bond are shared. A **nonpolar covalent bond** is one in which the electrons are shared equally, as in Cl_2 and N_2. In a **polar covalent bond**, one of the atoms exerts a greater attraction for the bonding electrons than the other. If the difference in relative ability to attract electrons is large enough, an ionic bond is formed.

Electronegativity

We use a quantity called electronegativity to estimate whether a given bond is nonpolar covalent, polar covalent, or ionic. **Electronegativity** is defined as the ability of an atom *in a molecule* to attract electrons to itself. The greater an atom's electronegativity, the greater its ability to attract electrons to itself. The electronegativity of an atom in a molecule is related to the atom's ionization energy and electron affinity, which are properties of isolated atoms. An atom with a very negative electron affinity and a high ionization energy both attracts electrons from other atoms and resists having its electrons attracted away; it is highly electronegative.

Electronegativity values can be based on a variety of properties, not just ionization energy and electron affinity. The American chemist Linus Pauling (1901–1994) developed the first and most widely used electronegativity scale, which is based on thermochemical data. As ▼ **FIGURE 8.7** shows, there is generally an increase in electronegativity from left to right across a period—that is, from the most metallic to the most nonmetallic elements. With some exceptions (especially in the transition metals), electronegativity decreases with increasing atomic number in a group. This is what we expect because we know that ionization energies decrease with increasing atomic number in a group and electron affinities do not change very much.

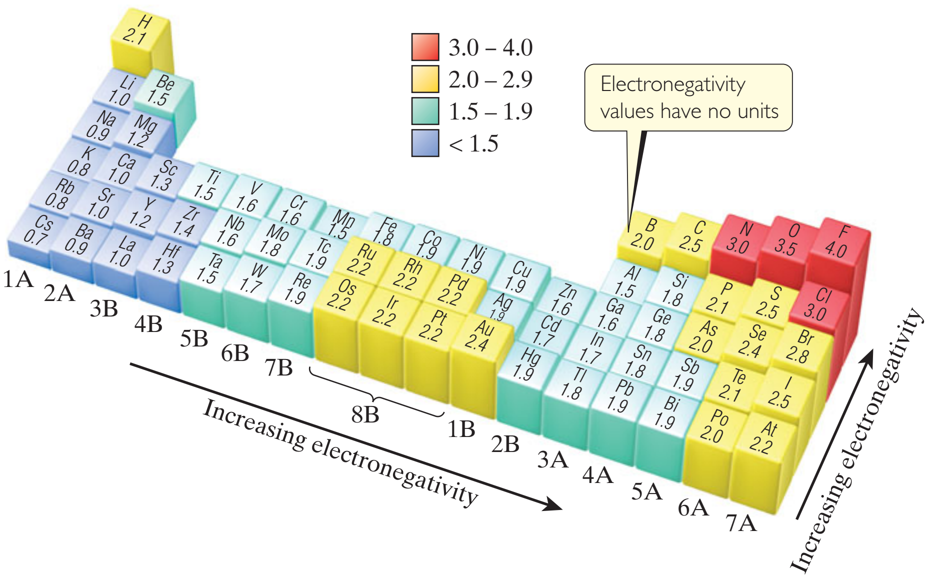
You do not need to memorize electronegativity values. Instead, you should know the periodic trends so that you can predict which of two elements is more electronegative.

GIVE IT SOME THOUGHT

How does the *electronegativity* of an element differ from its *electron affinity*?

GO FIGURE

For the group 6A elements, what is the trend in electronegativity with increasing atomic number?



◀ **FIGURE 8.7 Electronegativity values based on Pauling's thermochemical data.**

Electronegativity and Bond Polarity

We can use the difference in electronegativity between two atoms to gauge the polarity of the bond the atoms form. Consider these three fluorine-containing compounds:

	F_2	HF	LiF
Electronegativity difference	$4.0 - 4.0 = 0$	$4.0 - 2.1 = 1.9$	$4.0 - 1.0 = 3.0$
Type of bond	Nonpolar covalent	Polar covalent	Ionic

In F_2 the electrons are shared equally between the fluorine atoms and, thus, the covalent bond is *nonpolar*. A nonpolar covalent bond results when the electronegativities of the bonded atoms are equal.

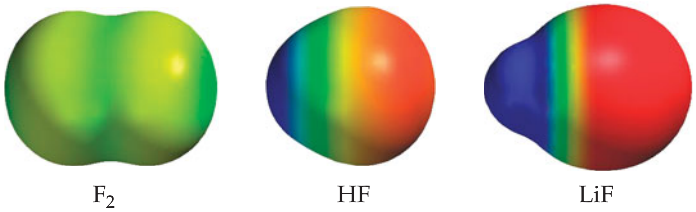
In HF the fluorine atom has a greater electronegativity than the hydrogen atom, with the result that the electrons are shared unequally—the bond is *polar*. In general, a polar covalent bond results when the atoms differ in electronegativity. In HF the more electronegative fluorine atom attracts electron density away from the less electronegative hydrogen atom, leaving a partial positive charge on the hydrogen atom and a partial negative charge on the fluorine atom. We can represent this charge distribution as

$$\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}}$$

The $\delta+$ and $\delta-$ (read "delta plus" and "delta minus") symbolize the partial positive and negative charges, respectively.

In LiF the electronegativity difference is very large, meaning that the electron density is shifted far toward F. The resultant bond is therefore most accurately described as *ionic*.

The shift of electron density toward the more electronegative atom in a bond can be seen in the results of calculations of electron density distributions. For the three species in our example, the calculated electron density distributions are shown in ▼ **FIGURE 8.8**. You can see that in F_2 the distribution is symmetrical, in HF the electron density is clearly shifted toward fluorine, and in LiF the shift is even greater. These examples illustrate, therefore, that *the greater the difference in electronegativity between two atoms, the more polar their bond.*



▲ **FIGURE 8.8** **Electron density distribution.** This computer-generated rendering shows the calculated electron-density distribution on the surface of the F_2, HF, and LiF molecules.

GIVE IT SOME THOUGHT

Based on differences in electronegativity, how would you characterize the bonding in sulfur dioxide, SO_2? Do you expect the bonds between S and O to be nonpolar, polar covalent, or ionic?

SAMPLE EXERCISE 8.4 Bond Polarity

In each case, which bond is more polar: **(a)** B—Cl or C—Cl, **(b)** P—F or P—Cl ? Indicate in each case which atom has the partial negative charge.

SOLUTION

Analyze We are asked to determine relative bond polarities, given nothing but the atoms involved in the bonds.

Plan Because we are not asked for quantitative answers, we can use the periodic table and our knowledge of electronegativity trends to answer the question.

Solve

(a) The chlorine atom is common to both bonds. Therefore, the analysis reduces to a comparison of the electronegativities of B and C. Because boron is to the left of carbon in the periodic table, we predict that boron has the lower electronegativity. Chlorine, being on the right side of the table, has a higher electronegativity. The more polar bond will be the one between the atoms having the lowest electronegativity (boron) and the highest electronegativity (chlorine). Consequently, the B—Cl bond is more polar; the chlorine atom carries the partial negative charge because it has a higher electronegativity.

(b) In this example phosphorus is common to both bonds, and the analysis reduces to a comparison of the electronegativities of F and Cl. Because fluorine is above chlorine in the periodic table, it should be more electronegative and will form the more polar bond with P. The higher electronegativity of fluorine means that it will carry the partial negative charge.

Check

(a) Using Figure 8.7: The difference in the electronegativities of chlorine and boron is $3.0 - 2.0 = 1.0$; the difference between chlorine and carbon is $3.0 - 2.5 = 0.5$. Hence, the B—Cl bond is more polar, as we had predicted.

(b) Using Figure 8.7: The difference in the electronegativities of chlorine and phosphorus is $3.0 - 2.1 = 0.9$; the difference between fluorine and phosphorus is $4.0 - 2.1 = 1.9$. Hence, the P—F bond is more polar, as we had predicted.

PRACTICE EXERCISE

Which of the following bonds is most polar: S—Cl, S—Br, Se—Cl, or Se—Br ?

Answer: Se—Cl

Dipole Moments

The difference in electronegativity between H and F leads to a polar covalent bond in the HF molecule. As a consequence, there is a concentration of negative charge on the more electronegative F atom, leaving the less electronegative H atom at the positive end of the molecule. A molecule such as HF, in which the centers of positive and negative charge do not coincide, is a **polar molecule**. Thus, we describe both bonds and entire molecules as being polar and nonpolar.

We can indicate the polarity of the HF molecule in two ways:

$$\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}} \quad \textit{or} \quad \overset{+\!\!\!\longrightarrow}{\mathrm{H}-\mathrm{F}}$$

In the notation on the right, the arrow denotes the shift in electron density toward the fluorine atom. The crossed end of the arrow can be thought of as a plus sign designating the positive end of the molecule.

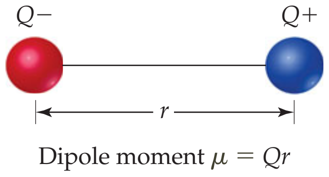
Polarity helps determine many properties we observe at the macroscopic level in the laboratory and in everyday life. Polar molecules align themselves with respect to one another, with the negative end of one molecule and the positive end of another attracting each other. Polar molecules are likewise attracted to ions. The negative end of a polar molecule is attracted to a positive ion, and the positive end is attracted to a negative ion. These interactions account for many properties of liquids, solids, and solutions, as you will see in Chapters 11, 12, and 13.

How can we quantify the polarity of a molecule? Whenever two electrical charges of equal magnitude but opposite sign are separated by a distance, a **dipole** is established. The quantitative measure of the magnitude of a dipole is called its **dipole moment**, denoted μ. If two equal and opposite charges $Q+$ and $Q-$ are separated by a distance r, as in ▶ **FIGURE 8.9**, the magnitude of the dipole moment is the product of Q and r:

$$\mu = Qr \qquad [8.11]$$

GO FIGURE

If the charged particles are moved closer together, does μ increase, decrease, or stay the same?



▲ **FIGURE 8.9 Dipole and dipole moment.** When charges of equal magnitude and opposite sign $Q+$ and $Q-$ are separated by a distance r, a dipole is produced.

This expression tells us that dipole moment increases as the magnitude of Q increases and as r increases. For a nonpolar molecule, such as F_2, the dipole moment is zero because there is no charge separation.

GIVE IT SOME THOUGHT

Chlorine monofluoride, ClF, and iodine monofluoride, IF, are *interhalogen* compounds—compounds that contain bonds between different halogen elements. Which of these molecules has the larger dipole moment?

Dipole moments are usually reported in *debyes* (D), a unit that equals 3.34×10^{-30} coulomb-meters (C-m). For molecules, we usually measure charge in units of the electronic charge e, 1.60×10^{-19} C, and distance in angstroms. This means we need to convert units whenever we want to report a dipole moment in debyes. Suppose that two charges 1+ and 1− (in units of e) are separated by 1.00 Å. The dipole moment produced is

$$\mu = Qr = (1.60 \times 10^{-19}\,\text{C})(1.00\,\text{Å})\left(\frac{10^{-10}\,\text{m}}{1\,\text{Å}}\right)\left(\frac{1\,\text{D}}{3.34 \times 10^{-30}\,\text{C-m}}\right) = 4.79\,\text{D}$$

Measurement of the dipole moments can provide us with valuable information about the charge distributions in molecules, as illustrated in Sample Exercise 8.5.

SAMPLE EXERCISE 8.5 Dipole Moments of Diatomic Molecules

The bond length in the HCl molecule is 1.27 Å. **(a)** Calculate the dipole moment, in debyes, that results if the charges on the H and Cl atoms were 1+ and 1−, respectively. **(b)** The experimentally measured dipole moment of HCl(g) is 1.08 D. What magnitude of charge, in units of e, on the H and Cl atoms leads to this dipole moment?

SOLUTION

Analyze and Plan We are asked in (a) to calculate the dipole moment of HCl that would result if there were a full charge transferred from H to Cl. We can use Equation 8.11 to obtain this result. In (b), we are given the actual dipole moment for the molecule and will use that value to calculate the actual partial charges on the H and Cl atoms.

Solve:

(a) The charge on each atom is the electronic charge, $e = 1.60 \times 10^{-19}$ C. The separation is 1.27 Å. The dipole moment is therefore

$$\mu = Qr = (1.60 \times 10^{-19}\,\text{C})(1.27\,\text{Å})\left(\frac{10^{-10}\,\text{m}}{1\,\text{Å}}\right)\left(\frac{1\,\text{D}}{3.34 \times 10^{-30}\,\text{C-m}}\right) = 6.08\,\text{D}$$

(b) We know the value of μ, 1.08 D, and the value of r, 1.27 Å. We want to calculate the value of Q:

$$Q = \frac{\mu}{r} = \frac{(1.08\,\text{D})\left(\dfrac{3.34 \times 10^{-30}\,\text{C-m}}{1\,\text{D}}\right)}{(1.27\,\text{Å})\left(\dfrac{10^{-10}\,\text{m}}{1\,\text{Å}}\right)} = 2.84 \times 10^{-20}\,\text{C}$$

We can readily convert this charge to units of e:

$$\text{Charge in } e = (2.84 \times 10^{-20}\,\text{C})\left(\frac{1\,e}{1.60 \times 10^{-19}\,\text{C}}\right) = 0.178e$$

Thus, the experimental dipole moment indicates that the charge separation in the HCl molecule is

$$\overset{0.178+}{\text{H}} - \overset{0.178-}{\text{Cl}}$$

Because the experimental dipole moment is less than that calculated in part (a), the charges on the atoms are much less than a full electronic charge. We could have anticipated this because the H—Cl bond is polar covalent rather than ionic.

PRACTICE EXERCISE

The dipole moment of chlorine monofluoride, ClF(g), is 0.88 D. The bond length of the molecule is 1.63 Å. **(a)** Which atom is expected to have the partial negative charge? **(b)** What is the charge on that atom in units of e?

Answers: **(a)** F, **(b)** 0.11−

TABLE 8.3 • Bond Lengths, Electronegativity Differences, and Dipole Moments of the Hydrogen Halides

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

▲ **TABLE 8.3** presents the bond lengths and dipole moments of the hydrogen halides. Notice that as we proceed from HF to HI, the electronegativity difference decreases and the bond length increases. The first effect decreases the amount of charge separated and causes the dipole moment to decrease from HF to HI, even though the bond length is increasing. Calculations identical to those used in Sample Exercise 8.5 show that the charges on the atoms decrease from 0.41+ and 0.41− in HF to 0.057+ and 0.057− in HI. We can visualize the varying degree of electronic charge shift in these substances from computer-generated renderings based on calculations of electron distribution, as shown in ▼ **FIGURE 8.10**. For these molecules, the change in the electronegativity difference has a greater effect on the dipole moment than does the change in bond length.

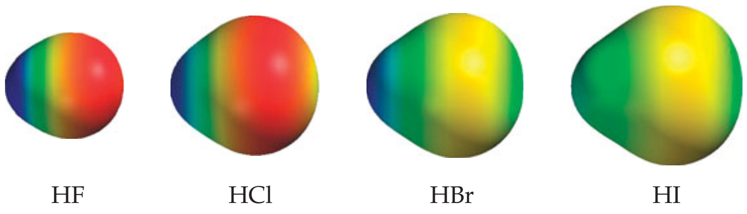
GIVE IT SOME THOUGHT

The bond between carbon and hydrogen is one of the most important types of bonds in chemistry. The length of a H—C bond is approximately 1.1 Å. Based on this distance and differences in electronegativity, do you expect the dipole moment of an individual H—C bond to be larger or smaller than that of the H—I bond?

Before leaving this section, let's return to the LiF molecule in Figure 8.8. Under standard conditions, LiF exists as an ionic solid with an arrangement of atoms analogous to the sodium chloride structure shown in Figure 8.3. However, it is possible to generate LiF *molecules* by vaporizing the ionic solid at high temperature. The molecules have a dipole moment of 6.28 D and a bond distance of 1.53 Å. From these values we can calculate the charge on lithium and fluorine to be 0.857+ and 0.857−, respectively. This bond is extremely polar, and the presence of such large charges strongly favors the formation of an extended ionic lattice in which each lithium ion is surrounded by fluoride ions and vice versa.

GO FIGURE

How do you interpret the fact that there is no red in the HBr and HI representations?



▲ **FIGURE 8.10 Charge separation in the hydrogen halides.** In HF, the strongly electronegative F pulls much of the electron density away from H. In HI, the I, being much less electronegative than F, does not attract the shared electrons as strongly and, consequently, there is far less polarization of the bond.

Differentiating Ionic and Covalent Bonding

To understand the interactions responsible for chemical bonding, it is advantageous to treat ionic and covalent bonding separately. That is the approach taken in this chapter, as well as in most other undergraduate-level chemistry texts. In reality, however, there is a continuum between the extremes of ionic and covalent bonding. This lack of a well-defined separation between the two types of bonding may seem unsettling or confusing at first.

The simple models of ionic and covalent bonding presented in this chapter go a long way toward understanding and predicting the structures and properties of chemical compounds. When covalent bonding is dominant, more often than not we expect compounds to exist as molecules,* having all the properties we associate with molecular substances, such as relatively low melting and boiling points and nonelectrolyte behavior when dissolved in water. When ionic bonding is dominant, we expect the compounds to be brittle, high-melting solids with extended lattice structures and exhibiting strong electrolyte behavior when dissolved in water.

There are, of course, exceptions to these general characterizations, some of which we examine later in the book. Nonetheless, the ability to quickly categorize the predominant bonding interactions in a substance as covalent or ionic imparts considerable insight into the properties of that substance. The question then becomes the best way to recognize which type of bonding dominates.

The simplest approach is to assume that the interaction between a metal and a nonmetal is ionic and that between two nonmetals is covalent. While this classification scheme is reasonably predictive, there are far too many exceptions to use it blindly. For example, tin is a metal and chlorine is a nonmetal, but $SnCl_4$ is a molecular substance that exists as a colorless liquid at room temperature. It freezes at $-33\ ^\circ C$ and boils at $114\ ^\circ C$. Clearly this substance does not have the characteristics of an ionic substance. A more sophisticated approach is to use the difference in electronegativity as the main criterion for determining whether ionic or covalent bonding will be dominant. This approach correctly predicts the bonding in $SnCl_4$ to be polar covalent based on an electronegativity difference of 1.2 and at the same time correctly predicts the bonding in NaCl to be predominantly ionic based on an electronegativity difference of 2.1.

Evaluating bonding based on electronegativity difference is a useful system, but it has one shortcoming. The electronegativity values given in Figure 8.7 do not take into account changes in bonding that accompany changes in the oxidation state of the metal. For example, Figure 8.7 gives the electronegativity difference between manganese and oxygen as $3.5 - 1.5 = 2.0$, which falls in the range where the bonding is normally considered ionic (the electronegativity difference for NaCl is $3.0 - 0.9 = 2.1$). Therefore, it is not surprising to learn that manganese(II) oxide, MnO, is a green solid that melts at $1842\ ^\circ C$ and has the same crystal structure as NaCl.

However, the bonding between manganese and oxygen is not always ionic. Manganese(VII) oxide, Mn_2O_7, is a green liquid that freezes at $5.9\ ^\circ C$, which indicates that covalent rather than ionic bonding dominates. The change in the oxidation state of manganese is responsible for the change in bonding. In general, as the oxidation state of a metal increases, so does the degree of covalent bonding. When the oxidation state of the metal is highly positive (roughly speaking, $+4$ or larger), we should expect significant covalency in the bonds it forms with nonmetals. Thus, with metals in high oxidation states we find molecular substances, such as Mn_2O_7, or polyatomic ions, such as MnO_4^- and CrO_4^{2-}, rather than ionic compounds.

GIVE IT SOME THOUGHT

You have a yellow solid that melts at $41\ ^\circ C$ and boils at $131\ ^\circ C$ and a green solid that melts at $2320\ ^\circ C$. If you are told that one of them is Cr_2O_3 and the other is OsO_4, which one do you expect to be the yellow solid?

---

*There are some exceptions to this statement, such as network solids, including diamond, silicon, and germanium, where an extended structure is formed even though the bonding is clearly covalent. These examples are discussed in Section 12.7.

8.5 | DRAWING LEWIS STRUCTURES

Lewis structures can help us understand the bonding in many compounds and are frequently used when discussing the properties of molecules. For this reason, drawing Lewis structures is an important skill that you should practice. To do so, you should use the following procedure.

1. **Sum the valence electrons from all atoms.** (Use the periodic table to help you determine the number of valence electrons in each atom.) For an anion, add one electron to the total for each negative charge. For a cation, subtract one electron from the total for each positive charge. Do not worry about keeping track of which electrons come from which atoms. Only the total number is important.
2. **Write the symbols for the atoms, show which atoms are attached to which, and connect them with a single bond (*a dash, representing* two *electrons*).** Chemical formulas are often written in the order in which the atoms are connected in the molecule or ion. The formula HCN, for example, tells you that the carbon atom is bonded to the H and to the N. In many polyatomic molecules and ions, the central atom is usually written first, as in CO_3^{2-} and SF_4. Remember that the central atom is generally less electronegative than the atoms surrounding it. In other cases, you may need more information before you can draw the Lewis structure.
3. **Complete the octets around all the atoms bonded to the central atom.** Remember, however, that a hydrogen atom has only a single pair of electrons around it.
4. **Place any leftover electrons on the central atom,** even if doing so results in more than an octet of electrons around the atom.
5. **If there are not enough electrons to give the central atom an octet, try multiple bonds.** Use one or more of the unshared pairs of electrons on the atoms bonded to the central atom to form double or triple bonds.

SAMPLE EXERCISE 8.6 **Drawing a Lewis Structure**

Draw the Lewis structure for phosphorus trichloride, PCl_3.

SOLUTION

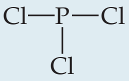
Analyze and Plan We are asked to draw a Lewis structure from a molecular formula. Our plan is to follow the five-step procedure just described.

Solve

First, we sum the valence electrons. Phosphorus (group 5A) has five valence electrons, and each chlorine (group 7A) has seven. The total number of valence electrons is therefore

$$5 + (3 \times 7) = 26$$

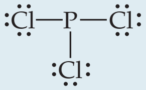
Second, we arrange the atoms to show which atom is connected to which, and we draw a single bond between them. There are various ways the atoms might be arranged. In binary compounds, however, the first element in the chemical formula is generally surrounded by the remaining atoms. Thus, we begin with a skeleton structure that shows a single bond between the P atom and each Cl atom:



$$\begin{array}{c}\mathrm{Cl{-}P{-}Cl}\\ | \\ \mathrm{Cl}\end{array}$$

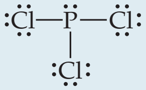
(It is not crucial that the Cl atoms be left of, right of, and below the P atom—any structure that shows each of the three Cl atoms bonded to P will work.)

Third, we complete the octets on the atoms bonded to the central atom. Placing octets around each Cl atom accounts for 24 electrons (remember, each line in our structure represents *two* electrons):



$$\begin{array}{c}:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}{-}\mathrm{P}{-}\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:\\ | \\ :\underset{\cdot\cdot}{\mathrm{Cl}}:\end{array}$$

Fourth, recalling that our total number of electrons is 26, we place the remaining two electrons on the central atom, completing the octet around it:



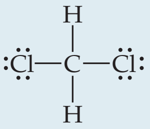
$$\begin{array}{c}:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}{-}\ddot{\mathrm{P}}{-}\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:\\ | \\ :\underset{\cdot\cdot}{\mathrm{Cl}}:\end{array}$$

This structure gives each atom an octet, so we stop at this point. (In checking for octets, remember to count both electrons in a single bond twice, once for each atom in the bond.)

PRACTICE EXERCISE

(a) How many valence electrons should appear in the Lewis structure for CH_2Cl_2?
(b) Draw the Lewis structure.

Answers: **(a)** 20, **(b)**



$$\begin{array}{c} H \\ | \\ :\underset{\cdot\cdot}{\ddot{Cl}}-C-\underset{\cdot\cdot}{\ddot{Cl}}: \\ | \\ H \end{array}$$

SAMPLE EXERCISE 8.7 Lewis Structure with a Multiple Bond

Draw the Lewis structure for HCN.

SOLUTION

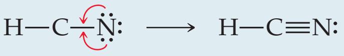
Hydrogen has one valence electron, carbon (group 4A) has four, and nitrogen (group 5A) has five. The total number of valence electrons is, therefore, $1 + 4 + 5 = 10$. In principle, there are different ways in which we might choose to arrange the atoms. Because hydrogen can accommodate only one electron pair, it always has only one single bond associated with it. Therefore, C—H—N is an impossible arrangement. The remaining two possibilities are H—C—N and H—N—C. The first is the arrangement found experimentally. You might have guessed this because **(a)** the formula is written with the atoms in this order and **(b)** carbon is less electronegative than nitrogen. Thus, we begin with the skeleton structure

$$H-C-N$$

The two bonds account for four electrons. The H atom can have only two electrons associated with it, and so we will not add any more electrons to it. If we place the remaining six electrons around N to give it an octet, we do not achieve an octet on C:

$$H-C-\underset{\cdot\cdot}{\ddot{N}}:$$

We therefore try a double bond between C and N, using one of the unshared pairs we placed on N. Again we end up with fewer than eight electrons on C, and so we next try a triple bond. This structure gives an octet around both C and N:



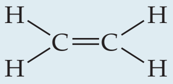
$$H-C-\underset{\cdot\cdot}{\ddot{N}}: \longrightarrow H-C\equiv N:$$

The octet rule is satisfied for the C and N atoms, and the H atom has two electrons around it. This is a correct Lewis structure.

PRACTICE EXERCISE

Draw the Lewis structure for **(a)** NO^+ ion, **(b)** C_2H_4.

Answers: **(a)** $[:N\equiv O:]^+$, **(b)**

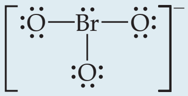


SAMPLE EXERCISE 8.8 Lewis Structure for a Polyatomic Ion

Draw the Lewis structure for the BrO_3^- ion.

SOLUTION

Bromine (group 7A) has seven valence electrons, and oxygen (group 6A) has six. We must add one more electron to our sum to account for the 1− charge of the ion. The total number of valence electrons is, therefore, $7 + (3 \times 6) + 1 = 26$. For oxyanions—$BrO_3^-$, SO_4^{2-}, NO_3^-, CO_3^{2-}, and so forth—the oxygen atoms surround the central nonmetal atom. After following this format and then putting in the single bonds and distributing the unshared electron pairs, we have



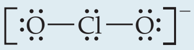
$$\left[\begin{array}{c} :\underset{\cdot\cdot}{\ddot{O}}-\ddot{Br}-\underset{\cdot\cdot}{\ddot{O}}: \\ | \\ :\underset{\cdot\cdot}{\ddot{O}}: \end{array}\right]^-$$

Notice that the Lewis structure for an ion is written in brackets and the charge is shown outside the brackets at the upper right.

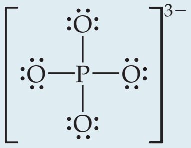
PRACTICE EXERCISE

Draw the Lewis structure for **(a)** ClO_2^-, **(b)** PO_4^{3-}.

Answers: **(a)**



(b)



Formal Charge and Alternative Lewis Structures

When we draw a Lewis structure, we are describing how the electrons are distributed in a molecule or polyatomic ion. In some instances we can draw more than one Lewis structure and have all of them obey the octet rule. All these structures can be thought of as contributing to the *actual* arrangement of the electrons in the molecule, but not all of them will contribute to the same extent. How do we decide which of several Lewis structures is the most important? One approach is to do some "bookkeeping" of the valence electrons to determine the *formal charge* of each atom in each Lewis structure. The **formal charge** of any atom in a molecule is the charge the atom would have if all the atoms in the molecule had the same electronegativity (that is, if each bonding electron pair in the molecule were shared equally between its two atoms).

To calculate the formal charge on any atom in a Lewis structure, we assign electrons to the atom as follows:

1. *All* unshared (nonbonding) electrons are assigned to the atom on which they are found.
2. For any bond—single, double, or triple—*half* of the bonding electrons are assigned to each atom in the bond.

The formal charge of each atom is calculated *by subtracting the number of electrons assigned to the atom from the number of valence electrons in the neutral atom.*

Let's practice by calculating the formal charges in the cyanide ion, CN^-, which has the Lewis structure

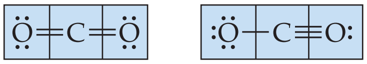
$$[:\mathrm{C}\equiv\mathrm{N}:]^-$$

For the C atom, there are two nonbonding electrons and three electrons from the six in the triple bond ($\frac{1}{2} \times 6 = 3$) for a total of five. The number of valence electrons on a neutral C atom is four. Thus, the formal charge on C is $4 - 5 = -1$. For N, there are two nonbonding electrons and three electrons from the triple bond. Because the number of valence electrons on a neutral N atom is five, its formal charge is $5 - 5 = 0$:

$$[:\overset{-1}{\mathrm{C}}\equiv\overset{0}{\mathrm{N}}:]^-$$

Notice that the sum of the formal charges equals the overall charge on the ion, 1−. The formal charges on a neutral molecule must add to zero, whereas those on an ion add to give the charge on the ion.

If we can draw several Lewis structures for a molecule, the concept of formal charge can help us decide which is the most important, which we shall call the *dominant* Lewis structure. One Lewis structure for CO_2, for instance, has two double bonds, as we saw on page 298. However, we can also satisfy the octet rule by drawing a Lewis structure having one single bond and one triple bond. Calculating formal charges in these structures, we have



	O	C	O	O	C	O
Valence electrons:	6	4	6	6	4	6
−(Electrons assigned to atom):	6	4	6	7	4	5
Formal charge:	0	0	0	−1	0	+1

Note that in both cases the formal charges add up to zero, as they must because CO_2 is a neutral molecule. So, which is the more correct structure? As a general rule, when more than one Lewis structure is possible, we will use the following guidelines to choose the dominant one:

1. The dominant Lewis structure is generally the one in which the atoms bear formal charges closest to zero.
2. A Lewis structure in which any negative charges reside on the more electronegative atoms is generally more dominant than one that has negative charges on the less electronegative atoms.

Thus, the first Lewis structure of CO_2 is the dominant one because the atoms carry no formal charges and so satisfy the first guideline. The other Lewis structure shown (and the similar one that has a triple bond to the left O and a single bond to the right O) do contribute to the actual structure but to a much smaller extent.

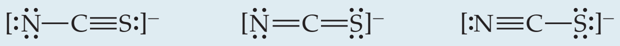
Although the concept of formal charge helps us to arrange alternative Lewis structures in order of importance, it is important that you remember that *formal charges do not represent real charges on atoms.* These charges are just a bookkeeping convention. The actual charge distributions in molecules and ions are determined not by formal charges but by a number of other factors, including electronegativity differences between atoms.

GIVE IT SOME THOUGHT

Suppose a Lewis structure for a neutral fluorine-containing molecule results in a formal charge on the fluorine atom of +1. What conclusion would you draw?

SAMPLE EXERCISE 8.9 Lewis Structures and Formal Charges

Three possible Lewis structures for the thiocyanate ion, NCS^-, are

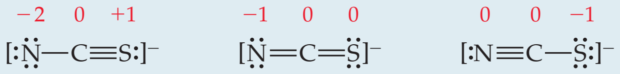


$$[:\overset{..}{\underset{..}{N}}-C\equiv S:]^- \qquad [\overset{..}{\underset{..}{N}}=C=\overset{..}{\underset{..}{S}}]^- \qquad [:N\equiv C-\overset{..}{\underset{..}{S}}:]^-$$

(**a**) Determine the formal charges in each structure. (**b**) Based on the formal charges, which Lewis structure is the dominant one?

SOLUTION

(**a**) Neutral N, C, and S atoms have five, four, and six valence electrons, respectively. We can determine the formal charges in the three structures by using the rules we just discussed:



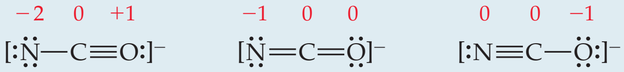
$$[:\overset{-2}{\overset{..}{\underset{..}{N}}}-\overset{0}{C}\equiv \overset{+1}{S}:]^- \qquad [\overset{-1}{\overset{..}{\underset{..}{N}}}=\overset{0}{C}=\overset{0}{\overset{..}{\underset{..}{S}}}]^- \qquad [:\overset{0}{N}\equiv \overset{0}{C}-\overset{-1}{\overset{..}{\underset{..}{S}}}:]^-$$

As they must, the formal charges in all three structures sum to 1−, the overall charge of the ion. (**b**) The dominant Lewis structure generally produces formal charges of the smallest magnitude (guideline 1). That rules out the left structure as the dominant one. Further, as discussed in Section 8.4, N is more electronegative than C or S. Therefore, we expect any negative formal charge to reside on the N atom (guideline 2). For these two reasons, the middle Lewis structure is the dominant one for NCS^-.

PRACTICE EXERCISE

The cyanate ion, NCO^-, has three possible Lewis structures. (**a**) Draw these three structures and assign formal charges in each. (**b**) Which Lewis structure is dominant?

Answers: (**a**)



$$[:\overset{-2}{\overset{..}{\underset{..}{N}}}-\overset{0}{C}\equiv \overset{+1}{O}:]^- \qquad [\overset{-1}{\overset{..}{\underset{..}{N}}}=\overset{0}{C}=\overset{0}{\overset{..}{\underset{..}{O}}}]^- \qquad [:\overset{0}{N}\equiv \overset{0}{C}-\overset{-1}{\overset{..}{\underset{..}{O}}}:]^-$$

(i) (ii) (iii)

(**b**) Structure (iii), which places a negative charge on oxygen, the most electronegative element in the ion, is the dominant Lewis structure.

A CLOSER LOOK

OXIDATION NUMBERS, FORMAL CHARGES, AND ACTUAL PARTIAL CHARGES

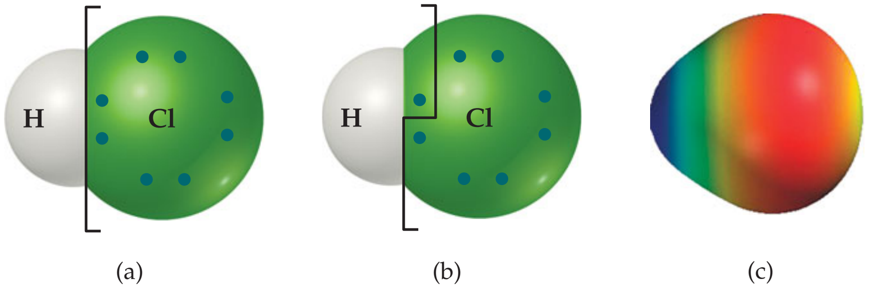
In Chapter 4 we introduced the rules for assigning *oxidation numbers* to atoms. The concept of electronegativity is the basis of these numbers. An atom's oxidation number is the charge the atom would have if its bonds were completely ionic. That is, in determining oxidation number, all shared electrons are counted with the more electronegative atom. For example, consider the Lewis structure of HCl in ▼ **FIGURE 8.11**(a). To assign oxidation numbers, both electrons in the covalent bond between the atoms are assigned to the more electronegative Cl atom. This procedure gives Cl eight valence electrons, one more than in the neutral atom. Thus, its oxidation number is −1. Hydrogen has no valence electrons when they are counted this way, giving it an oxidation number of +1.

To assign formal charges in this molecule, we ignore electronegativity and assign the electrons in bonds equally to the two bonded atoms. In the case of HCl, we divide the bonding pair of electrons equally between H and Cl, as in Figure 8.11(b). In this case Cl has seven assigned electrons, the same as that of the neutral Cl atom, and H has one assigned electron. Thus, the formal charges of both Cl and H in this compound are 0.

Neither oxidation number nor formal charge gives an accurate depiction of the actual charges on atoms because oxidation numbers overstate the role of electronegativity and formal charges ignore it. It seems reasonable that electrons in covalent bonds should be apportioned according to the relative electronegativities of the bonded atoms. From Figure 8.7 we see that Cl has an electronegativity of 3.0, while that of H is 2.1. The more electronegative Cl atom might therefore be expected to have roughly $3.0/(3.0 + 2.1) = 0.59$ of the electrical charge in the bonding pair, whereas the H atom has $2.1/(3.0 + 2.1) = 0.41$ of the charge. Because the bond consists of two electrons, the Cl atom's share is $0.59 \times 2e = 1.18e$, or $0.18e$ more than the neutral Cl atom. This gives rise to a partial negative charge of 0.18− on Cl and a partial positive charge of 0.18+ on H. (Notice again that we place the plus and minus signs *before* the magnitude in writing oxidation numbers and formal charges but *after* the magnitude in writing actual charges.)

The dipole moment of HCl gives an experimental measure of the partial charge on each atom. In Sample Exercise 8.5 we saw that the dipole moment of HCl indicates a partial charge of 0.178+ on H and 0.178− on Cl, in remarkably good agreement with our simple approximation based on electronegativities. Although our approximation method provides "ballpark" numbers for the magnitude of charge on atoms, the relationship between electronegativities and charge separation is generally more complicated. As we have already seen, computer programs employing quantum mechanical principles have been developed to obtain more accurate estimates of the partial charges on atoms, even in complex molecules. A computer-graphical representation of the charge distribution in HCl is shown in Figure 8.11(c).

RELATED EXERCISES 8.8, 8.49, 8.50, 8.51, 8.52, 8.86, 8.87, 8.90, and 8.91

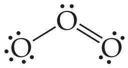


(a) (b) (c)

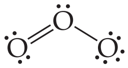
◀ **FIGURE 8.11** **Oxidation number, formal charge, and electron density distribution for the HCl molecule.**

8.6 RESONANCE STRUCTURES

We sometimes encounter molecules and ions in which the experimentally determined arrangement of atoms is not adequately described by a single dominant Lewis structure. Consider ozone, O_3, which is a bent molecule with two equal O—O bond lengths (▶ **FIGURE 8.12**). Because each oxygen atom contributes 6 valence electrons, the ozone molecule has 18 valence electrons. This means the Lewis structure must have one O—O single bond and one O═O double bond to attain an octet about each atom:

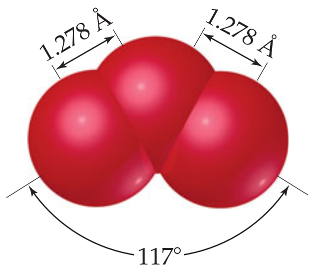


However, this single structure cannot by itself be dominant because it requires that one O—O bond be different from the other, contrary to the observed structure—we would expect the O═O double bond to be shorter than the O—O single bond. (Section 8.3) In drawing the Lewis structure, however, we could just as easily have put the O═O bond on the left:



GO FIGURE

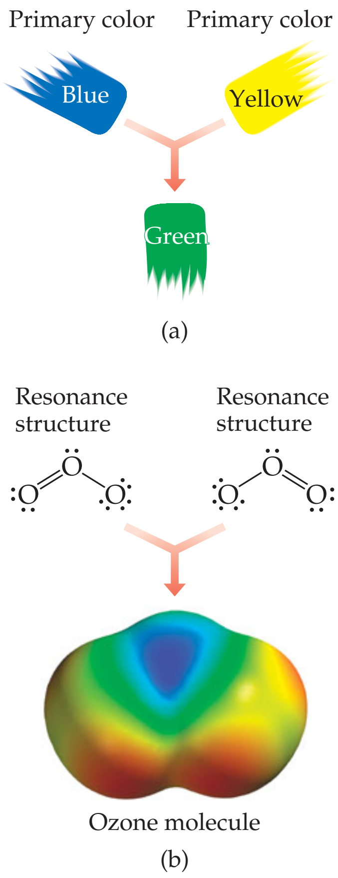
What feature of this structure suggests that the two outer O atoms are in some way equivalent to each other?



▲ **FIGURE 8.12** **Molecular structure of ozone.**

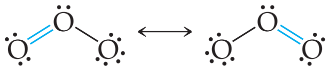
GO FIGURE

Is the electron density consistent with equal weights for the two resonance structures for O_3? Explain.



▲ **FIGURE 8.13 Resonance.** Describing a molecule as a blend of different resonance structures is similar to describing a paint color as a blend of primary colors. (a) Green paint is a blend of blue and yellow. We cannot describe green as a single primary color. (b) The ozone molecule is a blend of two resonance structures. We cannot describe the ozone molecule in terms of a single Lewis structure.

There is no reason for one of these Lewis structures to be dominant because they are equally valid representations of the molecule. The placement of the atoms in these two alternative but completely equivalent Lewis structures is the same, but the placement of the electrons is different. Lewis structures of this sort are called **resonance structures.** To describe the structure of ozone properly, we write both resonance structures and use a double-headed arrow to indicate that the real molecule is described by an average of the two:



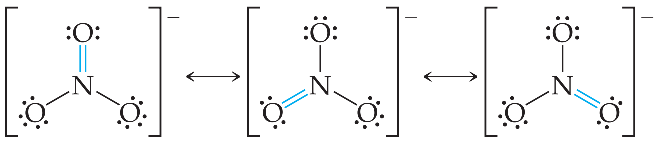
To understand why certain molecules require more than one resonance structure, we can draw an analogy to mixing paint (◀ **FIGURE 8.13**). Blue and yellow are both primary colors of paint pigment. An equal blend of blue and yellow pigments produces green pigment. We cannot describe green paint in terms of a single primary color, yet it still has its own identity. Green paint does not oscillate between its two primary colors: It is not blue part of the time and yellow the rest of the time. Similarly, molecules such as ozone cannot be described as oscillating between the two individual Lewis structures shown previously—there are two equivalent dominant Lewis structures that contribute equally to the actual structure of the molecule.

The actual arrangement of the electrons in molecules such as O_3 must be considered as a blend of two (or more) Lewis structures. By analogy to the green paint, the molecule has its own identity separate from the individual resonance structures. For example, the ozone molecule always has two equivalent O—O bonds whose lengths are intermediate between the lengths of an oxygen–oxygen single bond and an oxygen–oxygen double bond. Another way of looking at it is to say that the rules for drawing Lewis structures do not allow us to have a single dominant structure for the ozone molecule. For example, there are no rules for drawing half-bonds. We can get around this limitation by drawing two equivalent Lewis structures that, when averaged, amount to something very much like what is observed experimentally.

GIVE IT SOME THOUGHT

The O—O bonds in ozone are often described as "one-and-a-half" bonds. Is this description consistent with the idea of resonance?

As an additional example of resonance structures, consider the nitrate ion, NO_3^-, for which three equivalent Lewis structures can be drawn:



Notice that the arrangement of atoms is the same in each structure—only the placement of electrons differs. In writing resonance structures, the same atoms must be bonded to each other in all structures, so that the only differences are in the arrangements of electrons. All three NO_3^- Lewis structures are equally dominant and taken together adequately describe the ion, in which all three N—O bond lengths are the same.

GIVE IT SOME THOUGHT

In the same sense that we describe the O—O bonds in O_3 as "one-and-a-half" bonds, how would you describe the N—O bonds in NO_3^-?

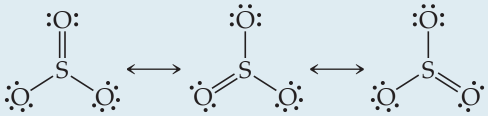
In some instances, all the possible Lewis structures for a species may not be equivalent to one another. Instead, one or more may be dominant. We will encounter examples of this as we proceed.

SAMPLE EXERCISE 8.10 **Resonance Structures**

Which is predicted to have the shorter sulfur–oxygen bonds, SO_3 or SO_3^{2-}?

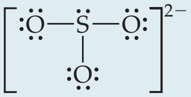
SOLUTION

The sulfur atom has six valence electrons, as does oxygen. Thus, SO_3 contains 24 valence electrons. In writing the Lewis structure, we see that three equivalent resonance structures can be drawn:



As with NO_3^-, the actual structure of SO_3 is an equal blend of all three. Thus, each S—O bond length should be about one-third of the way between the length of a single bond and the length of a double bond. That is, they should be shorter than single bonds but not as short as double bonds.

The SO_3^{2-} ion has 26 electrons, which leads to a dominant Lewis structure in which all the S—O bonds are single:

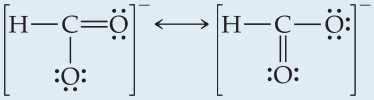


Our analysis of the Lewis structures leads us to conclude that SO_3 should have the shorter S—O bonds and SO_3^{2-} the longer ones. This conclusion is correct: The experimentally measured S—O bond lengths are 1.42 Å in SO_3 and 1.51 Å in SO_3^{2-}.

PRACTICE EXERCISE

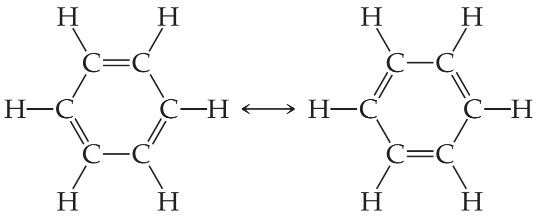
Draw two equivalent resonance structures for the formate ion, HCO_2^-.

Answer:



Resonance in Benzene

Resonance is an important concept in describing the bonding in organic molecules, particularly *aromatic* organic molecules, a category that includes the hydrocarbon *benzene*, C_6H_6. The six C atoms are bonded in a hexagonal ring, and one H atom is bonded to each C atom. We can write two equivalent dominant Lewis structures for benzene, each of which satisfies the octet rule. These two structures are in resonance:



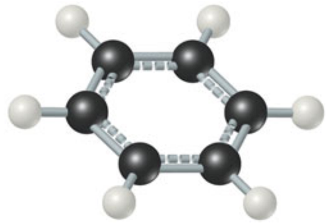
Note that the double bonds are in different places in the two structures. Each of these resonance structures shows three carbon–carbon single bonds and three carbon–carbon double bonds. However, experimental data show that all six C—C bonds are of equal length, 1.40 Å, intermediate between the typical bond lengths for a C—C single bond (1.54 Å) and a C═C double bond (1.34 Å). Each of the C—C bonds in benzene can be thought of as a blend of a single bond and a double bond (▶ **FIGURE 8.14**).

Benzene is commonly represented by omitting the hydrogen atoms and showing only the carbon–carbon framework with the vertices unlabeled. In this convention, the resonance in the molecule is represented either by two structures separated by a double-headed arrow or by a shorthand notation in which we draw a hexagon with a circle inside:

The shorthand notation reminds us that benzene is a blend of two resonance structures—it emphasizes that the C═C double bonds cannot be assigned to specific edges of the hexagon. Chemists use both representations of benzene interchangeably.

GO FIGURE

What is the significance of the dashed bonds in this ball-and-stick model?

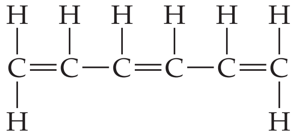


▲ **FIGURE 8.14** **Benzene, an "aromatic" organic compound.** The benzene molecule is a regular hexagon of carbon atoms with a hydrogen atom bonded to each one. The dashed lines represent the blending of two equivalent resonance structures, leading to C—C bonds that are intermediate between single and double bonds.

The bonding arrangement in benzene confers special stability to the molecule. As a result, millions of organic compounds contain the six-membered ring characteristic of benzene. Many of these compounds are important in biochemistry, in pharmaceuticals, and in the production of modern materials.

GIVE IT SOME THOUGHT

Each Lewis structure of benzene has three C═C double bonds. Another hydrocarbon containing three C═C double bonds is *hexatriene,* C_6H_8. A Lewis structure of hexatriene is



$$\begin{array}{cccccccccccc} H & & H & & H & & H & & H & & H \\ | & & | & & | & & | & & | & & | \\ C & = & C & - & C & = & C & - & C & = & C \\ | & & & & & & & & & & | \\ H & & & & & & & & & & H \end{array}$$

Do you expect hexatriene to have multiple resonance structures? If not, why is this molecule different from benzene with respect to resonance?

8.7 EXCEPTIONS TO THE OCTET RULE

The octet rule is so simple and useful in introducing the basic concepts of bonding that you might assume it is always obeyed. In Section 8.2, however, we noted its limitation in dealing with ionic compounds of the transition metals. The rule also fails in many situations involving covalent bonding. These exceptions to the octet rule are of three main types:

1. Molecules and polyatomic ions containing an odd number of electrons
2. Molecules and polyatomic ions in which an atom has fewer than an octet of valence electrons
3. Molecules and polyatomic ions in which an atom has more than an octet of valence electrons

Odd Number of Electrons

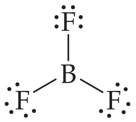
In the vast majority of molecules and polyatomic ions, the total number of valence electrons is even, and complete pairing of electrons occurs. However, in a few molecules and polyatomic ions, such as ClO_2, NO, NO_2, and O_2^-, the number of valence electrons is odd. Complete pairing of these electrons is impossible, and an octet around each atom cannot be achieved. For example, NO contains $5 + 6 = 11$ valence electrons. The two most important Lewis structures for this molecule are

GIVE IT SOME THOUGHT

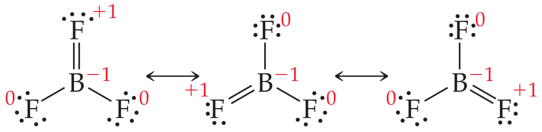
Which of the Lewis structures for NO is dominant based on analysis of the formal charges?

Less than an Octet of Valence Electrons

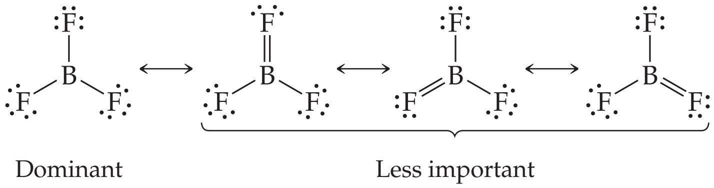
A second type of exception occurs when there are fewer than eight valence electrons around an atom in a molecule or polyatomic ion. This situation is also relatively rare (with the exception of hydrogen and helium as we have already discussed), most often encountered in compounds of boron and beryllium. As an example, let's consider boron trifluoride, BF_3. If we follow the first four steps of our procedure for drawing Lewis structures, we obtain the structure



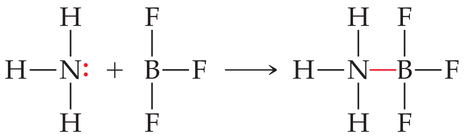
which has only six electrons around the boron atom. The formal charge is zero on both B and F, and we could complete the octet around boron by forming a double bond (step 5). In so doing, we see that there are three equivalent resonance structures (the formal charges are shown in red):



Each of these structures forces a fluorine atom to share additional electrons with the boron atom, which is inconsistent with the high electronegativity of fluorine. In fact, the formal charges tell us that this is an unfavorable situation. In each structure, the F atom involved in the B═F double bond has a formal charge of +1, while the less electronegative B atom has a formal charge of −1. Thus, the resonance structures containing a B═F double bond are less important than the one in which there are fewer than an octet of valence electrons around boron:



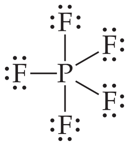
We usually represent BF_3 solely by the dominant resonance structure, in which there are only six valence electrons around boron. The chemical behavior of BF_3 is consistent with this representation. In particular, BF_3 reacts energetically with molecules having an unshared pair of electrons that can be used to form a bond with boron, as, for example, in the reaction

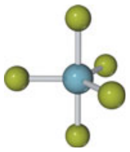


In the stable compound NH_3BF_3, boron has an octet of valence electrons.

More than an Octet of Valence Electrons

The third and largest class of exceptions consists of molecules or polyatomic ions in which there are more than eight electrons in the valence shell of an atom. When we draw the Lewis structure for PF_5, for example, we are forced to place ten electrons around the central phosphorus atom:





Molecules and ions with more than an octet of electrons around the central atom are often called *hypervalent*. Other examples of hypervalent species are SF_4, AsF_6^-, and ICl_4^-. The corresponding molecules with a second-period atom as the central atom, such as NCl_5 and OF_4, do *not* exist.

Hypervalent molecules are formed only for central atoms from period 3 and below in the periodic table. The principal reason for their formation is the relatively larger size of the central atom. For example, a P atom is large enough that five F (or even five Cl) atoms can be bonded to it without being too crowded. By contrast, an N atom is too small to accommodate five atoms bonded to it. Because size is a factor, hypervalent molecules occur most often when the central atom is bonded to the smallest and most electronegative atoms—F, Cl, and O.

The notion of a valence shell containing more than an octet of electrons is also consistent with the presence of unfilled *nd* orbitals in atoms from period 3 and below. By comparison, elements of the second period have only the 2*s* and 2*p* valence orbitals available for bonding. Detailed analyses of the bonding in molecules such as PF_5 and SF_6 suggest that the presence of unfilled 3*d* orbitals in P and S has a relatively minor impact on the formation of hypervalent molecules, and the general current belief is that the increased size of third-period atoms is the more important factor.

SAMPLE EXERCISE 8.11 Lewis Structure for an Ion with More than an Octet of Electrons

Draw the Lewis structure for ICl_4^-.

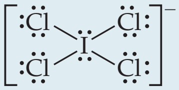
SOLUTION

Iodine (group 7A) has seven valence electrons. Each chlorine atom (group 7A) also has seven. An extra electron is added to account for the 1− charge of the ion. Therefore, the total number of valence electrons is

$$7 + (4 \times 7) + 1 = 36$$

The I atom is the central atom in the ion. Putting eight electrons around each Cl atom (including a pair of electrons between I and each Cl to represent the single bond between these atoms) requires $8 \times 4 = 32$ electrons.

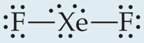
We are thus left with $36 - 32 = 4$ electrons to be placed on the larger iodine:



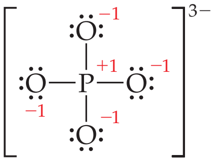
Iodine has 12 valence electrons around it, four more than needed for an octet.

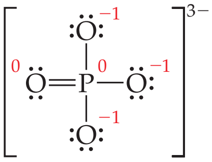
PRACTICE EXERCISE

(**a**) Which of the following atoms is never found with more than an octet of valence electrons around it: S, C, P, Br? (**b**) Draw the Lewis structure for XeF_2.

Answers: (**a**) C, (**b**) 

Finally, there are Lewis structures where you might have to choose between satisfying the octet rule and obtaining the most favorable formal charges by using more than an octet of electrons. For example, consider these Lewis structures for the phosphate ion, PO_4^{3-}:





The formal charges on the atoms are shown in red. In the left structure, the P atom obeys the octet rule. In the right structure, however, the P atom has five electron pairs, leading to smaller formal charges on the atoms. (You should be able to see that there are three additional resonance structures for the Lewis structure on the right.)

Chemists are still debating which of these two structures is dominant for PO_4^{3-}. Recent theoretical calculations based on quantum mechanics suggest to some researchers that the left structure is the dominant one. Other researchers claim that the bond lengths in the ion are more consistent with the right structure being dominant. This disagreement is a convenient reminder that, in general, multiple Lewis structures can contribute to the actual electron distribution in an atom or molecule.

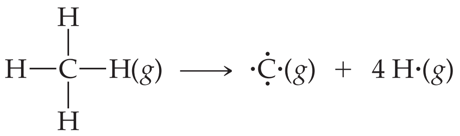
8.8 STRENGTHS OF COVALENT BONDS

The stability of a molecule is related to the strengths of its covalent bonds. The strength of a covalent bond between two atoms is determined by the energy required to break the bond. It is easiest to relate bond strength to the enthalpy change in reactions in which bonds are broken. ∞ (Section 5.4) The **bond enthalpy** is the enthalpy change, ΔH, for the breaking of a particular bond in one mole of a gaseous substance. For example, the bond enthalpy for the bond in Cl_2 is the enthalpy change when 1 mol of $Cl_2(g)$ dissociates into chlorine atoms:

$$:\underset{..}{\ddot{Cl}}-\underset{..}{\ddot{Cl}}:(g) \longrightarrow 2\,:\underset{..}{\ddot{Cl}}\cdot(g)$$

We use the letter D followed by the bond in question to represent bond enthalpies. Thus, for example, $D(Cl—Cl)$ is the bond enthalpy for the Cl_2 bond, and $D(H—Br)$ is the bond enthalpy for the HBr bond.

It is relatively simple to assign bond enthalpies to the bond in a diatomic molecule because in these cases the bond enthalpy is just the energy required to break the molecule into its atoms. However, many important bonds, such as the C—H bond, exist only in polyatomic molecules. For these bonds, we usually use *average* bond enthalpies. For example, the enthalpy change for the following process in which a methane molecule is decomposed into its five atoms (a process called *atomization*) can be used to define an average bond enthalpy for the C—H bond, $D(C—H)$:



$$\mathrm{CH_4}(g) \longrightarrow \cdot\dot{\underset{\cdot}{C}}\cdot(g) + 4\,H\cdot(g) \qquad \Delta H = 1660\ \text{kJ}$$

Because there are four equivalent C—H bonds in methane, the enthalpy of atomization is equal to the sum of the bond enthalpies of the four C—H bonds. Therefore, the average C—H bond enthalpy for CH_4 is $D(C—H) = (1660/4)\ \text{kJ/mol} = 415\ \text{kJ/mol}$.

The bond enthalpy for a given pair of atoms, say C—H, depends on the rest of the molecule containing the atom pair. However, the variation from one molecule to another is generally small, which supports the idea that bonding electron pairs are localized between atoms. If we consider C—H bond enthalpies in many different compounds, we find that the average bond enthalpy is 413 kJ/mol, close to the 415 kJ/mol we just calculated from CH_4.

GIVE IT SOME THOUGHT

How can you use the enthalpy of atomization of the hydrocarbon ethane, $C_2H_6(g)$, along with the value $D(C—H) = 413$ kJ/mol to estimate the value for $D(C—C)$?

▶ **TABLE 8.4** lists average bond enthalpies for a number of atom pairs. *The bond enthalpy is always a positive quantity*; energy is always required to break chemical bonds. Conversely, energy is *always* released when a bond forms between two gaseous atoms or molecular fragments. The greater the bond enthalpy, the stronger the bond. Further, a molecule with strong chemical bonds generally has less tendency to undergo chemical change than does one with weak bonds. For example, N_2, which has a very strong $N\equiv N$ triple bond, is very unreactive, whereas hydrazine, N_2H_4, which has an N—N single bond, is highly reactive.

GIVE IT SOME THOUGHT

Based on bond enthalpies, which do you expect to be more reactive, oxygen, O_2, or hydrogen peroxide, H_2O_2?

TABLE 8.4 • Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Si—Cl	464						

Multiple Bonds

C=C	614	N=N	418	O_2	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

Bond Enthalpies and the Enthalpies of Reactions

We can use average bond enthalpies to estimate the enthalpies of reactions in which bonds are broken and new bonds are formed. This procedure allows us to estimate quickly whether a given reaction will be endothermic ($\Delta H > 0$) or exothermic ($\Delta H < 0$) even if we do not know ΔH_f° for all the species involved.

Our strategy for estimating reaction enthalpies is a straightforward application of Hess's law. ∞ (Section 5.6) We use the fact that breaking bonds is always endothermic and forming bonds is always exothermic. We therefore imagine that the reaction occurs in two steps:

1. We supply enough energy to break those bonds in the reactants that are not present in the products. The enthalpy of the system is increased by the sum of the bond enthalpies of the bonds that are broken.
2. We form the bonds in the products that were not present in the reactants. This step releases energy and therefore lowers the enthalpy of the system by the sum of the bond enthalpies of the bonds that are formed.

The enthalpy of the reaction, ΔH_{rxn}, is estimated as the sum of the bond enthalpies of the bonds broken minus the sum of the bond enthalpies of the bonds formed:

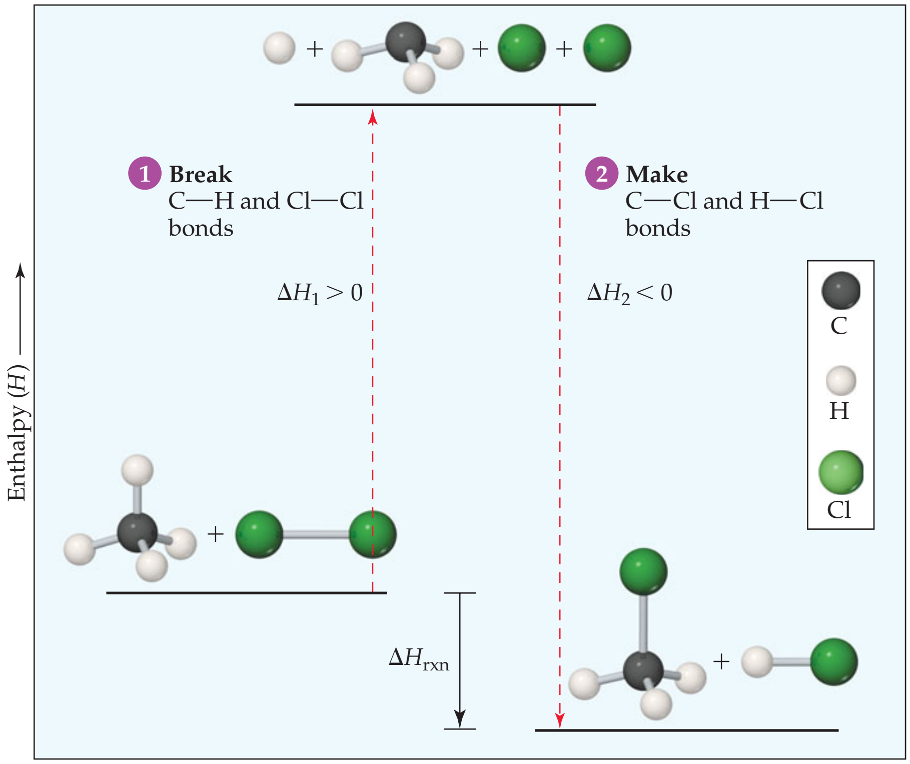
$$\Delta H_{\text{rxn}} = \sum(\text{bond enthalpies of bonds broken}) - \sum(\text{bond enthalpies of bonds formed}) \qquad [8.12]$$

Consider, for example, the gas-phase reaction between methane, CH_4, and chlorine to produce methyl chloride, CH_3Cl, and hydrogen chloride, HCl:

$$\mathrm{H{-}CH_3}(g) + \mathrm{Cl{-}Cl}(g) \longrightarrow \mathrm{Cl{-}CH_3}(g) + \mathrm{H{-}Cl}(g) \qquad \Delta H_{\text{rxn}} = ? \qquad [8.13]$$

GO FIGURE:

Is this reaction exothermic or endothermic?



◀ **FIGURE 8.15 Using bond enthalpies to calculate ΔH_{rxn}.** Average bond enthalpies are used to estimate ΔH_{rxn} for the reaction in Equation 8.13.

Our two-step procedure is outlined in ▲ **FIGURE 8.15**. We note that the following bonds are broken and made:

Bonds broken: 1 mol C—H, 1 mol Cl—Cl

Bonds made: 1 mol C—Cl, 1 mol H—Cl

We first supply enough energy to break the C—H and Cl—Cl bonds, which raises the enthalpy of the system (indicated as $\Delta H_1 > 0$ in Figure 8.15). We then form the C—Cl and H—Cl bonds, which release energy and lower the enthalpy of the system ($\Delta H_2 < 0$). We then use Equation 8.12 and data from Table 8.4 to estimate the enthalpy of the reaction:

$$\begin{aligned}\Delta H_{rxn} &= [D(\text{C—H}) + D(\text{Cl—Cl})] - [D(\text{Cl—Cl}) + D(\text{H—Cl})] \\ &= (413 \text{ kJ} + 242 \text{ kJ}) - (328 \text{ kJ} + 431 \text{ kJ}) = -104 \text{ kJ}\end{aligned}$$

The reaction is exothermic because the bonds in the products (especially the H—Cl bond) are stronger than the bonds in the reactants (especially the Cl—Cl bond).

We usually use bond enthalpies to estimate ΔH_{rxn} only if we do not have the needed ΔH_f° values readily available. For the preceding reaction, we cannot calculate ΔH_{rxn} from ΔH_f° values and Hess's law because ΔH_f° for $CH_3Cl(g)$ is not given in Appendix C. If we obtain the value of ΔH_f° for $CH_3Cl(g)$ from another source and use Equation 5.31,

$$\Delta H^\circ_{rxn} = \Sigma n \Delta H_f^\circ(\text{products}) - \Sigma m \Delta H_f^\circ(\text{reactants})$$

we find that $\Delta H_{rxn} = -99.8$ kJ for the reaction in Equation 8.13. Thus, the use of average bond enthalpies provides a reasonably accurate estimate of the actual reaction enthalpy change.

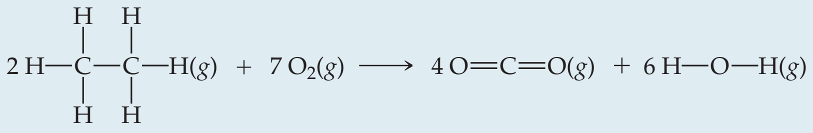
It is important to remember that bond enthalpies are derived for *gaseous* molecules and that they are often *averaged* values. Nonetheless, average bond enthalpies are useful for estimating reaction enthalpies quickly, especially for gas-phase reactions.

TABLE 8.5 • Average Bond Lengths for Some Single, Double, and Triple Bonds

Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C=C	1.34	N=N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C=N	1.38	N=O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O=O	1.21
C=O	1.23		
C≡O	1.13		

SAMPLE EXERCISE 8.12 Using Average Bond Enthalpies

Using data from Table 8.4, estimate ΔH for the reaction


$$2\,H_3C{-}CH_3(g) + 7\,O_2(g) \longrightarrow 4\,O{=}C{=}O(g) + 6\,H{-}O{-}H(g)$$

SOLUTION

Analyze We are asked to estimate the enthalpy change for a chemical reaction by using average bond enthalpies for the bonds broken and formed.

Plan In the reactants, we must break twelve C—H bonds and two C—C bonds in the two molecules of C_2H_6 and seven O_2 bonds in the seven O_2 molecules. In the products, we form eight C=O bonds (two in each CO_2) and twelve O—H bonds (two in each H_2O).

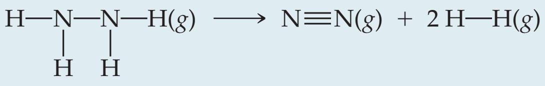
Solve Using Equation 8.12 and data from Table 8.4, we have

$$\begin{aligned}\Delta H &= [12D(\text{C—H}) + 2D(\text{C—C}) + 7D(\text{O}_2)] - [8D(\text{C=O}) + 12D(\text{O—H})]\\ &= [12(413\text{ kJ}) + 2(348\text{ kJ}) + 7(495\text{ kJ})] - [8(799\text{ kJ}) + 12(463\text{ kJ})]\\ &= 9117\text{ kJ} - 11948\text{ kJ}\\ &= -2831\text{ kJ}\end{aligned}$$

Check This estimate can be compared with the value of −2856 kJ calculated from more accurate thermochemical data; the agreement is good.

PRACTICE EXERCISE

Using Table 8.4, estimate ΔH for the reaction


$$H_2N{-}NH_2(g) \longrightarrow N{\equiv}N(g) + 2\,H{-}H(g)$$

Answer: −86 kJ

Bond Enthalpy and Bond Length

Just as we can define an average bond enthalpy, we can also define an average bond length for a number of common bonds (▲ TABLE 8.5). Of particular interest is the relationship, in any atom pair, among bond enthalpy, bond length, and number of bonds between the atoms. For example, we can use data in Tables 8.4 and 8.5 to compare the bond lengths and bond enthalpies of carbon–carbon single, double, and triple bonds:

C—C	C=C	C≡C
1.54 Å	1.34 Å	1.20 Å
348 kJ/mol	614 kJ/mol	839 kJ/mol

CHEMISTRY PUT TO WORK

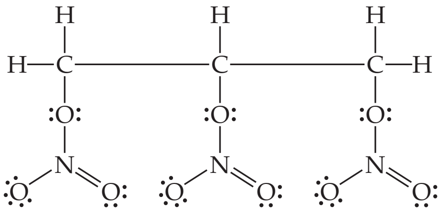
Explosives and Alfred Nobel

Enormous amounts of energy can be stored in chemical bonds. Perhaps the most graphic illustration of this fact is seen in certain molecular substances used as explosives. Our discussion of bond enthalpies allows us to examine more closely some of the properties of such explosive substances.

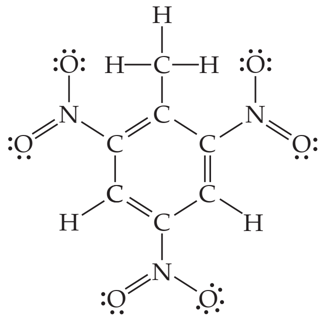
A useful explosive substance must (1) decompose very exothermically, (2) have gaseous products so that a tremendous gas pressure accompanies the decomposition, (3) decompose very rapidly, and (4) be stable enough so that it can be detonated predictably. The combination of the first three effects leads to the violent evolution of heat and gases.

To give the most exothermic reaction, an explosive should have weak chemical bonds and should decompose into molecules that have very strong bonds. Table 8.4 tells us that $N{\equiv}N$, $C{\equiv}O$, and $C{=}O$ bonds are among the strongest. Not surprisingly, explosives are usually designed to produce the gaseous products $N_2(g)$, $CO(g)$, and $CO_2(g)$. Water vapor is nearly always produced as well.

Many common explosives are organic molecules that contain nitro (NO_2) or nitrate (NO_3) groups attached to a carbon skeleton. The Lewis structures of two of the most familiar explosives, nitroglycerin and trinitrotoluene (TNT), are shown here (resonance structures are not shown for clarity). TNT contains the six-membered ring characteristic of benzene.



Nitroglycerin



Trinitrotoluene (TNT)

Nitroglycerin is a pale yellow, oily liquid. It is highly *shock-sensitive*: Merely shaking the liquid can cause its explosive decomposition into nitrogen, carbon dioxide, water, and oxygen gases:

$$4\,C_3H_5N_3O_9(l) \longrightarrow 6\,N_2(g) + 12\,CO_2(g) + 10\,H_2O(g) + O_2(g)$$

The large bond enthalpies of N_2 (941 kJ/mol), CO_2 (2×799 kJ/mol), and H_2O (2×463 kJ/mol) make this reaction enormously exothermic. Nitroglycerin is an exceptionally unstable explosive because it is in nearly perfect *explosive balance*: With the exception of a small amount of $O_2(g)$ produced, the only products are N_2, CO_2, and H_2O. Note also that, unlike combustion reactions (Section 3.2), explosions are entirely self-contained. No other reagent, such as $O_2(g)$, is needed for the explosive decomposition.

Because nitroglycerin is so unstable, it is difficult to use as a controllable explosive. The Swedish inventor Alfred Nobel (▼ **FIGURE 8.16**) found that mixing nitroglycerin with an absorbent solid material such as diatomaceous earth or cellulose gives a solid explosive (*dynamite*) that is much safer than liquid nitroglycerin.

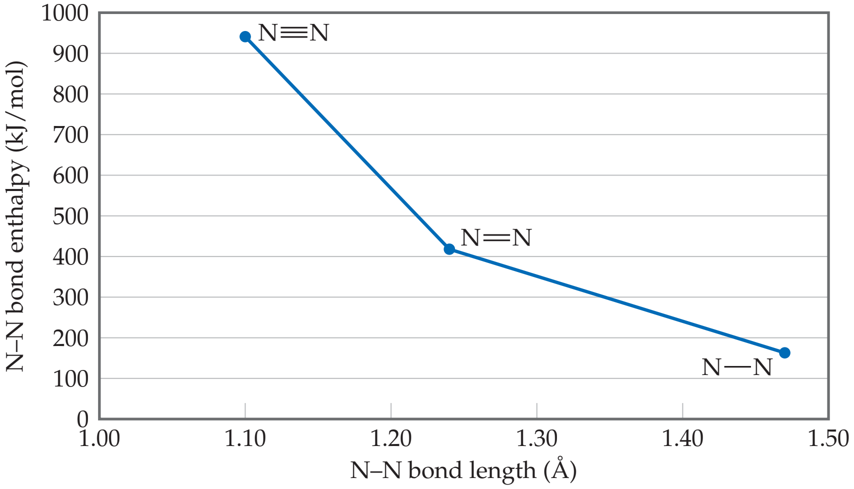
RELATED EXERCISES: 8.98 and 8.99

▲ **FIGURE 8.16 Alfred Nobel (1833–1896), Swedish inventor of dynamite.** By many accounts Nobel's discovery that nitroglycerin could be made more stable by absorbing it onto cellulose was an accident. This discovery made Nobel a wealthy man. He was also a complex and lonely man, however, who never married, was frequently ill, and suffered from chronic depression. He had invented the most powerful military explosive to date, but he strongly supported international peace movements. His will stated that his fortune be used to establish prizes awarding those who "have conferred the greatest benefit on mankind," including the promotion of peace and "fraternity between nations." The Nobel Prize is probably the most coveted award that a scientist, writer, or peace advocate can receive.

As the number of bonds between the carbon atoms increases, the bond length decreases and the bond enthalpy increases. That is, the carbon atoms are held more closely and more tightly together. In general, *as the number of bonds between two atoms increases, the bond grows shorter and stronger*. This trend is illustrated in ► **FIGURE 8.17** for N—N single, double, and triple bonds.

GO FIGURE

The line segments in the graph both have negative slopes. Why does this make sense?



▶ **FIGURE 8.17** **Bond strength versus bond length for N—N bonds.**

SAMPLE INTEGRATIVE EXERCISE Putting Concepts Together

Phosgene, a substance used in poisonous gas warfare during World War I, is so named because it was first prepared by the action of sunlight on a mixture of carbon monoxide and chlorine gases. Its name comes from the Greek words *phos* (light) and *genes* (born of). Phosgene has the following elemental composition:12.14% C, 16.17% O, and 71.69% Cl by mass. Its molar mass is 98.9 g/mol. **(a)** Determine the molecular formula of this compound. **(b)** Draw three Lewis structures for the molecule that satisfy the octet rule for each atom. (The Cl and O atoms bond to C.) **(c)** Using formal charges, determine which Lewis structure is the dominant one. **(d)** Using average bond enthalpies, estimate ΔH for the formation of gaseous phosgene from $CO(g)$ and $Cl_2(g)$.

SOLUTION

(a) The empirical formula of phosgene can be determined from its elemental composition. ∞ (Section 3.5) Assuming 100 g of the compound and calculating the number of moles of C, O, and Cl in this sample, we have

$$(12.14 \text{ g C})\left(\frac{1 \text{ mol C}}{12.01 \text{ g C}}\right) = 1.011 \text{ mol C}$$

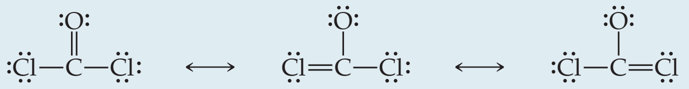
$$(16.17 \text{ g O})\left(\frac{1 \text{ mol O}}{16.00 \text{ g O}}\right) = 1.011 \text{ mol O}$$

$$(71.69 \text{ g Cl})\left(\frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}}\right) = 2.022 \text{ mol Cl}$$

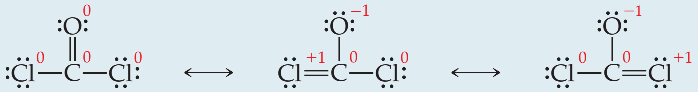
The ratio of the number of moles of each element, obtained by dividing each number of moles by the smallest quantity, indicates that there is one C and one O for each two Cl in the empirical formula, $COCl_2$.

The molar mass of the empirical formula is $12.01 + 16.00 + 2(35.45) = 98.91$ g/mol, the same as the molar mass of the molecule. Thus, $COCl_2$ is the molecular formula.

(b) Carbon has four valence electrons, oxygen has six, and chlorine has seven, giving $4 + 6 + 2(7) = 24$ electrons for the Lewis structures. Drawing a Lewis structure with all single bonds does not give the central carbon atom an octet. Using multiple bonds, three structures satisfy the octet rule:

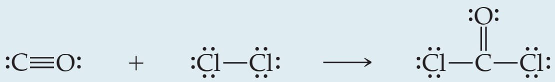


(c) Calculating the formal charges on each atom gives



The first structure is expected to be the dominant one because it has the lowest formal charges on each atom. Indeed, the molecule is usually represented by this single Lewis structure.

(d) Writing the chemical equation in terms of the Lewis structures of the molecules, we have



$$:C\equiv O: \; + \; :\ddot{Cl}-\ddot{Cl}: \; \longrightarrow \; :\ddot{Cl}-\overset{\overset{:O:}{\|}}{C}-\ddot{Cl}:$$

Thus, the reaction involves breaking a C$\equiv$O bond and a Cl—Cl bond and forming a C$=$O bond and two C—Cl bonds. Using bond enthalpies from Table 8.4, we have

$$\Delta H = D(C\equiv O) + D(Cl-Cl) - [D(C=O) + 2D(C-Cl)]$$
$$= 1072 \text{ kJ} + 242 \text{ kJ} - [799 \text{ kJ} + 2(328 \text{ kJ})] = -141 \text{ kJ}$$

Notice that the reaction is exothermic. Nevertheless, energy is needed from sunlight or another source for the reaction to begin, as is the case for the combustion of $H_2(g)$ and $O_2(g)$ to form $H_2O(g)$ (Figure 5.14).

CHAPTER SUMMARY AND KEY TERMS

INTRODUCTION AND SECTION 8.1 In this chapter we have focused on the interactions that lead to the formation of **chemical bonds**. We classify these bonds into three broad groups: **ionic bonds**, which result from the electrostatic forces that exist between ions of opposite charge; **covalent bonds**, which result from the sharing of electrons by two atoms; and **metallic bonds**, which result from a delocalized sharing of electrons in metals. The formation of bonds involves interactions of the outermost electrons of atoms, their valence electrons. The valence electrons of an atom can be represented by electron-dot symbols, called **Lewis symbols**. The tendencies of atoms to gain, lose, or share their valence electrons often follow the **octet rule**, which can be viewed as an attempt by atoms to achieve a noble-gas electron configuration.

SECTION 8.2 Ionic bonding results from the transfer of electrons from one atom to another, leading to the formation of a three-dimensional lattice of charged particles. The stabilities of ionic substances result from the strong electrostatic attractions between an ion and the surrounding ions of opposite charge. The magnitude of these interactions is measured by the **lattice energy**, which is the energy needed to separate an ionic lattice into gaseous ions. Lattice energy increases with increasing charge on the ions and with decreasing distance between the ions. The **Born–Haber cycle** is a useful thermochemical cycle in which we use Hess's law to calculate the lattice energy as the sum of several steps in the formation of an ionic compound.

SECTION 8.3 A covalent bond results from the sharing of electrons. We can represent the electron distribution in molecules by means of **Lewis structures**, which indicate how many valence electrons are involved in forming bonds and how many remain as unshared electron pairs. The octet rule helps determine how many bonds will be formed between two atoms. The sharing of one pair of electrons produces a **single bond**; the sharing of two or three pairs of electrons between two atoms produces **double** or **triple bonds**, respectively. Double and triple bonds are examples of multiple bonding between atoms. The bond length decreases as the number of bonds between the atoms increases.

SECTION 8.4 In covalent bonds, the electrons may not necessarily be shared equally between two atoms. **Bond polarity** helps describe unequal sharing of electrons in a bond. In a **nonpolar covalent bond** the electrons in the bond are shared equally by the two atoms; in a **polar covalent bond** one of the atoms exerts a greater attraction for the electrons than the other.

Electronegativity is a numerical measure of the ability of an atom to compete with other atoms for the electrons shared between them. Fluorine is the most electronegative element, meaning it has the greatest ability to attract electrons from other atoms. Electronegativity values range from 0.7 for Cs to 4.0 for F. Electronegativity generally increases from left to right in a row of the periodic table and decreases going down a column. The difference in the electronegativities of bonded atoms can be used to determine the polarity of a bond. The greater the electronegativity difference, the more polar the bond.

A **polar molecule** is one whose centers of positive and negative charge do not coincide. Thus, a polar molecule has a positive side and a negative side. This separation of charge produces a **dipole,** the magnitude of which is given by the **dipole moment**, which is measured in debyes (D). Dipole moments increase with increasing amount of charge separated and increasing distance of separation. Any diatomic molecule X—Y in which X and Y have different electronegativities is a polar molecule.

Most bonding interactions lie between the extremes of covalent and ionic bonding. While it is generally true that the bonding between a metal and a nonmetal is predominantly ionic, exceptions to this guideline are not uncommon when the difference in electronegativity of the atoms is relatively small or when the oxidation state of the metal becomes large.

SECTIONS 8.5 AND 8.6 If we know which atoms are connected to one another, we can draw Lewis structures for molecules and ions by a simple procedure. Once we do so, we can determine the **formal charge** of each atom in a Lewis structure, which is the charge that the atom would have if all atoms had the same electronegativity. In general, the dominant Lewis structure will have low formal charges with any negative formal charges residing on more electronegative atoms.

Sometimes a single dominant Lewis structure is inadequate to represent a particular molecule (or ion). In such situations, we describe the molecule by using two or more **resonance structures** for the molecule. The molecule is envisioned as a blend of these multiple resonance structures. Resonance structures are important in describing the bonding in molecules such as ozone, O_3, and the organic molecule benzene, C_6H_6.

SECTION 8.7 The octet rule is not obeyed in all cases. Exceptions occur when (a) a molecule has an odd number of electrons, (b) it is not possible to complete an octet around an atom without forcing an unfavorable distribution of electrons, or (c) a large atom is surrounded by a sufficiently large number of small electronegative atoms that it has more than an octet of electrons around it. Lewis structures with more than an octet of electrons are observed for atoms in the third row and beyond in the periodic table.

SECTION 8.8 The strength of a covalent bond is measured by its **bond enthalpy**, which is the molar enthalpy change upon breaking a particular bond. Average bond enthalpies can be determined for a wide variety of covalent bonds. The strengths of covalent bonds increase with the number of electron pairs shared between two atoms. We can use bond enthalpies to estimate the enthalpy change during chemical reactions in which bonds are broken and new bonds formed. The average bond length between two atoms decreases as the number of bonds between the atoms increases, consistent with the bond being stronger as the number of bonds increases.

KEY SKILLS

- Write Lewis symbols for atoms and ions. (Section 8.1)
- Understand lattice energy and be able to arrange compounds in order of increasing lattice energy based on the charges and sizes of the ions involved. (Section 8.2)
- Use atomic electron configurations and the octet rule to write Lewis structures for molecules to determine their electron distribution. (Section 8.3)
- Use electronegativity differences to identify nonpolar covalent, polar covalent, and ionic bonds. (Section 8.4)
- Calculate charge separation in diatomic molecules based on the experimentally measured dipole moment and bond distance. (Section 8.4)
- Calculate formal charges from Lewis structures and use those formal charges to identify the dominant Lewis structure for a molecule or ion. (Section 8.5)
- Recognize molecules where resonance structures are needed to describe the bonding. (Section 8.6)
- Recognize exceptions to the octet rule and draw accurate Lewis structures even when the octet rule is not obeyed. (Section 8.7)
- Understand the relationship between bond type (single, double, and triple), bond strength (or enthalpy), and bond length. (Section 8.8)
- Use bond enthalpies to estimate enthalpy changes for reactions involving gas-phase reactants and products. (Section 8.8)

KEY EQUATIONS

• $E_{el} = \dfrac{\kappa Q_1 Q_2}{d}$	[8.4]	The potential energy of two interacting charges
• $\mu = Qr$	[8.11]	The dipole moment of two charges of equal magnitude but opposite sign, separated by a distance *r*
• $\Delta H_{rxn} = \sum(\text{bond enthalpies of bonds broken}) - \sum(\text{bond enthalpies of bonds formed})$	[8.12]	The enthalpy change as a function of bond enthalpies for reactions involving gas-phase molecules

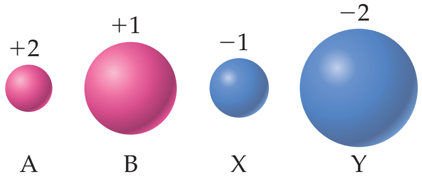
EXERCISES

VISUALIZING CONCEPTS

8.1 For each of these Lewis symbols, indicate the group in the periodic table in which the element X belongs: [Section 8.1]

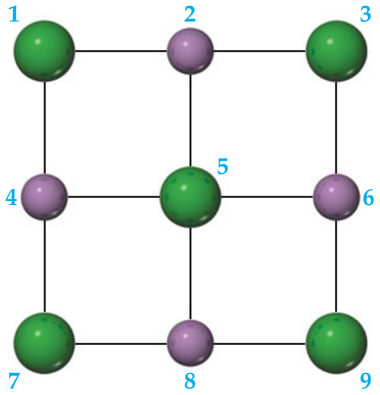
(a) $\cdot\underset{\cdot}{\dot{X}}\cdot$ **(b)** $\cdot X\cdot$ **(c)** $:\underset{\cdot}{\dot{X}}\cdot$

8.2 Illustrated are four ions—A, B, X, and Y— showing their relative ionic radii. The ions shown in red carry positive charges: a

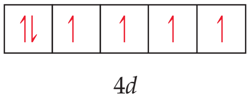


2+ charge for A and a 1+ charge for B. Ions shown in blue carry negative charges: a 1− charge for X and a 2− charge for Y. **(a)** Which combinations of these ions produce ionic compounds where there is a 1∶1 ratio of cations and anions? **(b)** Among the combinations in part (a), which leads to the ionic compound having the largest lattice energy? **(c)** Which combination of ions leads to the ionic compound having the smallest lattice energy? [Section 8.2]

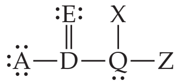
8.3 A portion of a two-dimensional "slab" of NaCl(*s*) is shown here (see Figure 8.3) in which the ions are numbered. **(a)** Of the following types of interactions (identified by color), which are attractive and which are repulsive: "purple-purple," "purple-green," "green-green"? Explain. **(b)** Consider the "green-green" interactions between ions 1 and 3, ions 1 and 5, and ions 3 and 5. Which one or more of these three will result in the interaction of largest magnitude? Which one or more will result in the interaction of the smallest magnitude? **(c)** Consider the "green-green" interactions between ions 1 and 5 and the "green-purple" interactions between ions 1 and 2. Which of these will have the greater magnitude? **(d)** Does your answer to part (c) help explain why NaCl is a stable ionic solid? [Section 8.2]



8.4 The orbital diagram that follows shows the valence electrons for a 2+ ion of an element. **(a)** What is the element? **(b)** What is the electron configuration of an atom of this element? [Section 8.2]



8.5 In the Lewis structure shown here, A, D, E, Q, X, and Z represent elements in the first two rows of the periodic table (H—Ne). Identify all six elements so that the formal charges of all atoms are zero. [Section 8.3]



$$:\ddot{\mathrm{A}}-\overset{\overset{:\mathrm{E}:}{\|}}{\mathrm{D}}-\overset{\overset{\mathrm{X}}{|}}{\underset{..}{\mathrm{Q}}}-\mathrm{Z}$$

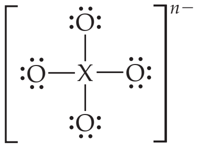
8.6 Incomplete Lewis structures for the nitrous acid molecule, HNO_2, and the nitrite ion, NO_2^-, are shown below. **(a)** Complete each Lewis structure by adding electron pairs as needed. **(b)** Is the formal charge on N the same or different in these two species? **(c)** Would either HNO_2 or NO_2^- be expected to exhibit resonance? **(d)** Would you expect the N═O bond in HNO_2 to be longer, shorter, or the same length as the N—O bonds in NO_2^-? Explain. [Sections 8.5 and 8.6]

H—O—N═O   O—N═O

8.7 The partial Lewis structure that follows is for a hydrocarbon molecule. In the full Lewis structure, each carbon atom satisfies the octet rule, and there are no unshared electron pairs in the molecule. The carbon–carbon bonds are labeled 1, 2, and 3. **(a)** Determine where the hydrogen atoms are in the molecule. **(b)** Rank the carbon–carbon bonds in order of increasing bond length. **(c)** Rank the carbon–carbon bonds in order of increasing bond enthalpy. [Sections 8.3 and 8.8]

$$\mathrm{C}\overset{1}{=}\mathrm{C}\overset{2}{-}\mathrm{C}\overset{3}{\equiv}\mathrm{C}$$

8.8 Consider the Lewis structure for the polyatomic oxyanion shown here, where X is an element from the third period (Na—Ar). By changing the overall charge, *n*, from 1− to 2− to 3− we get three different polyatomic ions. For each of these ions **(a)** identify the central atom, X; **(b)** determine the formal charge of the central atom, X; **(c)** draw a Lewis structure that makes the formal charge on the central atom equal to zero. [Sections 8.5, 8.6, and 8.7]



$$\left[\begin{array}{c} :\ddot{\mathrm{O}}: \\ | \\ :\ddot{\mathrm{O}}-\mathrm{X}-\ddot{\mathrm{O}}: \\ | \\ :\underset{..}{\mathrm{O}}: \end{array}\right]^{n-}$$

LEWIS SYMBOLS (section 8.1)

8.9 **(a)** What are valence electrons? **(b)** How many valence electrons does a nitrogen atom possess? **(c)** An atom has the electron configuration $1s^22s^22p^63s^23p^2$. How many valence electrons does the atom have?

8.10 **(a)** What is the octet rule? **(b)** How many electrons must a sulfur atom gain to achieve an octet in its valence shell? **(c)** If an atom has the electron configuration $1s^22s^22p^3$, how many electrons must it gain to achieve an octet?

8.11 Write the electron configuration for silicon. Identify the valence electrons in this configuration and the nonvalence electrons. From the standpoint of chemical reactivity, what is the important difference between them?

8.12 **(a)** Write the electron configuration for the element titanium, Ti. How many valence electrons does this atom possess? **(b)** Hafnium, Hf, is also found in group 4B. Write the electron configuration for Hf. **(c)** Ti and Hf behave as though they possess the same number of valence electrons. Which of the subshells in the electron configuration of Hf behave as valence orbitals? Which behave as core orbitals?

8.13 Write the Lewis symbol for atoms of each of the following elements: **(a)** Al, **(b)** Br, **(c)** Ar, **(d)** Sr.

8.14 What is the Lewis symbol for each of the following atoms or ions: **(a)** K, **(b)** As, **(c)** Sn^{2+}, **(d)** N^{3-}?

IONIC BONDING (section 8.2)

8.15 Using Lewis symbols, diagram the reaction between magnesium and oxygen atoms to give the ionic substance MgO.

8.16 Use Lewis symbols to represent the reaction that occurs between Ca and F atoms.

8.17 Predict the chemical formula of the ionic compound formed between the following pairs of elements: **(a)** Al and F, **(b)** K and S, **(c)** Y and O, **(d)** Mg and N.

8.18 Which ionic compound is expected to form from combining the following pairs of elements: **(a)** barium and fluorine, **(b)** cesium and chlorine, **(c)** lithium and nitrogen, **(d)** aluminum and oxygen?

8.19 Write the electron configuration for each of the following ions, and determine which ones possess noble-gas configurations: **(a)** Sr^{2+}, **(b)** Ti^{2+}, **(c)** Se^{2-}, **(d)** Ni^{2+}, **(e)** Br^{-}, **(f)** Mn^{3+}.

8.20 Write electron configurations for the following ions, and determine which have noble-gas configurations: **(a)** Cd^{2+}, **(b)** P^{3-}, **(c)** Zr^{4+}, **(d)** Ru^{3+}, **(e)** As^{3-}, **(f)** Ag^{+}.

8.21 **(a)** Define the term *lattice energy*. **(b)** Which factors govern the magnitude of the lattice energy of an ionic compound?

8.22 NaCl and KF have the same crystal structure. The only difference between the two is the distance that separates cations and anions. **(a)** The lattice energies of NaCl and KF are given in Table 8.2. Based on the lattice energies, would you expect the Na—Cl or the K—F distance to be longer? **(b)** Use the ionic radii given in Figure 7.7 to estimate the Na—Cl and K—F distances. Does this estimate agree with the prediction you made based on the lattice energies?

8.23 The ionic substances KF, CaO, and ScN are isoelectronic (they have the same number of electrons). Examine the lattice energies for these substances in Table 8.2, and account for the trends you observe.

8.24 **(a)** Does the lattice energy of an ionic solid increase or decrease (i) as the charges of the ions increase, (ii) as the sizes of the ions increase? **(b)** Arrange the following substances not listed in Table 8.2 according to their expected lattice energies, listing them from lowest lattice energy to the highest: MgS, KI, GaN, LiBr.

8.25 The lattice energies of KBr and CsCl are nearly equal (Table 8.2). What can you conclude from this observation?

8.26 Explain the following trends in lattice energy:
(a) $NaCl > RbBr > CsBr$; **(b)** $BaO > KF$; **(c)** $SrO > SrCl_2$.

8.27 Energy is required to remove two electrons from Ca to form Ca^{2+} and is required to add two electrons to O to form O^{2-}. Why, then, is CaO stable relative to the free elements?

8.28 List the individual steps used in constructing a Born–Haber cycle for the formation of BaI_2 from the elements. Which of the steps would you expect to be exothermic?

8.29 Use data from Appendix C, Figure 7.9, and Figure 7.11 to calculate the lattice energy of RbCl. Is this value greater than or less than the lattice energy of NaCl? Explain.

8.30 **(a)** Based on the lattice energies of $MgCl_2$ and $SrCl_2$ given in Table 8.2, what is the range of values that you would expect for the lattice energy of $CaCl_2$? **(b)** Using data from Appendix C, Figure 7.9, and Figure 7.11 and the value of the second ionization energy for Ca, 1145 kJ/mol, calculate the lattice energy of $CaCl_2$.

COVALENT BONDING, ELECTRONEGATIVITY, AND BOND POLARITY (sections 8.3 and 8.4)

8.31 **(a)** What is meant by the term *covalent bond*? **(b)** Give three examples of covalent bonding. **(c)** A substance XY, formed from two different elements, boils at −33 °C. Is XY likely to be a covalent or an ionic substance? Explain.

8.32 Which of these elements are unlikely to form covalent bonds: S, H, K, Ar, Si? Explain your choices.

8.33 Using Lewis symbols and Lewis structures, diagram the formation of $SiCl_4$ from Si and Cl atoms.

8.34 Use Lewis symbols and Lewis structures to diagram the formation of PF_3 from P and F atoms.

8.35 **(a)** Construct a Lewis structure for O_2 in which each atom achieves an octet of electrons. **(b)** Explain why it is necessary to form a double bond in the Lewis structure. **(c)** The bond in O_2 is shorter than the O—O bond in compounds that contain an O—O single bond. Explain this observation.

8.36 **(a)** Construct a Lewis structure for hydrogen peroxide, H_2O_2, in which each atom achieves an octet of electrons. **(b)** Do you expect the O—O bond in H_2O_2 to be longer or shorter than the O—O bond in O_2?

8.37 **(a)** What is meant by the term *electronegativity*? **(b)** On the Pauling scale what is the range of electronegativity values for the elements? **(c)** Which element has the greatest electronegativity? **(d)** Which element has the smallest electronegativity?

8.38 **(a)** What is the trend in electronegativity going from left to right in a row of the periodic table? **(b)** How do electronegativity values generally vary going down a column in the periodic table? **(c)** How do periodic trends in electronegativity relate to those for ionization energy and electron affinity?

8.39 Using only the periodic table as your guide, select the most electronegative atom in each of the following sets: **(a)** Na, Mg, K, Ca; **(b)** P, S, As, Se; **(c)** Be, B, C, Si; **(d)** Zn, Ge, Ga, As.

8.40 By referring only to the periodic table, select **(a)** the most electronegative element in group 6A; **(b)** the least electronegative element in the group Al, Si, P; **(c)** the most electronegative element in the group Ga, P, Cl, Na; **(d)** the element in the group K, C, Zn, F that is most likely to form an ionic compound with Ba.

8.41 Which of the following bonds are polar: **(a)** B—F, **(b)** Cl—Cl, **(c)** Se—O, **(d)** H—I ? Which is the more electronegative atom in each polar bond?

8.42 Arrange the bonds in each of the following sets in order of increasing polarity: **(a)** C—F, O—F, Be—F; **(b)** O—Cl, S—Br, C—P; **(c)** C—S, B—F, N—O.

8.43 **(a)** From the data in Table 8.3, calculate the effective charges on the H and Br atoms of the HBr molecule in units of the electronic charge, *e*. **(b)** Compare your answers to part

(a) with those in Sample Exercise 8.5 for the HCl molecule. Can you explain why the values are different?

8.44 The iodine monobromide molecule, IBr, has a bond length of 2.49 Å and a dipole moment of 1.21 D. **(a)** Which atom of the molecule is expected to have a negative charge? Explain. **(b)** Calculate the effective charges on the I and Br atoms in IBr, in units of the electronic charge, *e*.

8.45 In the following pairs of binary compounds determine which one is a molecular substance and which one is an ionic substance. Use the appropriate naming convention (for ionic or molecular substances) to assign a name to each compound: **(a)** SiF_4 and LaF_3, **(b)** $FeCl_2$ and $ReCl_6$, **(c)** $PbCl_4$ and RbCl.

8.46 In the following pairs of binary compounds determine which one is a molecular substance and which one is an ionic substance. Use the appropriate naming convention (for ionic or molecular substances) to assign a name to each compound: **(a)** $TiCl_4$ and CaF_2, **(b)** ClF_3 and VF_3, **(c)** $SbCl_5$ and AlF_3.

LEWIS STRUCTURES; RESONANCE STRUCTURES (sections 8.5 and 8.6)

8.47 Draw Lewis structures for the following: **(a)** SiH_4, **(b)** CO, **(c)** SF_2, **(d)** H_2SO_4 (H is bonded to O), **(e)** ClO_2^-, **(f)** NH_2OH.

8.48 Write Lewis structures for the following: **(a)** H_2CO (both H atoms are bonded to C), **(b)** H_2O_2, **(c)** C_2F_6 (contains a C—C bond), **(d)** AsO_3^{3-}, **(e)** H_2SO_3 (H is bonded to O), **(f)** C_2H_2.

8.49 **(a)** When talking about atoms in a Lewis structure, what is meant by the term *formal charge*? **(b)** Does the formal charge of an atom represent the actual charge on that atom? Explain. **(c)** How does the formal charge of an atom in a Lewis structure differ from the oxidation number of the atom?

8.50 **(a)** Write a Lewis structure for the phosphorus trifluoride molecule, PF_3. Is the octet rule satisfied for all the atoms in your structure? **(b)** Determine the oxidation numbers of the P and F atoms. **(c)** Determine the formal charges of the P and F atoms. **(d)** Is the oxidation number for the P atom the same as its formal charge? Explain.

8.51 Write Lewis structures that obey the octet rule for each of the following, and assign oxidation numbers and formal charges to each atom: **(a)** OCS, **(b)** $SOCl_2$ (S is bonded to the two Cl atoms and to the O), **(c)** BrO_3^-, **(d)** $HClO_2$ (H is bonded to O).

8.52 For each of the following molecules or ions of sulfur and oxygen, write a single Lewis structure that obeys the octet rule, and calculate the oxidation numbers and formal charges on all the atoms: **(a)** SO_2, **(b)** SO_3, **(c)** SO_3^{2-}. **(d)** Arrange these molecules/ions in order of increasing S—O bond distance.

8.53 **(a)** Write one or more appropriate Lewis structures for the nitrite ion, NO_2^-. **(b)** With what allotrope of oxygen is it isoelectronic? **(c)** What would you predict for the lengths of the bonds in NO_2^- relative to N—O single bonds and double bonds?

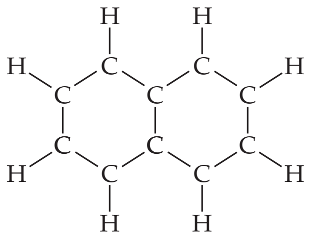
8.54 Consider the formate ion, HCO_2^-, which is the anion formed when formic acid loses an H^+ ion. The H and the two O atoms are bonded to the central C atom. **(a)** Write one or more appropriate Lewis structures for this ion. **(b)** Are resonance structures needed to describe the structure? **(c)** What would you predict for the C—O bond lengths in the formate ion relative to those in CO_2?

8.55 Predict the ordering of the C—O bond lengths in CO, CO_2, and CO_3^{2-}.

8.56 Based on Lewis structures, predict the ordering of N—O bond lengths in NO^+, NO_2^-, and NO_3^-.

8.57 **(a)** Use the concept of resonance to explain why all six C—C bonds in benzene are equal in length. **(b)** Are the C—C bond lengths in benzene shorter than C—C single bonds? Are they shorter than C=C double bonds?

8.58 Mothballs are composed of naphthalene, $C_{10}H_8$, a molecule of which consists of two six-membered rings of carbon fused along an edge, as shown in this incomplete Lewis structure:



(a) Write two complete Lewis structures for naphthalene. **(b)** The observed C—C bond lengths in the molecule are intermediate between C—C single and C=C double bonds. Explain. **(c)** Represent the resonance in naphthalene in a way analogous to that used to represent it in benzene.

EXCEPTIONS TO THE OCTET RULE (section 8.7)

8.59 **(a)** State the octet rule. **(b)** Does the octet rule apply to ionic as well as to covalent compounds? Explain using examples as appropriate.

8.60 Considering the nonmetals, what is the relationship between the group number for an element (carbon, for example, belongs to group 4A; see the periodic table on the inside front cover) and the number of single covalent bonds that element needs to form to conform to the octet rule?

8.61 The chlorine oxides, in which a chlorine atom is bonded to one or more oxygen atoms, are important molecules in the chemistry of the atmosphere. Will any of the chlorine oxides obey the octet rule? Why or why not?

8.62 For elements in the third row of the periodic table and beyond, the octet rule is often not obeyed. What factors are usually cited to explain this fact?

8.63 Draw the Lewis structures for each of the following ions or molecules. Identify those that do not obey the octet rule, and explain why they do not: **(a)** SO_3^{2-}, **(b)** AlH_3, **(c)** N_3^-, **(d)** CH_2Cl_2, **(e)** SbF_5.

8.64 Draw the Lewis structures for each of the following molecules or ions. Which do not obey the octet rule? **(a)** NO, **(b)** BF_3, **(c)** ICl_2^-, **(d)** $OPBr_3$ (the P is the central atom), **(e)** XeF_4.

8.65 In the vapor phase, $BeCl_2$ exists as a discrete molecule. **(a)** Draw the Lewis structure of this molecule, using only single bonds. Does this Lewis structure satisfy the octet rule? **(b)** What other resonance structures are possible that satisfy the octet rule? **(c)** On the basis of the formal charges, which Lewis structure is expected to be dominant for $BeCl_2$?

8.66 **(a)** Describe the molecule xenon trioxide, XeO_3, using four possible Lewis structures, one each with zero, one, two, or three Xe—O double bonds. **(b)** Do any of these resonance structures satisfy the octet rule for every atom in the molecule? **(c)** Do any of the four Lewis structures have multiple resonance structures? If so, how many resonance structures do you find? **(d)** Which of the Lewis structures in (a) yields the most favorable formal charges for the molecule?

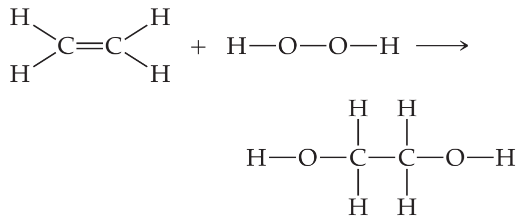
8.67 Consider the following statement: "For some molecules and ions, a Lewis structure that satisfies the octet rule does not lead to the lowest formal charges, and a Lewis structure that leads to the lowest formal charges does not satisfy the octet rule." Illustrate this statement using the hydrogen sulfite ion, HSO_3^-, as an example (the H atom is bonded to one of the O atoms).

8.68 Some chemists believe that satisfaction of the octet rule should be the top criterion for choosing the dominant Lewis structure of a molecule or ion. Other chemists believe that achieving the best formal charges should be the top criterion. Consider the dihydrogen phosphate ion, $H_2PO_4^-$, in which the H atoms are bonded to O atoms. **(a)** What would be the predicted dominant Lewis structure if satisfying the octet rule is the top criterion? **(b)** What would it be if achieving the best formal charges is the top criterion? **(c)** Is there another Lewis structure you can draw that satisfies neither of these criteria?

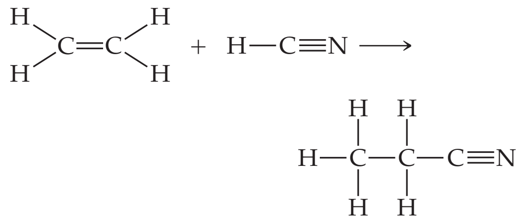
BOND ENTHALPIES (section 8.8)

8.69 Using Table 8.4, estimate ΔH for each of the following gas-phase reactions:

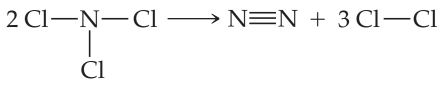
(a)



(b)



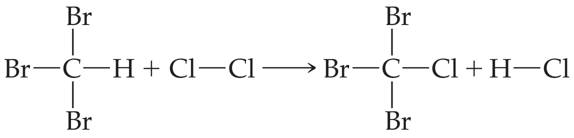
(c)



$$2\,\mathrm{Cl{-}\underset{\underset{Cl}{|}}{N}{-}Cl \longrightarrow N{\equiv}N + 3\,Cl{-}Cl}$$

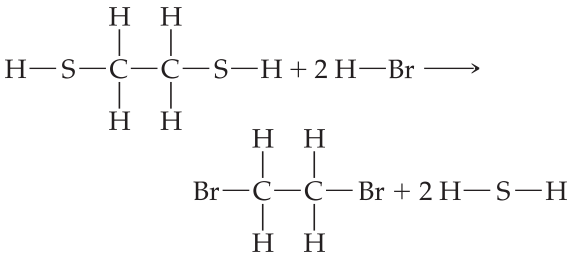
8.70 Using Table 8.4, estimate ΔH for the following gas-phase reactions:

(a)



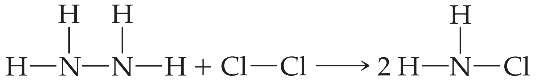
$$\mathrm{Br{-}\underset{Br}{\overset{Br}{C}}{-}H + Cl{-}Cl \longrightarrow Br{-}\underset{Br}{\overset{Br}{C}}{-}Cl + H{-}Cl}$$

(b)



$$\mathrm{H{-}S{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}S{-}H + 2\,H{-}Br \longrightarrow Br{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}Br + 2\,H{-}S{-}H}$$

(c)



$$\mathrm{H{-}\overset{H}{N}{-}\overset{H}{N}{-}H + Cl{-}Cl \longrightarrow 2\,H{-}\overset{H}{N}{-}Cl}$$

8.71 Using Table 8.4, estimate ΔH for each of the following reactions:

(a) $2\,CH_4(g) + O_2(g) \longrightarrow 2\,CH_3OH(g)$

(b) $H_2(g) + Br_2(g) \longrightarrow 2\,HBr(g)$

(c) $2\,H_2O_2(g) \longrightarrow 2\,H_2O(g) + O_2(g)$

8.72 Use Table 8.4 to estimate the enthalpy change for each of the following reactions:

(a) $H_2C{=}O(g) + HCl(g) \longrightarrow H_3C{-}O{-}Cl(g)$

(b) $H_2O_2(g) + 2\,CO(g) \longrightarrow H_2(g) + 2\,CO_2(g)$

(c) $3\,H_2C{=}CH_2(g) \longrightarrow C_6H_{12}(g)$ (the six carbon atoms form a six-membered ring with two H atoms on each C atom)

8.73 Ammonia is produced directly from nitrogen and hydrogen by using the Haber process. The chemical reaction is

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

(a) Use Table 8.4 to estimate the enthalpy change for the reaction. Is it exothermic or endothermic? **(b)** Compare the enthalpy change you calculate in (a) to the true enthalpy change as obtained using ΔH_f° values.

8.74 **(a)** Use bond enthalpies to estimate the enthalpy change for the reaction of hydrogen with ethylene:

$$H_2(g) + C_2H_4(g) \longrightarrow C_2H_6(g)$$

(b) Calculate the standard enthalpy change for this reaction, using heats of formation. Why does this value differ from that calculated in (a)?

8.75 Given the following bond-dissociation energies, calculate the average bond enthalpy for the Ti—Cl bond.

	ΔH(kJ/mol)
$TiCl_4(g) \longrightarrow TiCl_3(g) + Cl(g)$	335
$TiCl_3(g) \longrightarrow TiCl_2(g) + Cl(g)$	423
$TiCl_2(g) \longrightarrow TiCl(g) + Cl(g)$	444
$TiCl(g) \longrightarrow Ti(g) + Cl(g)$	519

[8.76] **(a)** Using average bond enthalpies, predict which of the following reactions will be most exothermic:

(i) $C(g) + 2\,F_2(g) \longrightarrow CF_4(g)$

(ii) $CO(g) + 3\,F_2 \longrightarrow CF_4(g) + OF_2(g)$

(iii) $CO_2(g) + 4\,F_2 \longrightarrow CF_4(g) + 2\,OF_2(g)$

(b) Explain the trend, if any, that exists between reaction exothermicity and the extent to which the carbon atom is bonded to oxygen.

ADDITIONAL EXERCISES

8.77 How many elements in the periodic table are represented by a Lewis symbol with a single dot? Are all these elements in the same group? Explain.

[8.78] From Equation 8.4 and the ionic radii given in Figure 7.7, calculate the potential energy of the following pairs of ions. Assume that the ions are separated by a distance equal to the sum of their ionic radii: **(a)** Na^+, Br^-; **(b)** Rb^+, Br^-; **(c)** Sr^{2+}, S^{2-}.

8.79 **(a)** Explain the following trend in lattice energy: BeH_2, 3205 kJ/mol; MgH_2, 2791 kJ/mol; CaH_2, 2410 kJ/mol; SrH_2, 2250 kJ/mol; BaH_2, 2121 kJ/mol. **(b)** The lattice energy of ZnH_2 is 2870 kJ/mol. Based on the data given in part (a), the radius of the Zn^{2+} ion is expected to be closest to that of which group 2A element?

8.80 Based on data in Table 8.2, estimate (within 30 kJ/mol) the lattice energy for **(a)** LiBr, **(b)** CsBr, **(c)** $CaCl_2$.

8.81 An ionic substance of formula MX has a lattice energy of 6×10^3 kJ/mol. Is the charge on the ion M likely to be $1+$, $2+$ or $3+$? Explain your reasoning.

[8.82] From the ionic radii given in Figure 7.7, calculate the potential energy of a Ca^{2+} and O^{2-} ion pair that is just touching (the magnitude of the electronic charge is given on the back inside cover). Calculate the energy of a mole of such pairs. How does this value compare with the lattice energy of CaO (Table 8.2)? Explain the difference.

8.83 Construct a Born–Haber cycle for the formation of the hypothetical compound $NaCl_2$, where the sodium ion has a $2+$ charge (the second ionization energy for sodium is given in Table 7.2). **(a)** How large would the lattice energy need to be for the formation of $NaCl_2$ to be exothermic? **(b)** If we were to estimate the lattice energy of $NaCl_2$ to be roughly equal to that of $MgCl_2$ (2326 kJ/mol from Table 8.2), what value would you obtain for the standard enthalpy of formation, ΔH_f°, of $NaCl_2$?

8.84 **(a)** How does a polar molecule differ from a nonpolar one? **(b)** Atoms X and Y have different electronegativities. Will the diatomic molecule X—Y necessarily be polar? Explain. **(c)** What factors affect the size of the dipole moment of a diatomic molecule?

8.85 For the following collection of nonmetallic elements, O, P, Te, I, B, **(a)** which two would form the most polar single bond? **(b)** Which two would form the longest single bond? **(c)** Which two would be likely to form a compound of formula XY_2? **(d)** Which combinations of elements would likely yield a compound of empirical formula X_2Y_3? In each case explain your answer.

8.86 The substance chlorine monoxide, ClO(*g*), is important in atmospheric processes that lead to depletion of the ozone layer. The ClO molecule has a dipole moment of 1.24 D and the Cl—O bond length is 1.60 Å. **(a)** Determine the magnitude of the charges on the Cl and O atoms in units of the electronic charge, *e*. **(b)** Based on the electronegativities of the elements, which atom would you expect to have a negative charge in the ClO molecule? **(c)** By using formal charges as a guide, propose the dominant Lewis structure for the molecule. Are the formal charges consistent with your answers to parts (a) and (b)? Can you reconcile any differences you find?

[8.87] Using the electronegativities of Br and Cl, estimate the partial charges on the atoms in the Br—Cl molecule. Using these partial charges and the atomic radii given in Figure 7.7, estimate the dipole moment of the molecule. The measured dipole moment is 0.57 D.

8.88 A major challenge in implementing the "hydrogen economy" is finding a safe, lightweight, and compact way of storing hydrogen for use as a fuel. The hydrides of light metals are attractive for hydrogen storage because they can store a high weight percentage of hydrogen in a small volume. For example, $NaAlH_4$ can release 5.6% of its mass as H_2 upon decomposing to NaH(*s*), Al(*s*), and $H_2(g)$. $NaAlH_4$ possesses both covalent bonds, which hold polyatomic anions together, and ionic bonds. **(a)** Write a balanced equation for the decomposition of $NaAlH_4$. **(b)** Which element in $NaAlH_4$ is the most electronegative? Which one is the least electronegative? **(c)** Based on electronegativity differences, what do you think is the identity of the polyatomic anion? Draw a Lewis structure for this ion.

8.89 Although I_3^- is known, F_3^- is not. Using Lewis structures, explain why F_3^- does not form.

8.90 Calculate the formal charge on the indicated atom in each of the following molecules or ions: **(a)** the central oxygen atom in O_3, **(b)** phosphorus in PF_6^-, **(c)** nitrogen in NO_2, **(d)** iodine in ICl_3, **(e)** chlorine in $HClO_4$ (hydrogen is bonded to O).

8.91 **(a)** Determine the formal charge on the chlorine atom in the hypochlorite ion, ClO^-, and the perchlorate ion, ClO_4^-, using resonance structures where the Cl atom has an octet. **(b)** What are the oxidation numbers of chlorine in ClO^- and in ClO_4^-? **(c)** Is it uncommon for the formal charge and the oxidation state to be different? Explain. **(d)** Perchlorate is a much stronger oxidizing agent than hypochlorite. Would you expect there to be any relationship between the oxidizing power of the oxyanion and either the oxidation state or the formal charge of chlorine?

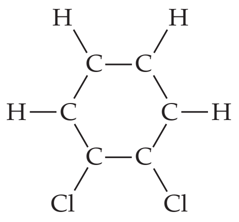
8.92 The following three Lewis structures can be drawn for N_2O:

$$:N{\equiv}N{-}\underset{\cdot\cdot}{\ddot{O}}: \longleftrightarrow :\underset{\cdot\cdot}{\ddot{N}}{-}N{\equiv}O: \longleftrightarrow :\ddot{N}{=}N{=}\ddot{O}:$$

(a) Using formal charges, which of these three resonance forms is likely to be the most important? **(b)** The N—N bond length in N_2O is 1.12 Å, slightly longer than a typical N≡N bond; and the N—O bond length is 1.19 Å, slightly shorter than a typical N=O bond. (See Table 8.5.) Rationalize these observations in terms of the resonance structures shown previously and your conclusion for part (a).

[8.93] **(a)** Triazine, $C_3H_3N_3$, is like benzene except that in triazine every other C—H group is replaced by a nitrogen atom. Draw the Lewis structure(s) for the triazine molecule. **(b)** Estimate the carbon–nitrogen bond distances in the ring.

[8.94] Ortho-dichlorobenzene, $C_6H_4Cl_2$, is obtained when two of the adjacent hydrogen atoms in benzene are replaced with Cl atoms. A skeleton of the molecule is shown here. **(a)** Complete a Lewis structure for the molecule using bonds and electron pairs as needed. **(b)** Are there any resonance structures for the molecule? If so, sketch them. **(c)** Are the resonance structures in (a) and (b) equivalent to one another as they are in benzene? If not, explain what makes them different.



8.95 Consider the hypothetical molecule B—A═B. How could you use an experimentally determined structure of the molecule to decide whether resonance is important in it?

8.96 An important reaction for the conversion of natural gas to other useful hydrocarbons is the conversion of methane to ethane.

$$2\,CH_4(g) \longrightarrow C_2H_6(g) + H_2(g)$$

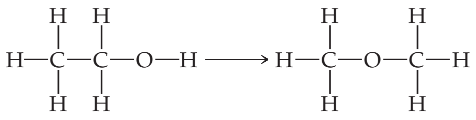
In practice, this reaction is carried out in the presence of oxygen, which converts the hydrogen produced to water.

$$2\,CH_4(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow C_2H_6(g) + H_2O(g)$$

Use Table 8.4 to estimate ΔH for these two reactions. Why is the conversion of methane to ethane more favorable when oxygen is used?

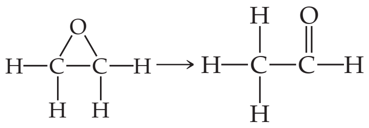
8.97 Two compounds are isomers if they have the same chemical formula but a different arrangement of atoms. Use Table 8.4 to estimate ΔH for each of the following gas-phase isomerization reactions, and indicate which isomer has the lower enthalpy:

(a)



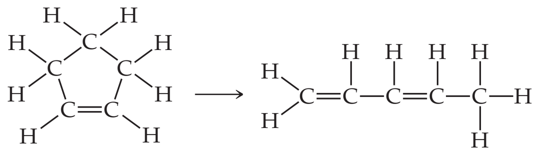
Ethanol Dimethyl ether

(b)



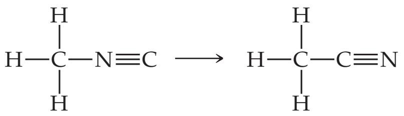
Ethylene oxide Acetaldehyde

(c)



Cyclopentene Pentadiene

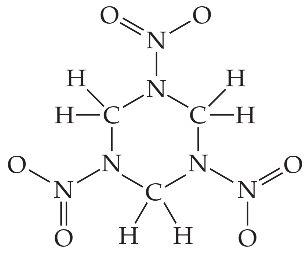
(d)



Methyl isocyanide Acetonitrile

[8.98] With reference to the "Chemistry Put to Work" box on explosives, **(a)** use bond enthalpies to estimate the enthalpy change for the explosion of 1.00 g of nitroglycerin. **(b)** Write a balanced equation for the decomposition of TNT. Assume that, upon explosion, TNT decomposes into $N_2(g)$, $CO_2(g)$, $H_2O(g)$, and $C(s)$.

[8.99] The "plastic" explosive C-4, often used in action movies, contains the molecule *cyclotrimethylenetrinitramine,* which is often called RDX (for Royal Demolition eXplosive):



Cyclotrimethylenetrinitramine (RDX)

(a) Complete the Lewis structure for the molecule by adding unshared electron pairs where they are needed. **(b)** Does the Lewis structure you drew in part (a) have any resonance structures? If so, how many? **(c)** The molecule causes an explosion by decomposing into $CO(g)$, $N_2(g)$, and $H_2O(g)$. Write a balanced equation for the decomposition reaction. **(d)** With reference to Table 8.4, which is the weakest type of bond in the molecule? **(e)** Use average bond enthalpies to estimate the enthalpy change when 5.0 g of RDX decomposes.

8.100 The bond lengths of carbon–carbon, carbon–nitrogen, carbon–oxygen, and nitrogen–nitrogen single, double, and triple bonds are listed in Table 8.5. Plot bond enthalpy (Table 8.4) versus bond length for these bonds (as in Figure 8.17). What do you conclude about the relationship between bond length and bond enthalpy? What do you conclude about the relative strengths of C—C, C—N, C—O, and N—N bonds?

INTEGRATIVE EXERCISES

8.101 The Ti^{2+} ion is isoelectronic with the Ca atom. **(a)** Are there any differences in the electron configurations of Ti^{2+} and Ca? **(b)** With reference to Figure 6.24, comment on the changes in the ordering of the 4*s* and 3*d* subshells in Ca and Ti^{2+}. **(c)** Will Ca and Ti^{2+} have the same number of unpaired electrons? Explain.

[8.102] **(a)** Write the chemical equations that are used in calculating the lattice energy of $SrCl_2(s)$ via a Born–Haber cycle. **(b)** The second ionization energy of $Sr(g)$ is 1064 kJ/mol. Use this fact along with data in Appendix C, Figure 7.9, Figure 7.11, and Table 8.2 to calculate ΔH_f° for $SrCl_2(s)$.

[8.103] The electron affinity of oxygen is −141 kJ/mol, corresponding to the reaction

$$O(g) + e^- \longrightarrow O^-(g)$$

The lattice energy of $K_2O(s)$ is 2238 kJ/mol. Use these data along with data in Appendix C and Figure 7.9 to calculate the "second electron affinity" of oxygen, corresponding to the reaction

$$O^-(g) + e^- \longrightarrow O^{2-}(g)$$

8.104 You and a partner are asked to complete a lab entitled "Oxides of Ruthenium" that is scheduled to extend over two lab periods. The first lab, which is to be completed by your partner, is devoted to carrying out compositional analysis. In the second lab, you are to determine melting points. Upon going to lab you find two unlabeled vials, one containing a soft yellow substance and the other a black powder. You also find the following notes in your partner's notebook—*Compound 1*: 76.0% Ru and 24.0% O (by mass), *Compound 2*: 61.2% Ru and

38.8% O (by mass). (**a**) What is the empirical formula for Compound 1? (**b**) What is the empirical formula for Compound 2? (**c**) Upon determining the melting points of these two compounds, you find that the yellow compound melts at 25 °C, while the black powder does not melt up to the maximum temperature of your apparatus, 1200 °C. What is the identity of the yellow compound? What is the identity of the black compound? Be sure to use the appropriate naming convention depending on whether the compound is better described as a molecular or ionic compound.

[8.105] One scale for electronegativity is based on the concept that the electronegativity of any atom is proportional to the ionization energy of the atom minus its electron affinity: electronegativity $= k(\text{IE} - \text{EA})$, where k is a proportionality constant. (**a**) How does this definition explain why the electronegativity of F is greater than that of Cl even though Cl has the greater electron affinity? (**b**) Why are both ionization energy and electron affinity relevant to the notion of electronegativity? (**c**) By using data in Chapter 7, determine the value of k that would lead to an electronegativity of 4.0 for F under this definition. (**d**) Use your result from part (c) to determine the electronegativities of Cl and O using this scale. Do these values follow the trend shown in Figure 8.7?

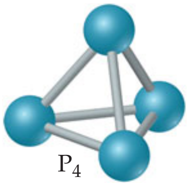
8.106 The compound chloral hydrate, known in detective stories as knockout drops, is composed of 14.52% C, 1.83% H, 64.30% Cl, and 19.35% O by mass and has a molar mass of 165.4 g/mol. (**a**) What is the empirical formula of this substance? (**b**) What is the molecular formula of this substance? (**c**) Draw the Lewis structure of the molecule, assuming that the Cl atoms bond to a single C atom and that there are a C—C bond and two C—O bonds in the compound.

8.107 Barium azide is 62.04% Ba and 37.96% N. Each azide ion has a net charge of 1−. (**a**) Determine the chemical formula of the azide ion. (**b**) Write three resonance structures for the azide ion. (**c**) Which structure is most important? (**d**) Predict the bond lengths in the ion.

8.108 Acetylene (C_2H_2) and nitrogen (N_2) both contain a triple bond, but they differ greatly in their chemical properties. (**a**) Write the Lewis structures for the two substances. (**b**) By referring to Appendix C, look up the enthalpies of formation of acetylene and nitrogen and compare their reactivities. (**c**) Write balanced chemical equations for the complete oxidation of N_2 to form $N_2O_5(g)$ and of acetylene to form $CO_2(g)$ and $H_2O(g)$. (**d**) Calculate the enthalpy of oxidation per mole of N_2 and C_2H_2 (the enthalpy of formation of $N_2O_5(g)$ is 11.30 kJ/mol). How do these comparative values relate to your response to part (b)? Both N_2 and C_2H_2 possess triple bonds with quite high bond enthalpies (Table 8.4). What aspect of chemical bonding in these molecules or in the oxidation products seems to account for the difference in chemical reactivities?

[8.109] Under special conditions, sulfur reacts with anhydrous liquid ammonia to form a binary compound of sulfur and nitrogen. The compound is found to consist of 69.6% S and 30.4% N. Measurements of its molecular mass yield a value of 184.3 g mol^{-1}. The compound occasionally detonates on being struck or when heated rapidly. The sulfur and nitrogen atoms of the molecule are joined in a ring. All the bonds in the ring are of the same length. (**a**) Calculate the empirical and molecular formulas for the substance. (**b**) Write Lewis structures for the molecule, based on the information you are given. (*Hint:* You should find a relatively small number of dominant Lewis structures.) (**c**) Predict the bond distances between the atoms in the ring. (*Note*: The S—S distance in the S_8 ring is 2.05 Å.) (**d**) The enthalpy of formation of the compound is estimated to be 480 kJ mol^{-1}. ΔH_f° of $S(g)$ is 222.8 kJ mol^{-1}. Estimate the average bond enthalpy in the compound.

[8.110] A common form of elemental phosphorus is the tetrahedral P_4 molecule, where all four phosphorus atoms are equivalent:



P_4

At room temperature phosphorus is a solid. (**a**) Do you think there are any unshared pairs of electrons in the P_4 molecule? (**b**) How many P—P bonds are there in the molecule? (**c**) Can you draw a Lewis structure for a linear P_4 molecule that satisfies the octet rule? (**d**) Using formal charges, what can you say about the stability of the linear molecule versus that of the tetrahedral molecule?

[8.111] Consider benzene (C_6H_6) in the gas phase. (**a**) Write the reaction for breaking all the bonds in $C_6H_6(g)$, and use data in Appendix C to determine the enthalpy change for this reaction. (**b**) Write a reaction that corresponds to breaking all the carbon–carbon bonds in $C_6H_6(g)$. (**c**) By combining your answers to parts (a) and (b) and using the average bond enthalpy for C—H from Table 8.4, calculate the average bond enthalpy for the carbon–carbon bonds in $C_6H_6(g)$. (**d**) Comment on your answer from part (c) as compared to the values for C—C single bonds and C═C double bonds in Table 8.4.

8.112 Average bond enthalpies are generally defined for gas-phase molecules. Many substances are liquids in their standard state. (Section 5.7) By using appropriate thermochemical data from Appendix C, calculate average bond enthalpies in the liquid state for the following bonds, and compare these values to the gas-phase values given in Table 8.4: (**a**) Br—Br, from $Br_2(l)$; (**b**) C—Cl, from $CCl_4(l)$; (**c**) O—O, from $H_2O_2(l)$ (assume that the O—H bond enthalpy is the same as in the gas phase). (**d**) What can you conclude about the process of breaking bonds in the liquid as compared to the gas phase? Explain the difference in the ΔH values between the two phases.

WHAT'S AHEAD

9.1 MOLECULAR SHAPES

We begin by discussing *molecular shapes* and examining some shapes commonly encountered in molecules.

9.2 THE VSEPR MODEL

We consider how molecular geometries can be predicted using the *valence-shell electron-pair repulsion,* or *VSEPR,* model, which is based on Lewis structures and the repulsions between regions of high electron density.

9.3 MOLECULAR SHAPE AND MOLECULAR POLARITY

Once we know the geometry of a molecule and the types of bonds it contains, we can determine whether the molecule is *polar* or *nonpolar*.

9.4 COVALENT BONDING AND ORBITAL OVERLAP

We recognize that electrons are shared between atoms in a covalent bond. In *valence-bond theory,* the bonding electrons are visualized as originating in atomic orbitals on two atoms. A covalent bond is formed when these orbitals overlap.

9

THE DRUG SHOWN HERE IS DIAZEPAM, better known as Valium. It is commonly prescribed for a wide range of disorders, including *anxiety*, *insomnia*, *seizures*, *muscle spasms*, *restless legs syndrome*, and *obsessive-compulsive disorder*. Valium was invented by Leo Sternbach at Hoffmann-LaRoche Pharmaceuticals and first licensed for use in 1960. It was the top-selling pharmaceutical in the United States from 1969 to 1982, with peak sales in 1978 of 2.3 billion tablets! It continues to be an important medication and is on the World Health Organization's Essential Drugs list.

9.5 HYBRID ORBITALS

To account for molecular shape, we consider how the orbitals of one atom mix with one another, or *hybridize,* to create *hybrid orbitals*.

9.6 MULTIPLE BONDS

Atomic orbitals that contribute to covalent bonding in a molecule can overlap in multiple ways to produce *sigma* and *pi* bonds between atoms. Single bonds generally consist of one sigma bond; multiple bonds involve one sigma and one or more pi bonds. We examine the geometric arrangements of these bonds and how they are exemplified in organic compounds.

9.7 MOLECULAR ORBITALS

We examine a more sophisticated treatment of bonding called *molecular orbital theory,* which introduces the concepts of *bonding* and *antibonding molecular orbitals*.

9.8 PERIOD 2 DIATOMIC MOLECULES

We consider how molecular orbital theory is used to construct *energy-level diagrams* for second-row diatomic molecules.

MOLECULAR GEOMETRY AND BONDING THEORIES

WE SAW IN CHAPTER 8 THAT LEWIS STRUCTURES help us understand the compositions of molecules and their covalent bonds. However, Lewis structures do not show one of the most important aspects of molecules—their overall shapes. The shape and size of molecules—sometimes referred to as molecular *architecture*—are defined by the angles and distances between the nuclei of the component atoms.

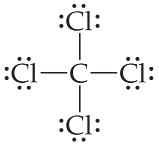
The shape and size of a molecule of a substance, together with the strength and polarity of its bonds, largely determine the properties of that substance. Some of the most dramatic examples of the important roles of molecular architecture are seen in biochemical reactions. For example, the chapter-opening photograph shows a molecular model of diazepam, better known as Valium. In the body, this relatively simple molecule enters into an extraordinary array of biochemical interactions. Valium works by binding to certain important sites in the central nervous system. Its effectiveness is highly dependent on the shape and size of the molecule as well on the charge distributions within it. Even a small modification to molecular shape or size alters the drug's effectiveness.

One of our goals in this chapter is to develop a sense of the shapes of molecules and how those shapes are governed in large measure by the kinds of bonds that exist between the atoms making up the molecules.

Our first goal is to learn the relationship between two-dimensional Lewis structures and three-dimensional molecular shapes. Armed with this knowledge, we can examine the nature of covalent bonds. The lines used to depict bonds in Lewis structures provide important clues about the orbitals that molecules use in bonding. By examining these orbitals, we can gain a greater understanding of the behavior of molecules. Mastering the material in this chapter will help you in later discussions of the physical and chemical properties of substances.

9.1 MOLECULAR SHAPES

In Chapter 8 we used Lewis structures to account for the formulas of covalent compounds. (Section 8.5) Lewis structures, however, do not indicate the shapes of molecules; they simply show the number and types of bonds. For example, the Lewis structure of CCl_4 tells us only that four Cl atoms are bonded to a central C atom:



$$\begin{array}{c} :\ddot{\text{Cl}}: \\ | \\ :\underset{..}{\ddot{\text{Cl}}}-\text{C}-\underset{..}{\ddot{\text{Cl}}}: \\ | \\ :\underset{..}{\text{Cl}}: \end{array}$$

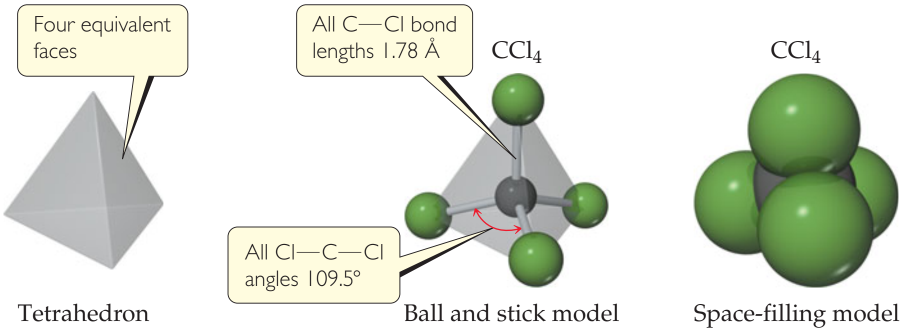
The Lewis structure is drawn with the atoms all in the same plane. As shown in ▼ **FIGURE 9.1**, however, the actual arrangement is the Cl atoms at the corners of a *tetrahedron,* a geometric object with four corners and four faces, each an equilateral triangle.

The shape of a molecule is determined by its **bond angles**, the angles made by the lines joining the nuclei of the atoms in the molecule. The bond angles of a molecule, together with the bond lengths (Section 8.8), define the shape and size of the molecule. In Figure 9.1, you should be able to see that there are six Cl—C—Cl bond angles in CCl_4 and that they all have the same value of 109.5°, the angle size characteristic of a tetrahedron. In addition, all four C—Cl bonds are the same length (1.78 Å). Thus, the shape and size of CCl_4 are completely described by stating that the molecule is tetrahedral with C—Cl bonds of length 1.78 Å.

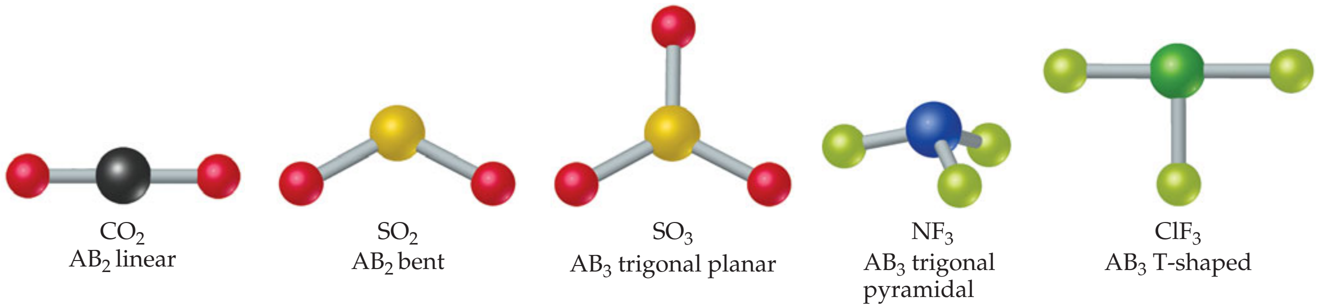
We begin our discussion of molecular shapes with molecules (and ions) that, like CCl_4, have a single central atom bonded to two or more atoms of the same type. Such molecules have the general formula AB_n in which the central atom A is bonded to n

GO FIGURE

In the space-filling model, what determines the relative sizes of the spheres?



▲ **FIGURE 9.1 Tetrahedral shape of CCl_4.**



▲ **FIGURE 9.2** **Shapes of AB_2 and AB_3 molecules.**

B atoms. Both CO_2 and H_2O are AB_2 molecules, for example, whereas SO_3 and NH_3 are AB_3 molecules, and so on.

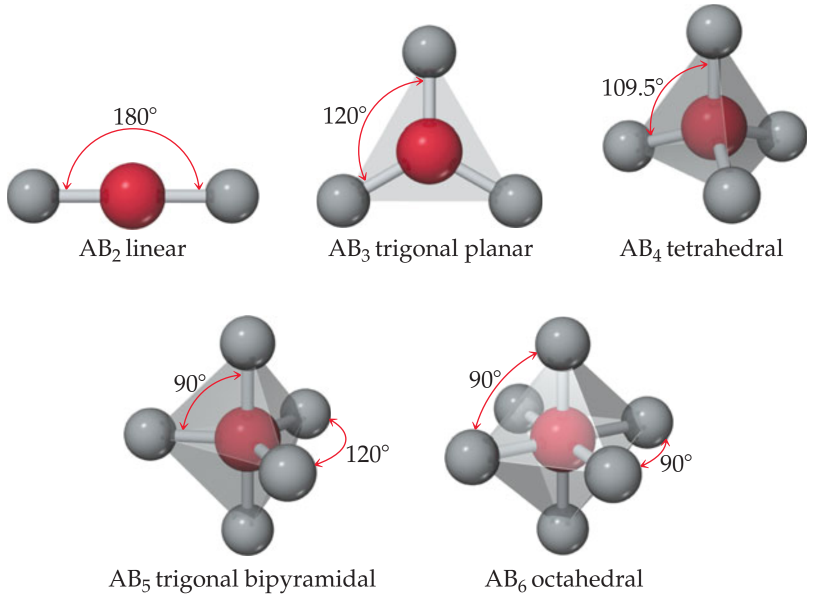
The number of shapes possible for AB_n molecules depends on the value of n. Those commonly found for AB_2 and AB_3 molecules are shown in ▲ **FIGURE 9.2**. An AB_2 molecule must be either linear (bond angle $= 180°$) or bent (bond angle $\neq 180°$). For AB_3 molecules, the two most common shapes place the B atoms at the corners of an equilateral triangle. If the A atom lies in the same plane as the B atoms, the shape is *trigonal planar*. If the A atom lies above the plane of the B atoms, the shape is *trigonal pyramidal* (a pyramid with an equilateral triangle as its base). Some AB_3 molecules, such as ClF_3, are *T-shaped*, the relatively unusual shape shown in Figure 9.2. The atoms lie in one plane, but the angles between them vary as shown.

Compare Figures 9.1 and 9.2 to notice the difference between NF_3 and CCl_4. The CCl_4 molecule is tetrahedral because the four atoms bonded to the carbon are disposed at the four apexes of a tetrahedron around the central atom. The NF_3 molecule is pyramidal because the three atoms bonded to nitrogen lie at the base of a trigonal pyramid.

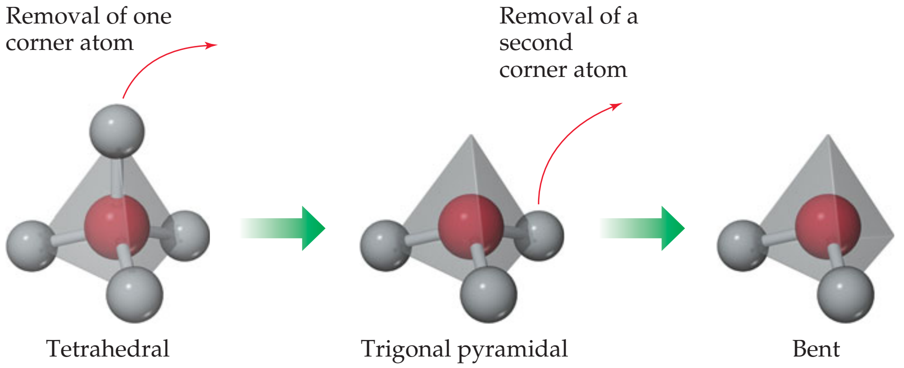
The shapes that maximize the separation of outer atoms are shown in ▼ **FIGURE 9.3**. In addition to the shapes we have already seen, this figure shows those encountered when there are five or six atoms surrounding a central atom. The trigonal bipyramid can be thought of as two face-to-face trigonal pyramids; the octahedron is like two face-to-face square pyramids.

GO FIGURE

Which of these molecular shapes do you expect for the SF_6 molecule?



◀ **FIGURE 9.3** **Shapes allowing maximum distances between atoms in AB_n molecules.**



▶ **FIGURE 9.4 Derivatives of the tetrahedral molecular shape.**

Some molecules have shapes other than those shown in Figure 9.3, but we can usually derive the shape of those molecules from Figure 9.3. Neither trigonal pyramidal nor bent is shown in Figure 9.3, for instance, but ▲ **FIGURE 9.4** shows how we can arrive at these shapes by removing atoms from the tetrahedral shape.

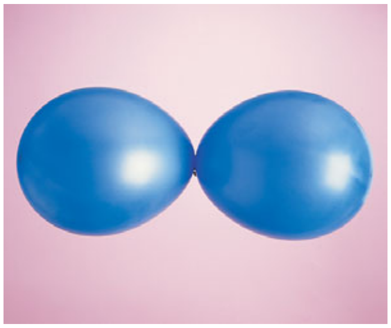
Why do so many AB_n molecules have shapes related to those shown in Figure 9.3, and can we predict these shapes? When A is a representative element (one from the *s* block or *p* block of the periodic table), we can answer these questions by using the **valence-shell electron-pair repulsion (VSEPR) model**. Although the name is rather imposing, the model is quite simple. It has useful predictive capabilities, as we will see in Section 9.2.

GIVE IT SOME THOUGHT

In addition to tetrahedral, another common shape for AB_4 molecules is *square planar.* All five atoms lie in the same plane, with the B atoms at the corners of a square and the A atom at the center of the square. Which shape in Figure 9.3 could lead to a square-planar shape upon removal of one or more atoms?

9.2 THE VSEPR MODEL

Imagine tying two identical balloons together at their ends. As shown in ◀ **FIGURE 9.5**, the two balloons naturally orient themselves to point away from each other; that is, they try to "get out of each other's way" as much as possible. If we add a third balloon, the balloons orient themselves toward the vertices of an equilateral triangle, and if we add a fourth balloon, they adopt a tetrahedral shape. We see that an optimum geometry exists for each number of balloons.



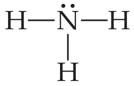
Two balloons
linear orientation

Three balloons
trigonal-planar orientation

Four balloons
tetrahedral orientation

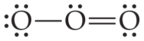
▲ **FIGURE 9.5 A balloon analogy for electron domains.**

In some ways, the electrons in molecules behave like these balloons. We have seen that a single covalent bond is formed between two atoms when a pair of electrons occupies the space between the atoms. (Section 8.3) A **bonding pair** of electrons thus defines a region in which the electrons are most likely to be found. We will refer to such a region as an **electron domain**. Likewise, a **nonbonding pair** (or **lone pair**) of electrons defines an electron domain that is located principally on one atom. For example, the Lewis structure of NH_3 has four electron domains around the central nitrogen atom (three bonding pairs, represented as usual by short lines, and one nonbonding pair, represented by dots):



$$\begin{array}{ccc} H & -\ddot{N}- & H \\ & | & \\ & H & \end{array}$$

Each multiple bond in a molecule also constitutes a single electron domain. Thus, the resonance structure for O_3 has three electron domains around the central oxygen atom (a single bond, a double bond, and a nonbonding pair of electrons):

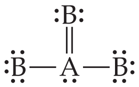


$$:\underset{..}{\ddot{O}}-\ddot{O}=\underset{..}{\ddot{O}}$$

In general, *each nonbonding pair, single bond, or multiple bond produces a single electron domain around the central atom in a molecule.*

GIVE IT SOME THOUGHT

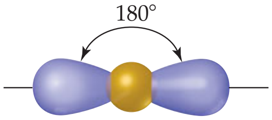
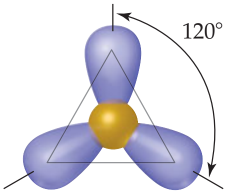
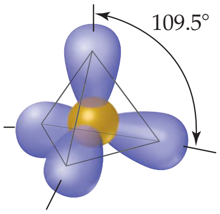
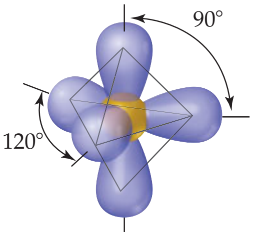
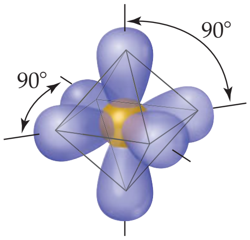
Suppose a particular AB_3 molecule has the resonance structure



Does this structure follow the octet rule? How many electron domains are there around the A atom?

The VSEPR model is based on the idea that electron domains are negatively charged and therefore repel one another. Like the balloons in Figure 9.5, electron domains try to stay out of one another's way. *The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them.* In fact, the analogy between electron domains and balloons is so close that the same preferred geometries are found in both cases. Like the balloons in Figure 9.5, two electron domains orient *linearly,* three domains orient in a *trigonal-planar* fashion, and four orient *tetrahedrally*. These arrangements, together with those for five- and six-electron domains, are summarized in ▼ **TABLE 9.1**. If you compare the geometries in Table 9.1 with those in Figure 9.3,

TABLE 9.1 • Electron-Domain Geometries as a Function of Number of Electron Domains

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

you will see that they are the same. *The shapes of different AB_n molecules or ions depend on the number of electron domains surrounding the central atom.*

The arrangement of electron domains about the central atom of an AB_n molecule or ion is called its **electron-domain geometry**. In contrast, the **molecular geometry** is the arrangement of *only the atoms* in a molecule or ion—any nonbonding pairs in the molecule are *not* part of the description of the molecular geometry.

In determining the shape of any molecule, we first use the VSEPR model to predict the electron-domain geometry. From knowing how many of the domains are due to nonbonding pairs, we can then predict the molecular geometry. When all the electron domains in a molecule arise from bonds, the molecular geometry is identical to the electron-domain geometry. When, however, one or more domains involve nonbonding pairs of electrons, we must remember to ignore those domains when talking about molecular shape.

We can generalize the steps we follow in using the VSEPR model to predict the shapes of molecules or ions:

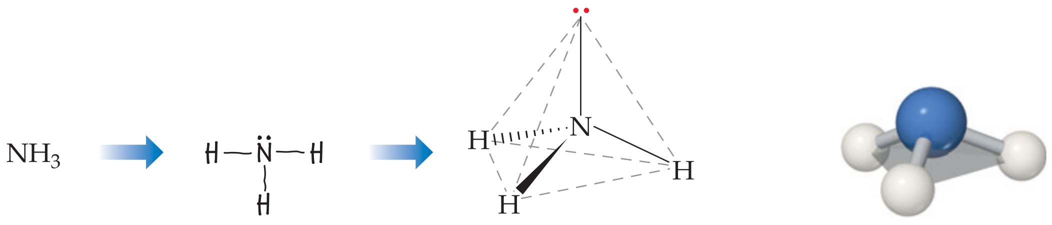
1. Draw the *Lewis structure* of the molecule or ion, and count the number of electron domains around the central atom. Each nonbonding electron pair, each single bond, each double bond, and each triple bond counts as one electron domain.
2. Determine the *electron-domain geometry* by arranging the electron domains about the central atom so that the repulsions among them are minimized, as shown in Table 9.1.
3. Use the arrangement of the bonded atoms to determine the *molecular geometry*.

▼ **FIGURE 9.6** shows how these steps are applied to predict the geometry of the NH_3 molecule. The three bonds and one nonbonding pair in the Lewis structure tell us we have four electron domains. We know from Table 9.1 that the repulsions among four electron domains are minimized when the domains point toward the vertices of a tetrahedron, so the electron-domain geometry of NH_3 is tetrahedral. We know from the Lewis structure that one electron domain holds a nonbonding pair of electrons, which occupies one of the four vertices of the tetrahedron. The bonding arrangement is therefore three atoms bonded to a central atom, with the central atom not in the same plane as the three others. This is just the situation we find in the middle molecule of Figure 9.4. Hence, the molecular geometry of NH_3 is trigonal pyramidal. Notice that the tetrahedral arrangement of the four electron domains leads us to predict the trigonal-pyramidal molecular geometry.

Because the trigonal-pyramidal molecular geometry is based on a tetrahedral electron-domain geometry, the *ideal bond angles* are 109.5°. As we will soon see, bond angles deviate from ideal values when the surrounding atoms and electron domains are not identical.

GIVE IT SOME THOUGHT

From the standpoint of the VSEPR model, what do nonbonding electron pairs, single bonds, and multiple bonds have in common?



1. Draw Lewis structure

2. Determine electron-domain geometry by counting *all* electron domains, then use Table 9.1 to determine appropriate electron domain geomtry.

3. Determine molecular geometry by counting *only bonding* electron domains to see arrangement of bonded atoms (trigonal pyramidal)

► **FIGURE 9.6 Determining the molecular geometry of NH_3.**

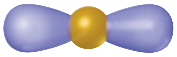
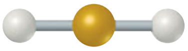
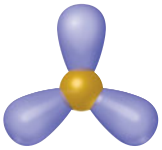
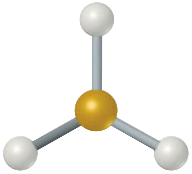
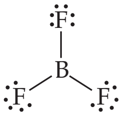
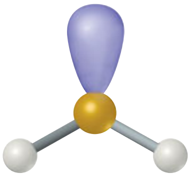
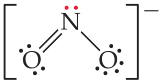
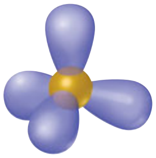
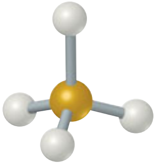
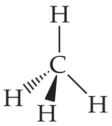
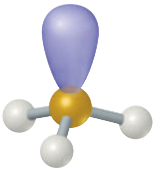
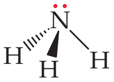
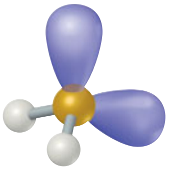
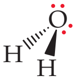
As one more example, let's determine the shape of the CO_2 molecule. Its Lewis structure reveals two electron domains (each one a double bond) around the central carbon:

$$\ddot{\underset{\cdot\cdot}{O}}=C=\ddot{\underset{\cdot\cdot}{O}}$$

Two electron domains orient in a linear electron-domain geometry (Table 9.1). Because neither domain is a nonbonding pair of electrons, the molecular geometry is also linear, and the O—C—O bond angle is 180°.

▼ **TABLE 9.2** summarizes the possible molecular geometries when an AB_n molecule has four or fewer electron domains about A. These geometries are important because they include all the shapes usually seen in molecules or ions that obey the octet rule.

TABLE 9.2 • Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	$\ddot{\underset{\cdot\cdot}{O}}=C=\ddot{\underset{\cdot\cdot}{O}}$
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

SAMPLE EXERCISE 9.1 Using the VSEPR Model

Use the VSEPR model to predict the molecular geometry of (**a**) O_3, (**b**) $SnCl_3^-$.

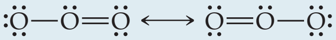
SOLUTION

Analyze We are given the molecular formulas of a molecule and a polyatomic ion, both conforming to the general formula AB_n and both having a central atom from the *p* block of the periodic table.

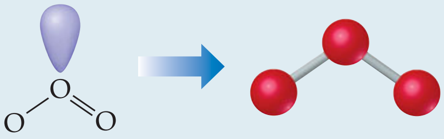
Plan To predict the molecular geometries, we draw their Lewis structures and count electron domains around the central atom to get the electron-domain geometry. We then obtain the molecular geometry from the arrangement of the domains that are due to bonds.

Solve

(**a**) We can draw two resonance structures for O_3:

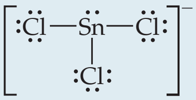


Because of resonance, the bonds between the central O atom and the outer O atoms are of equal length. In both resonance structures the central O atom is bonded to the two outer O atoms and has one nonbonding pair. Thus, there are three electron domains about the central O atoms. (Remember that a double bond counts as a single electron domain.) The arrangement of three electron domains is trigonal planar (Table 9.1). Two of the domains are from bonds, and one is due to a nonbonding pair. So, the molecule has a bent shape with an ideal bond angle of 120° (Table 9.2).

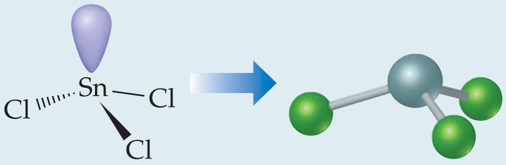


Comment As this example illustrates, when a molecule exhibits resonance, any one of the resonance structures can be used to predict the molecular geometry.

(**b**) The Lewis structure for $SnCl_3^-$ is



The central Sn atom is bonded to the three Cl atoms and has one nonbonding pair; thus, we have four electron domains, meaning tetrahedral electron-domain geometry (Table 9.1) with one vertex occupied by a nonbonding pair of electrons. Tetrahedral electron-domain geometry with three bonding and one nonbonding domains means the molecular geometry is trigonal pyramidal (Table 9.2).



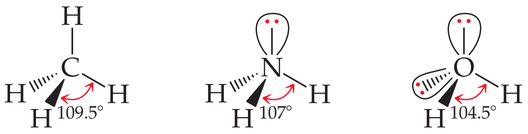
PRACTICE EXERCISE

Predict the electron-domain and molecular geometries for (**a**) $SeCl_2$, (**b**) CO_3^{2-}.

Answers: (**a**) tetrahedral, bent; (**b**) trigonal planar, trigonal planar

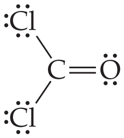
Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

We can refine the VSEPR model to explain slight distortions from the ideal geometries summarized in Table 9.2. For example, consider methane (CH_4), ammonia (NH_3), and water (H_2O). All three have a tetrahedral electron-domain geometry, but their bond angles differ slightly:

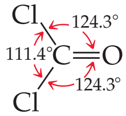


Notice that the bond angles decrease as the number of nonbonding electron pairs increases. A bonding pair of electrons is attracted by both nuclei of the bonded atoms, but a nonbonding pair is attracted primarily by only one nucleus. Because a nonbonding pair experiences less nuclear attraction, its electron domain is spread out more in space than is the electron domain for a bonding pair (▶ **FIGURE 9.7**). Nonbonding electron pairs therefore take up more space than bonding pairs. As a result, *electron domains for nonbonding electron pairs exert greater repulsive forces on adjacent electron domains and tend to compress bond angles.*

Because multiple bonds contain a higher electronic-charge density than single bonds, multiple bonds also represent enlarged electron domains. Consider the Lewis structure of phosgene:



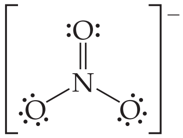
Because three electron domains surround the central atom, we might expect a trigonal-planar geometry with 120° bond angles. The double bond, however, seems to act much like a nonbonding pair of electrons, reducing the Cl—C—Cl bond angle to 111.4°:



In general, *electron domains for multiple bonds exert a greater repulsive force on adjacent electron domains than do electron domains for single bonds.*

GIVE IT SOME THOUGHT

One resonance structure of the nitrate ion is



The bond angles in this ion are 120°. Is this observation consistent with the preceding discussion of the effect of multiple bonds on bond angles?

Molecules with Expanded Valence Shells

Atoms from period 3 and beyond may be surrounded by more than four electron pairs. (Section 8.7) Molecules with five or six electron domains around the central atom have molecular geometries based on either a *trigonal-bipyramidal* (five domains) or *octahedral* (six domains) electron-domain geometry (▶ **TABLE 9.3**).

The most stable electron-domain geometry for five electron domains is the trigonal bipyramid (two trigonal pyramids sharing a base). Unlike the other arrangements we have seen, the electron domains in a trigonal bipyramid can point toward two geometrically distinct types of positions. Two domains point toward *axial positions* and three point toward *equatorial positions* (▶ **FIGURE 9.8**). Each axial domain makes a 90° angle with any equatorial domain. Each equatorial domain makes a 120° angle with either of the other two equatorial domains and a 90° angle with either axial domain.

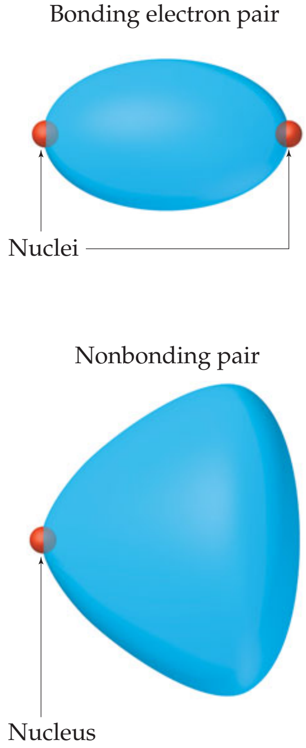
Suppose a molecule has five electron domains, and there are one or more nonbonding pairs. Will the domains from the nonbonding pairs occupy axial or equatorial positions? To answer this question, we must determine which location minimizes repulsion between domains. Repulsion between two domains is much greater when they are situated 90° from each other than when they are at 120°. An equatorial domain is 90° from only two other domains (the axial domains), but an axial domain is 90° from *three* other domains (the equatorial domains). Hence, an equatorial domain experiences less repulsion than an axial domain. Because the domains from nonbonding pairs exert larger repulsions than those from bonding pairs, nonbonding domains always occupy the equatorial positions in a trigonal bipyramid.

GIVE IT SOME THOUGHT

It might seem that a square-planar geometry of four electron domains around a central atom would be more favorable than a tetrahedron. Can you rationalize why the tetrahedron is preferred, based on angles between electron domains?

GO FIGURE

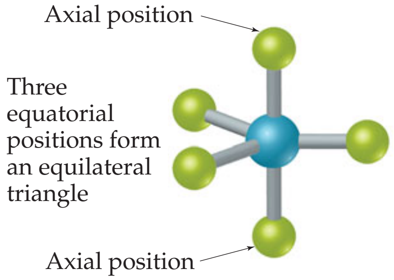
Why is the volume occupied by the nonbonding electron pair domain larger than the volume occupied by the bonding domain?



▲ **FIGURE 9.7 Relative volumes occupied by bonding and nonbonding electron domains.**

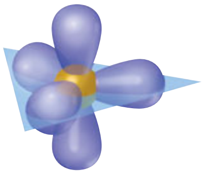
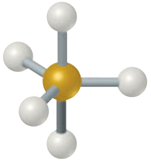
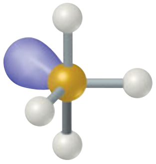
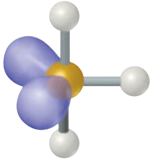
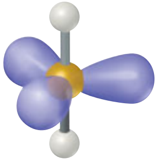
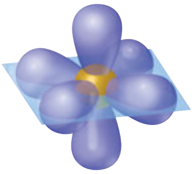
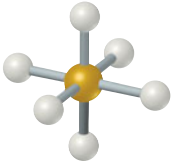
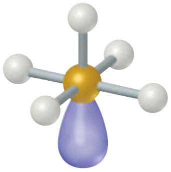
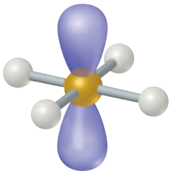
GO FIGURE

What is the bond angle formed by an axial atom, the central atom, and any equatorial atom?



▲ **FIGURE 9.8 In a trigonal-bipyramidal geometry, there are two types of positions for the outer atoms.**

TABLE 9.3 • Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

The most stable electron-domain geometry for six electron domains is the *octahedron*. An octahedron is a polyhedron with six vertices and eight faces, each an equilateral triangle. An atom with six electron domains around it can be visualized as being at the center of the octahedron with the electron domains pointing toward the six vertices, as shown in Table 9.3. All the bond angles are 90°, and all six vertices are equivalent. Therefore, if an atom has five bonding electron domains and one nonbonding domain, we can put the nonbonding domain at any of the six vertices of the octahedron. The result is always a *square-pyramidal* molecular geometry. When there are two nonbonding electron domains, however, their repulsions are minimized by pointing them toward opposite sides of the octahedron, producing a *square-planar* molecular geometry, as shown in Table 9.3.

SAMPLE EXERCISE 9.2 Molecular Geometries of Molecules with Expanded Valence Shells

Use the VSEPR model to predict the molecular geometry of (**a**) SF_4, (**b**) IF_5.

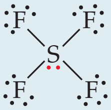
SOLUTION

Analyze The molecules are of the AB_n type with a central *p*-block atom.

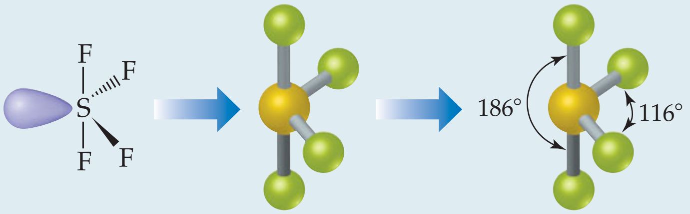
Plan We first draw Lewis structures and then use the VSEPR model to determine the electron-domain geometry and molecular geometry.

Solve

(**a**) The Lewis structure for SF_4 is

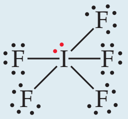


The sulfur has five electron domains around it: four from the S—F bonds and one from the nonbonding pair. Each domain points toward a vertex of a trigonal bipyramid. The domain from the nonbonding pair will point toward an equatorial position. The four bonds point toward the remaining four positions, resulting in a molecular geometry that is described as seesaw-shaped:

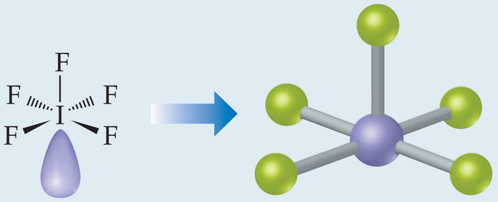


Comment The experimentally observed structure is shown on the right. We can infer that the nonbonding electron domain occupies an equatorial position, as predicted. The axial and equatorial S—F bonds are slightly bent away from the nonbonding domain, suggesting that the bonding domains are "pushed" by the nonbonding domain, which exerts a greater repulsion (Figure 9.7).

(**b**) The Lewis structure of IF_5 is



The iodine has six electron domains around it, one of which is nonbonding. The electron-domain geometry is therefore octahedral, with one position occupied by the nonbonding pair, and the molecular geometry is *square pyramidal* (Table 9.3):



Comment Because the nonbonding domain is larger than the bonding domains, we predict that the four F atoms in the base of the pyramid will be tipped up slightly toward the top F atom. Experimentally, we find that the angle between the base atoms and top F atom is 82°, smaller than the ideal 90° angle of an octahedron.

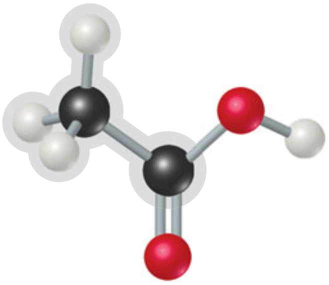
PRACTICE EXERCISE

Predict the electron-domain and molecular geometries of (**a**) BrF_3, (**b**) ICl_4^-.

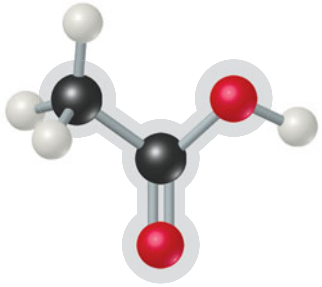
Answers: (**a**) trigonal bipyramidal, T-shaped; (**b**) octahedral, square planar

GO FIGURE

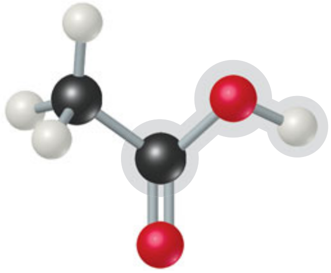
Although the electron-domain geometry around the right O is tetrahedral, the C—O—H bond is slightly less than 109.5°. Explain.



Electron-domain geometry tetrahedral, molecular geometry tetrahedral



Electron-domain geometry trigonal planar, molecular geometry trigonal planar

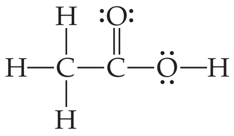


Electron-domain geometry tetrahedral, molecular geometry bent

▲ **FIGURE 9.9** **Acetic acid, CH_3COOH.**

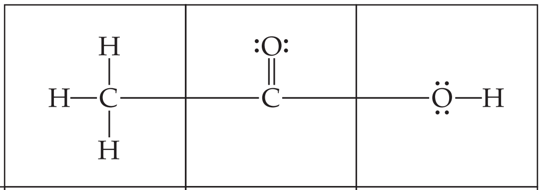
Shapes of Larger Molecules

Although the molecules and ions we have considered contain only a single central atom, the VSEPR model can be extended to more complex molecules. For the acetic acid molecule, for example,



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}{-}\overset{\displaystyle :O:}{\overset{\|}{C}}{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{-}H}$$

we can use the VSEPR model to predict the geometry about each atom:



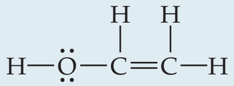
Number of electron domains	4	3	4
Electron-domain geometry	Tetrahedral	Trigonal planar	Tetrahedral
Predicted bond angles	109.5°	120°	109.5°

The left C has four electron domains (all bonding), and so the electron-domain and molecular geometries around that atom are both tetrahedral. The central C has three electron domains (counting the double bond as one domain), making both the electron-domain and the molecular geometries trigonal planar. The O on the right has four electron domains (two bonding, two nonbonding), so its electron-domain geometry is tetrahedral and its molecular geometry is bent. The bond angles about the central C atom and the O atom are expected to deviate slightly from the ideal values of 120° and 109.5° because of the spatial demands of multiple bonds and nonbonding electron pairs.

The structure of the acetic acid molecule is shown in ◀ **FIGURE 9.9**.

SAMPLE EXERCISE 9.3 **Predicting Bond Angles**

Eyedrops for dry eyes usually contain a water-soluble polymer called *poly(vinyl alcohol)*, which is based on the unstable organic molecule *vinyl alcohol*:



$$\mathrm{H{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{-}\overset{\displaystyle H}{\overset{|}{C}}{=}\overset{\displaystyle H}{\overset{|}{C}}{-}H}$$

Predict the approximate values for the H—O—C and O—C—C bond angles in vinyl alcohol.

SOLUTION

Analyze We are given a Lewis structure and asked to determine two bond angles.

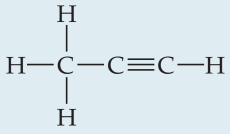
Plan To predict a bond angle, we determine the number of electron domains surrounding the middle atom in the bond. The ideal angle corresponds to the electron-domain geometry around the atom. The angle will be compressed somewhat by nonbonding electrons or multiple bonds.

Solve In H—O—C, the O atom has four electron domains (two bonding, two nonbonding). The electron-domain geometry around O is therefore tetrahedral, which gives an ideal angle of 109.5°. The H—O—C angle is compressed somewhat by the nonbonding pairs, so we expect this angle to be slightly less than 109.5°.

To predict the O—C—C bond angle, we examine the middle atom in the angle. In the molecule, there are three atoms bonded to this C atom and no nonbonding pairs, and so it has three electron domains about it. The predicted electron-domain geometry is trigonal planar, resulting in an ideal bond angle of 120°. Because of the larger size of the C═C domain, the bond angle should be slightly greater than 120°.

PRACTICE EXERCISE

Predict the H—C—H and C—C—C bond angles in *propyne*:



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H-C-C{\equiv}C-H} \\ | \\ \mathrm{H} \end{array}$$

Answers: 109.5°, 180°

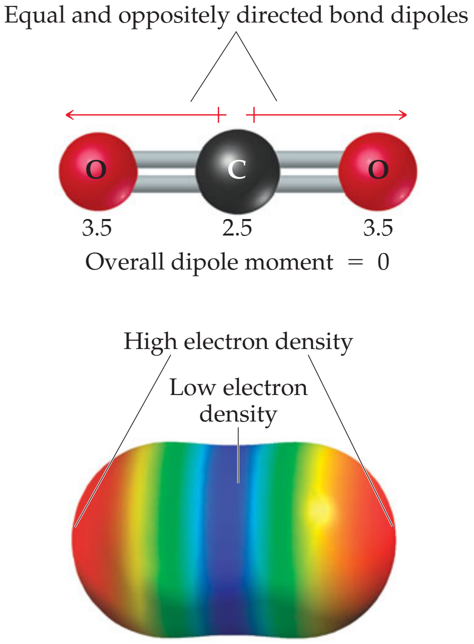
9.3 | MOLECULAR SHAPE AND MOLECULAR POLARITY

Recall that bond polarity is a measure of how equally the electrons in a bond are shared between the two atoms of the bond. As the difference in electronegativity between the two atoms increases, so does the bond polarity. (Section 8.4) We saw that the dipole moment of a diatomic molecule is a measure of the amount of charge separation in the molecule.

For a molecule consisting of more than two atoms, *the dipole moment depends on both the polarities of the individual bonds and the geometry of the molecule*. For each bond in the molecule, we consider the **bond dipole**, which is the dipole moment due only to the two atoms in that bond. Consider the linear CO_2 molecule, for example. As shown in ▶ **FIGURE 9.10**, each C═O bond is polar, and because the C═O bonds are identical, the bond dipoles are equal in magnitude. A plot of the molecule's electron density clearly shows that the individual bonds are polar, but what can we say about the *overall* dipole moment of the molecule?

GO FIGURE

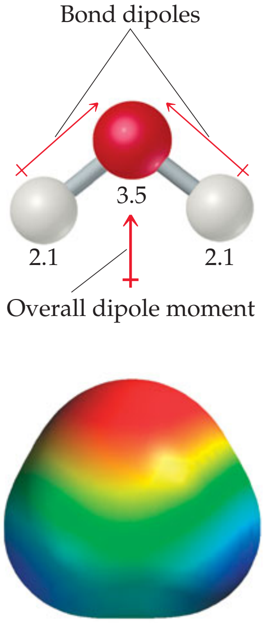
Explain how the directions of the red bond dipole arrows relate to the electron density picture.



▲ **FIGURE 9.10** **CO_2, a nonpolar molecule.** The numbers are electronegativity values for these two atoms.

Bond dipoles and dipole moments are vector quantities; that is, they have both a magnitude and a direction. The dipole moment of a polyatomic molecule is the vector sum of its bond dipoles. Both the magnitudes *and* the directions of the bond dipoles must be considered when summing vectors. The two bond dipoles in CO_2, although equal in magnitude, are opposite in direction. Adding them is the same as adding two numbers that are equal in magnitude but opposite in sign, such as 100 + (−100). The bond dipoles, like the numbers, "cancel" each other. Therefore, the dipole moment of CO_2 is zero, even though the individual bonds are polar. The geometry of the molecule dictates that the overall dipole moment be zero, making CO_2 a *nonpolar* molecule.

Now consider H_2O, a bent molecule with two polar bonds (▶ **FIGURE 9.11**). Again, the two bonds are identical, and the bond dipoles are equal in magnitude. Because the molecule is bent, however, the bond dipoles do not directly oppose each other and therefore do not cancel. Hence, the H_2O molecule has an overall nonzero dipole moment (μ = 1.85 D) and is therefore a *polar* molecule. The oxygen atom carries a partial negative charge, and the hydrogen atoms each have a partial positive charge, as shown in the electron-density model.

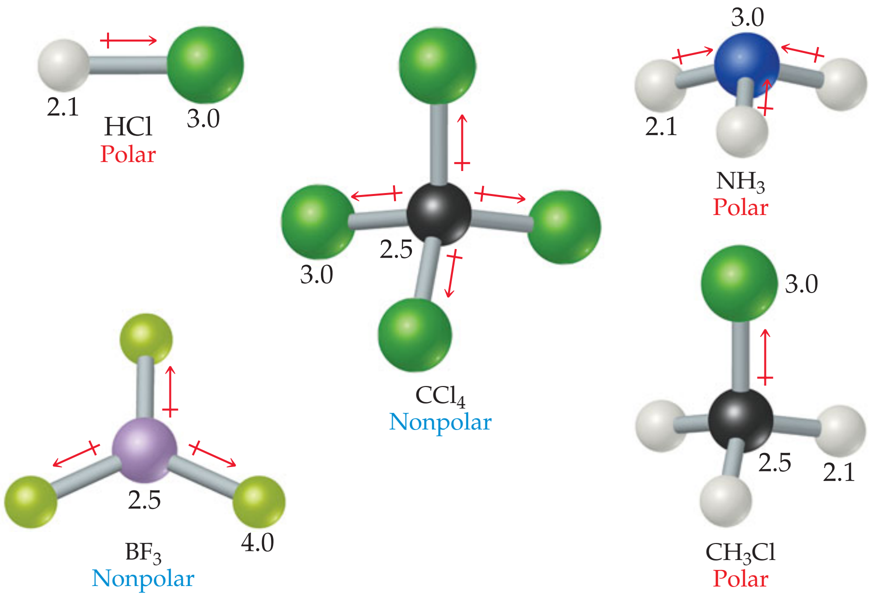


▲ **FIGURE 9.11** **H_2O, a polar molecule.** The numbers are electronegativity values.

GIVE IT SOME THOUGHT

The molecule O═C═S is linear and has a Lewis structure analogous to that of CO_2. Would you expect this molecule to have a dipole moment?

▶ **FIGURE 9.12** shows some polar and nonpolar molecules, all with polar bonds. The molecules in which the central atom is symmetrically surrounded by identical atoms (BF_3 and CCl_4) are nonpolar. For AB_n molecules in which all the B atoms are the same, certain symmetrical shapes—linear (AB_2), trigonal planar (AB_3), tetrahedral and square planar (AB_4), trigonal bipyramidal (AB_5), and octahedral (AB_6)—must lead to nonpolar molecules even though the individual bonds might be polar.



▶ **FIGURE 9.12 Polar and nonpolar molecules containing polar bonds.** The numbers are electronegativity values.

SAMPLE EXERCISE 9.4 Polarity of Molecules

Predict whether these molecules are polar or nonpolar: (**a**) BrCl, (**b**) SO_2, (**c**) SF_6.

SOLUTION

Analyze We are given three molecular formulas and asked to predict whether the molecules are polar.

Plan A molecule containing only two atoms is polar if the atoms differ in electronegativity. The polarity of a molecule containing three or more atoms depends on both the molecular geometry and the individual bond polarities. Thus, we must draw a Lewis structure for each molecule containing three or more atoms and determine its molecular geometry. We then use electronegativity values to determine the direction of the bond dipoles. Finally, we see whether the bond dipoles cancel to give a nonpolar molecule or reinforce each other to give a polar one.

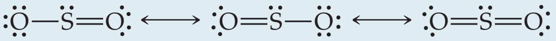
Solve

(**a**) Chlorine is more electronegative than bromine. All diatomic molecules with polar bonds are polar molecules. Consequently, BrCl is polar, with chlorine carrying the partial negative charge:

$$\overset{+\!\!\!\longrightarrow}{\mathrm{Br}-\mathrm{Cl}}$$

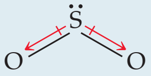
The measured dipole moment of BrCl is $\mu = 0.57$ D.

(**b**) Because oxygen is more electronegative than sulfur, SO_2 has polar bonds. Three resonance forms can be written:



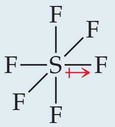
$$:\ddot{\underset{..}{\mathrm{O}}}-\ddot{\mathrm{S}}=\ddot{\mathrm{O}}: \longleftrightarrow :\ddot{\mathrm{O}}=\ddot{\mathrm{S}}-\ddot{\underset{..}{\mathrm{O}}}: \longleftrightarrow :\ddot{\mathrm{O}}=\ddot{\mathrm{S}}=\ddot{\mathrm{O}}:$$

For each of these, the VSEPR model predicts a bent molecular geometry. Because the molecule is bent, the bond dipoles do not cancel, and the molecule is polar:



Experimentally, the dipole moment of SO_2 is $\mu = 1.63$ D.

(**c**) Fluorine is more electronegative than sulfur, so the bond dipoles point toward fluorine. For clarity, only one S—F dipole is shown. The six S—F bonds are arranged octahedrally around the central sulfur:



Because the octahedral molecular geometry is symmetrical, the bond dipoles cancel, and the molecule is nonpolar, meaning that $\mu = 0$.

PRACTICE EXERCISE

Determine whether the following molecules are polar or nonpolar: (**a**) NF_3, (**b**) BCl_3.

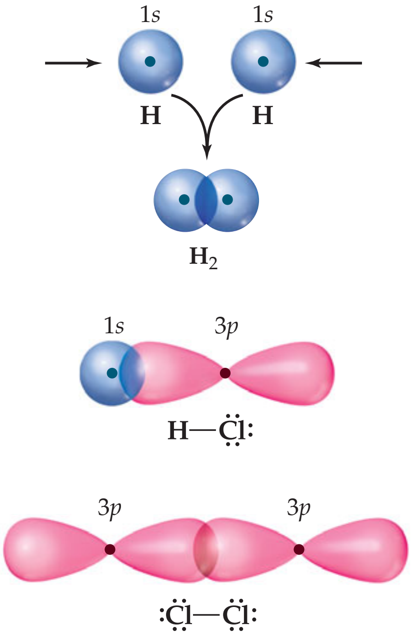
Answers: (**a**) polar because polar bonds are arranged in a trigonal-pyramidal geometry, (**b**) nonpolar because polar bonds are arranged in a trigonal-planar geometry

9.4 COVALENT BONDING AND ORBITAL OVERLAP

The VSEPR model provides a simple means for predicting molecular geometries but does not explain why bonds exist between atoms. In developing theories of covalent bonding, chemists have approached the problem from another direction, using quantum mechanics. How can we use atomic orbitals to explain bonding and to account for molecular geometries? The marriage of Lewis's notion of electron-pair bonds and the idea of atomic orbitals leads to a model of chemical bonding, called **valence-bond theory**, in which bonding electron pairs are concentrated in the regions between atoms and nonbonding electron pairs lie in directed regions of space. By extending this approach to include the ways in which atomic orbitals can mix with one another, we obtain an explanatory picture that corresponds to the VSEPR model.

In Lewis theory, covalent bonding occurs when atoms share electrons because the sharing concentrates electron density between the nuclei. In valence-bond theory, we visualize the buildup of electron density between two nuclei as occurring when a valence atomic orbital of one atom shares space, or *overlaps,* with a valence atomic orbital of another atom. The overlap of orbitals allows two electrons of opposite spin to share the space between the nuclei, forming a covalent bond.

The coming together of two H atoms to form H_2 is depicted in ▶ **FIGURE 9.13**. Each atom has a single electron in a 1*s* orbital. As the orbitals overlap, electron density is concentrated between the nuclei. Because the electrons in the overlap region are simultaneously attracted to both nuclei, they hold the atoms together, forming a covalent bond.



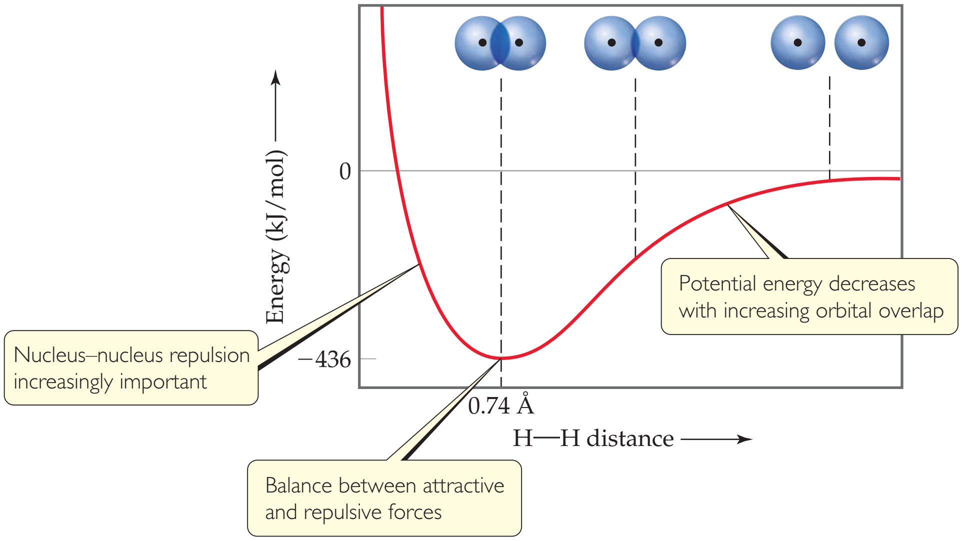
▲ **FIGURE 9.13 Covalent bonds in H_2, HCl, and Cl_2 result from overlap of atomic orbitals.**

The idea of orbital overlap producing a covalent bond applies equally well to other molecules. In HCl, for example, chlorine has the electron configuration $[Ne]3s^2 3p^5$. All the valence orbitals of chlorine are full except one 3*p* orbital, which contains a single electron. This 3*p* electron pairs with the single 1*s* electron of H to form a covalent bond (Figure 9.13). Because the other two chlorine 3*p* orbitals are already filled with a pair of electrons, they do not participate in the bonding to hydrogen. Likewise, we can explain the covalent bond in Cl_2 in terms of the overlap of the singly occupied 3*p* orbital of one Cl atom with the singly occupied 3*p* orbital of another.

There is always an optimum distance between the two nuclei in any covalent bond. ▶ **FIGURE 9.14** shows how the potential energy of a system consisting of two H atoms changes as the atoms come together to form an H_2 molecule. When the atoms are infinitely far apart, they do not "feel" each other and so the energy approaches zero. As the distance between the atoms decreases, the overlap between their 1*s* orbitals increases. Because of the resultant increase in electron density between the nuclei, the potential energy of the system decreases. That is, the strength of the bond increases, as shown by the decrease in the potential energy of the two-atom system. However, Figure 9.14 also shows that as the atoms come closer together than 0.74 Å, the energy increases sharply. This increase, which becomes significant at short internuclear distances, is due mainly to the electrostatic repulsion between the nuclei. The internuclear distance, or bond length, is the distance that corresponds to the minimum of the potential-energy curve. The potential energy at this minimum corresponds to the bond strength. Thus, the observed bond length is the distance at which the attractive forces between unlike charges (electrons and nuclei) are balanced by the repulsive forces between like charges (electron–electron and nucleus–nucleus).

GO FIGURE

On the left part of the curve the potential energy rises above zero. What causes this to happen?



▲ **FIGURE 9.14** **Formation of the H_2 molecule as atomic orbitals overlap.**

9.5 HYBRID ORBITALS

The VSEPR model, simple as it is, does a surprisingly good job at predicting molecular shape, despite the fact that it has no obvious relationship to the filling and shapes of atomic orbitals. For example, based on the shapes and orientations of the 2*s* and 2*p* orbitals on a carbon atom, it is not obvious why a CH_4 molecule should have a tetrahedral geometry. How can we reconcile the notion that covalent bonds are formed from overlap of atomic orbitals with the molecular geometries that come from the VSEPR model?

To begin with, we recall that atomic orbitals are mathematical functions that come from the quantum mechanical model for atomic structure. ∞ (Section 6.5) To explain molecular geometries, we can assume that the atomic orbitals on an atom (usually the central atom) mix to form new orbitals called **hybrid orbitals**. The shape of any hybrid orbital is different from the shapes of the original atomic orbitals. The process of mixing atomic orbitals is a mathematical operation called **hybridization**. The total number of atomic orbitals on an atom remains constant, so the number of hybrid orbitals on an atom equals the number of atomic orbitals that are mixed.

As we examine the common types of hybridization, notice the connection between the type of hybridization and certain of the molecular geometries predicted by the VSEPR model: linear, bent, trigonal planar, and tetrahedral.

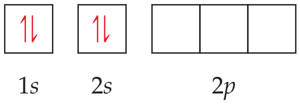
sp Hybrid Orbitals

To illustrate the process of hybridization, consider the BeF_2 molecule, which has the Lewis structure

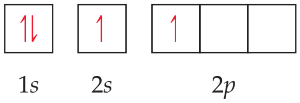

$$:\ddot{\underset{..}{F}}—Be—\ddot{\underset{..}{F}}:$$

The VSEPR model correctly predicts that BeF_2 is linear with two identical Be—F bonds. How can we use valence-bond theory to describe the bonding? The electron configuration of F ($1s^22s^22p^5$) indicates an unpaired electron in a 2*p* orbital. This electron can be paired with an unpaired Be electron to form a polar covalent bond. Which orbitals on the Be atom, however, overlap with those on the F atoms to form the Be—F bonds?

The orbital diagram for a ground-state Be atom is

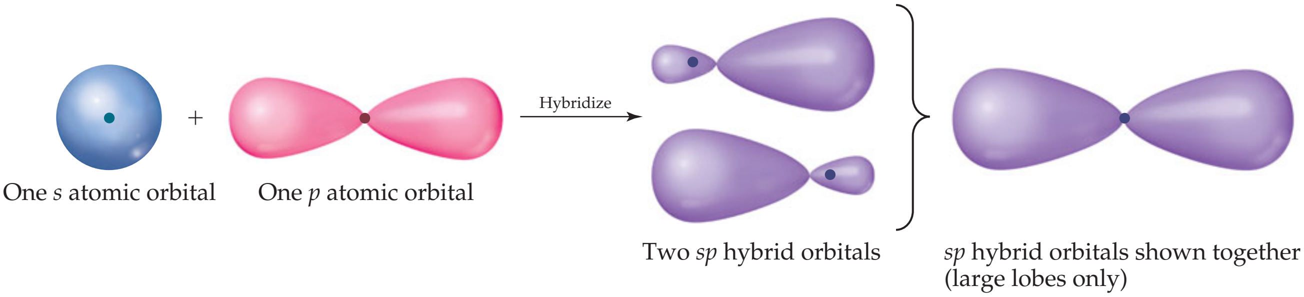


Because it has no unpaired electrons, the Be atom in its ground state cannot bond with the fluorine atoms. The Be atom could form two bonds, however, by "promoting" one of the 2*s* electrons to a 2*p* orbital:



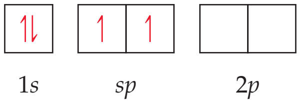
The Be atom now has two unpaired electrons and can therefore form two polar covalent bonds with F atoms. The two bonds would not be identical, however, because a Be 2*s* orbital would be used to form one of the bonds and a 2*p* orbital would be used to form the other. Therefore, although the promotion of an electron allows two Be—F bonds to form, we still have not explained the structure of BeF_2.

We can solve this dilemma by "mixing" the 2*s* orbital with one 2*p* orbital to generate two new orbitals, as shown in ▼ **FIGURE 9.15**. Like *p* orbitals, each new orbital has two lobes. Unlike *p* orbitals, however, one lobe is much larger than the other. The two new orbitals are identical in shape, but their large lobes point in opposite directions. These two new orbitals, which we color-code purple in Figure 9.15, are hybrid orbitals. Because we have hybridized one *s* and one *p* orbital, we call each hybrid an *sp* hybrid orbital. *According to the valence-bond model, a linear arrangement of electron domains implies* sp *hybridization.*



▲ **FIGURE 9.15 Formation of *sp* hybrid orbitals.**

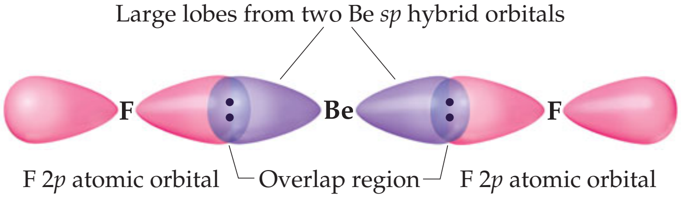
For the Be atom of BeF_2, we write the orbital diagram for the formation of two *sp* hybrid orbitals as



The electrons in the *sp* hybrid orbitals can form bonds with the two fluorine atoms (▼ **FIGURE 9.16**). Because the *sp* hybrid orbitals are equivalent but point in opposite

GO FIGURE

Why is it reasonable to take account of only the large lobes of the Be hybrid orbitals in considering the bonding to F?



◀ **FIGURE 9.16 Formation of two equivalent Be—F bonds in BeF_2.**

directions, BeF_2 has two identical bonds and a linear geometry. The remaining two 2*p* atomic orbitals of Be remain unhybridized and are vacant. Remember also that each fluorine atom has two other valence *p* atomic orbitals, each containing one nonbonding electron pair. Those atomic orbitals are omitted from Figure 9.16 to keep the illustration simpler.

GIVE IT SOME THOUGHT

What is the orientation of the two unhybridized *p* orbitals on Be with respect to the two Be—F bonds?

sp^2 and sp^3 Hybrid Orbitals

Whenever we mix a certain number of atomic orbitals, we get the same number of hybrid orbitals. Each hybrid orbital is equivalent to the others but points in a different direction. Thus, mixing one 2*s* and one 2*p* atomic orbital yields two equivalent *sp* hybrid orbitals that point in opposite directions (Figure 9.15). Other combinations of atomic orbitals can be hybridized to obtain different geometries. In BF_3, for example, mixing the 2*s* and two of the 2*p* atomic orbitals yields three equivalent sp^2 (pronounced "*s-p*-two") hybrid orbitals (▼ **FIGURE 9.17**).

The three sp^2 hybrid orbitals lie in the same plane, 120° apart from one another. They are used to make three equivalent bonds with the three fluorine atoms, leading to the trigonal-planar molecular geometry of BF_3. Notice that an unfilled 2*p* atomic orbital remains unhybridized. This unhybridized orbital will be important when we discuss double bonds in Section 9.6.

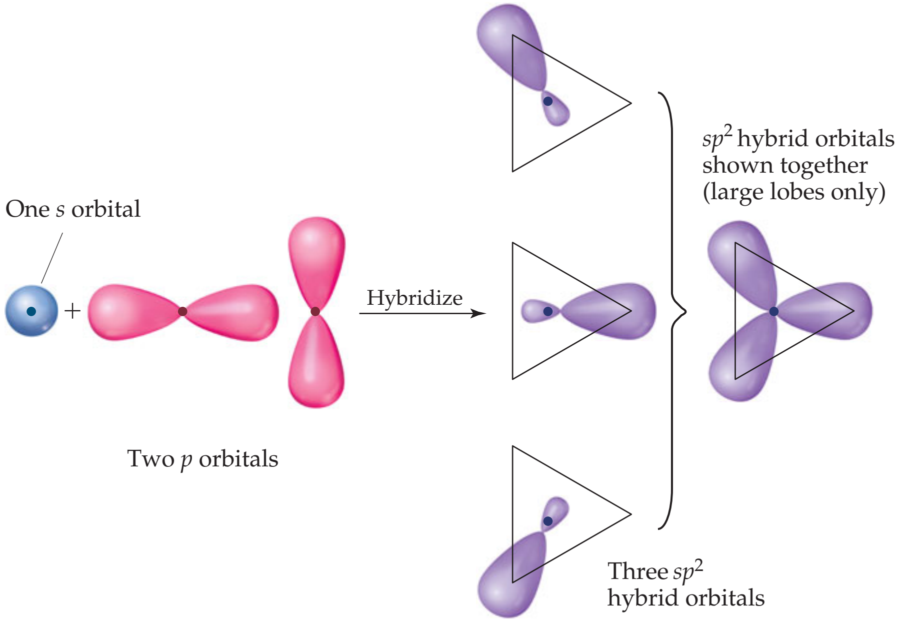
GIVE IT SOME THOUGHT

In an sp^2 hybridized atom, what is the orientation of the unhybridized *p* atomic orbital relative to the three sp^2 hybrid orbitals?

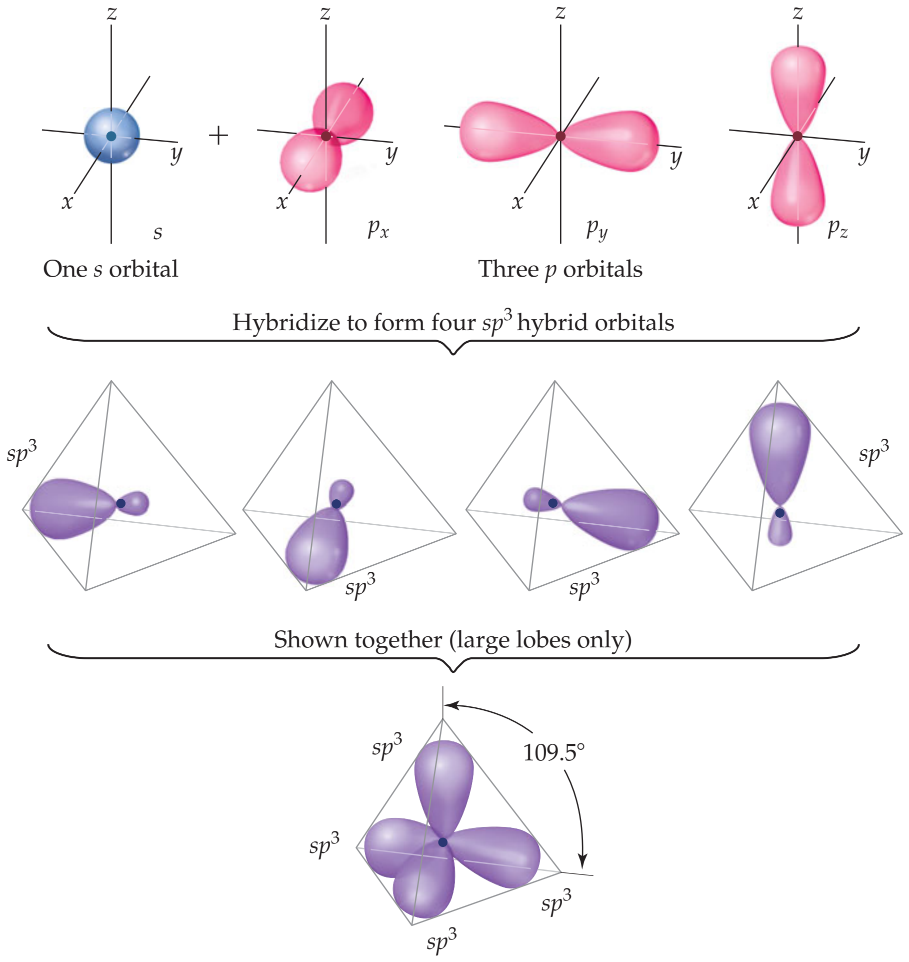
An *s* atomic orbital can also mix with all three *p* atomic orbitals in the same subshell. For example, the carbon atom in CH_4 forms four equivalent bonds with the four

GO FIGURE.

How many atomic orbitals contribute to form the three sp^2 hybrid orbitals?



▶ **FIGURE 9.17 Formation of sp^2 hybrid orbitals.**



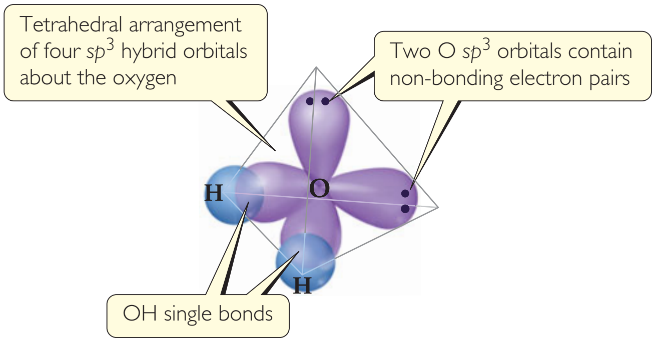
◀ **FIGURE 9.18 Formation of sp^3 hybrid orbitals.**

hydrogen atoms. We envision this process as resulting from the mixing of the 2*s* and all three 2*p* atomic orbitals of carbon to create four equivalent sp^3 (pronounced "*s*-*p*-three") hybrid orbitals. Each sp^3 hybrid orbital has a large lobe that points toward one vertex of a tetrahedron (▲ **FIGURE 9.18**). These hybrid orbitals can be used to form two-electron bonds by overlap with the atomic orbitals of another atom, such as H. Using valence-bond theory, we can describe the bonding in CH_4 as the overlap of four equivalent sp^3 hybrid orbitals on C with the 1*s* orbitals of the four H atoms to form four equivalent bonds.

The idea of hybridization is also used to describe the bonding in molecules containing nonbonding pairs of electrons. In H_2O, for example, the electron-domain geometry around the central O atom is approximately tetrahedral (▶ **FIGURE 9.19**). Thus, the four electron pairs can be envisioned as occupying sp^3 hybrid orbitals. Two of the hybrid orbitals contain nonbonding pairs of electrons, and the other two form bonds with the hydrogen atoms.

So far our discussion of hybridization has extended only to period 2 elements, specifically carbon, nitrogen, and oxygen. The elements of period 3 and beyond introduce a new consideration because in many of their compounds these elements have more than an octet of electrons in the valence shell, as we saw in Section 9.2. How do we analyze the bonding in compounds such as PCl_5, SF_6, or BrF_5? The use of only *s* and *p* orbitals on the central atom limits us to four hybrid orbitals, yet in these compounds the central atom is involved in bonding to five or six other atoms.

For such elements, the number of hybrid orbitals formed could be increased by including valence-shell *d* orbitals. For example, to explain the bonding in SF_6 we could include two sulfur 3*d* orbitals



▲ **FIGURE 9.19 Hybrid orbital description of H_2O.**

in addition to the *3s* and three *3p* orbitals. These six atomic orbitals could make six hybrid orbitals, but there is more involved in hybridization than simply finding a set of orbitals that point in the right directions; we must also consider orbital energies. The sulfur *3d* orbitals lie substantially higher in energy than the *3s* and *3p* orbitals. The amount of energy needed to form the six hybrid orbitals is greater than the amount returned by forming bonds with the six fluorine atoms. Theoretical calculations seem to show that the sulfur *3d* orbitals do not participate to a significant degree in the bonding between sulfur and the six fluorine atoms.

The valence-bond model we have developed for period 2 elements works well for compounds of period 3 elements so long as we have no more than an octet of electrons in the valence-shell orbitals. Thus, for example, it is appropriate to discuss the bonding in PF_3 or H_2Se in terms of hybrid *s* and *p* orbitals on the central atom. However, the model turns out not to be appropriate when there is more than an octet of electrons about the central atom. How then do we account for the bonding in SF_6 and other compounds of the main group elements in which the central atom has more than an octet of valence electrons? To address that question from the viewpoint of bonding theory requires a treatment beyond the scope of a general chemistry text. Fortunately, the VSEPR model, although it does not explain the bonding in such molecules, can accurately predict their geometries.

This discussion points up the important fact that models in science are not reality but rather are our attempts to describe aspects of reality that we have been able to measure, such as bond distances, bond energies, molecular geometries, and so on. A model may work well up to a certain point but not beyond it, as with the idea of hybrid orbitals. The hybrid orbital model for period 2 elements has proven very useful and is an essential part of any modern discussion of bonding and molecular geometry in organic chemistry. When it comes to substances such as SF_6, however, we encounter the limitations of the model.

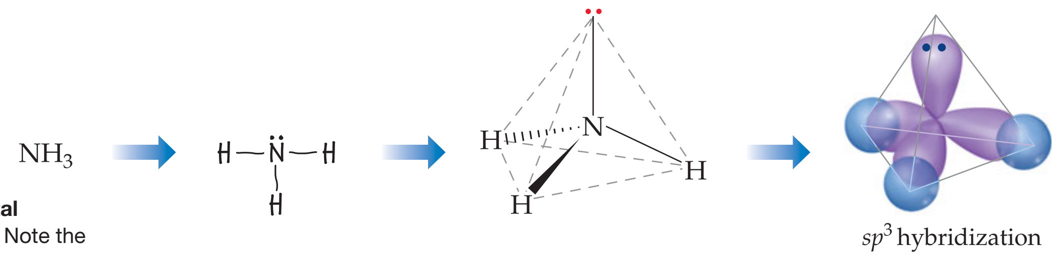
Hybrid Orbital Summary

Overall, hybrid orbitals provide a convenient model for using valence-bond theory to describe covalent bonds in molecules in which the molecular geometry conforms to the electron-domain geometry predicted by the VSEPR model. The picture of hybrid orbitals has limited predictive value. When we know the electron-domain geometry, however, we can employ hybridization to describe the atomic orbitals used by the central atom in bonding.

The following steps allow us to describe the hybrid orbitals used by an atom in bonding:

1. Draw the *Lewis structure* for the molecule or ion.
2. Use the VSEPR model to determine the electron-domain geometry around the central atom.
3. Specify the *hybrid orbitals* needed to accommodate the electron pairs based on their geometric arrangement (▶ **TABLE 9.4**).

These steps are illustrated in ▼ **FIGURE 9.20**, which shows how the hybridization at N in NH_3 is determined.



sp^3 hybridization

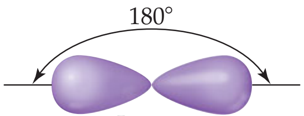
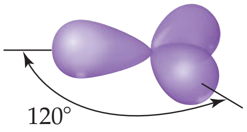
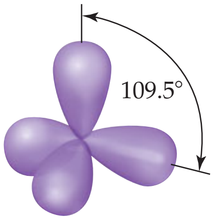
1. Draw Lewis structure

2. Determine electron-domain geometry about central atom from VSEPR model and Table 9.1

3. Using Table 9.4, select sp^3 hybrid orbital set

▶ **FIGURE 9.20 Hybrid orbital description of bonding in NH_3.** Note the comparison with Figure 9.6. Here we focus on the hybrid orbitals used to make bonds and hold nonbonding electron pairs.

TABLE 9.4 • Geometric Arrangements Characteristic of Hybrid Orbital Sets

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two *sp*	 Linear	BeF_2, $HgCl_2$
s,p,p	Three sp^2	 Trigonal planar	BF_3, SO_3
s,p,p,p	Four sp^3	 Tetrahedral	CH_4, NH_3, H_2O, NH_4^+

SAMPLE EXERCISE 9.5 Hybridization

Indicate the orbital hybridization around the central atom in NH_2^-.

SOLUTION

Analyze We are given the chemical formula for a polyatomic anion and asked to describe the type of hybrid orbitals surrounding the central atom.

Plan To determine the central atom hybrid orbitals, we must know the electron-domain geometry around the atom. Thus, we draw the Lewis structure to determine the number of electron domains around the central atom. The hybridization conforms to the number and geometry of electron domains around the central atom as predicted by the VSEPR model.

Solve The Lewis structure is

$$\left[\mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{N}}}:\mathrm{H}\right]^-$$

Because there are four electron domains around N, the electron-domain geometry is tetrahedral. The hybridization that gives a tetrahedral electron-domain geometry is sp^3 (Table 9.4). Two of the sp^3 hybrid orbitals contain nonbonding pairs of electrons, and the other two are used to make bonds with the hydrogen atoms.

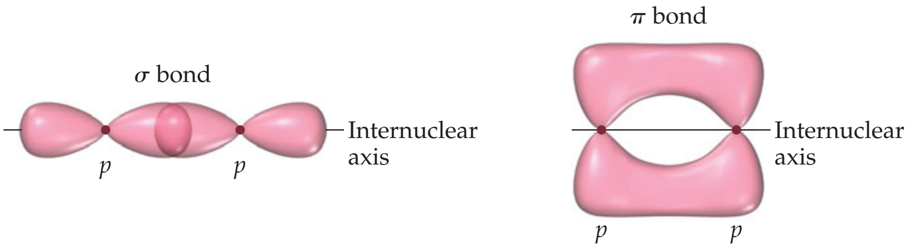
PRACTICE EXERCISE

Predict the electron-domain geometry and hybridization of the central atom in SO_3^{2-}.

Answer: tetrahedral, sp^3

9.6 | MULTIPLE BONDS

In the covalent bonds we have considered thus far, the electron density is concentrated along the line connecting the nuclei (the *internuclear axis*). In other words, the line joining the two nuclei passes through the middle of the overlap region. These bonds are called **sigma (σ) bonds.** The overlap of two *s* orbitals in H_2, the overlap of an *s* and a *p*

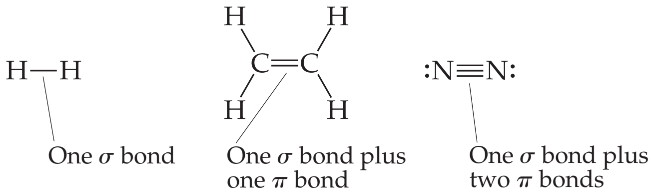


▶ **FIGURE 9.21 Comparison of σ and π bonds.** Note that the two regions of overlap in the π bond, above and below the internuclear axis, constitute a *single* π bond.

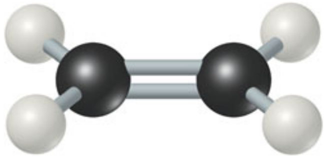
orbital in HCl, the overlap of two *p* orbitals in Cl_2 (all shown in Figure 9.13), and the overlap of a *p* orbital and an *sp* hybrid orbital in BeF_2 (Figure 9.16) are all σ bonds.

To describe multiple bonding, we must consider a second kind of bond, this one the result of overlap between two *p* orbitals oriented perpendicularly to the internuclear axis (▲ **FIGURE 9.21**). This sideways overlap of *p* orbitals produces a **pi (π) bond**. A π bond is one in which the overlap regions lie above and below the internuclear axis. Unlike in a σ bond, in a π bond the electron density is not concentrated on the internuclear axis. Although it is not evident in Figure 9.21, the sideways orientation of *p* orbitals in a π bond makes for weaker overlap. As a result, π bonds are generally weaker than σ bonds.

In almost all cases, single bonds are σ bonds. A double bond consists of one σ bond and one π bond, and a triple bond consists of one σ bond and two π bonds:



To see how these ideas are used, consider ethylene (C_2H_4), which has a C=C double bond. As illustrated by the ball-and-stick model of ◀ **FIGURE 9.22**, the three bond angles about each carbon are all approximately 120°, suggesting that each carbon atom uses sp^2 hybrid orbitals (Figure 9.17) to form σ bonds with the other carbon and with two hydrogens. Because carbon has four valence electrons, after sp^2 hybridization one electron in each carbon remains in the unhybridized 2*p* orbital, which is directed perpendicular to the plane that contains the three sp^2 hybrid orbitals.



▲ **FIGURE 9.22 Trigonal-planar molecular geometry of ethylene.** The double bond is made up of one C—C σ bond and one C—C π bond.

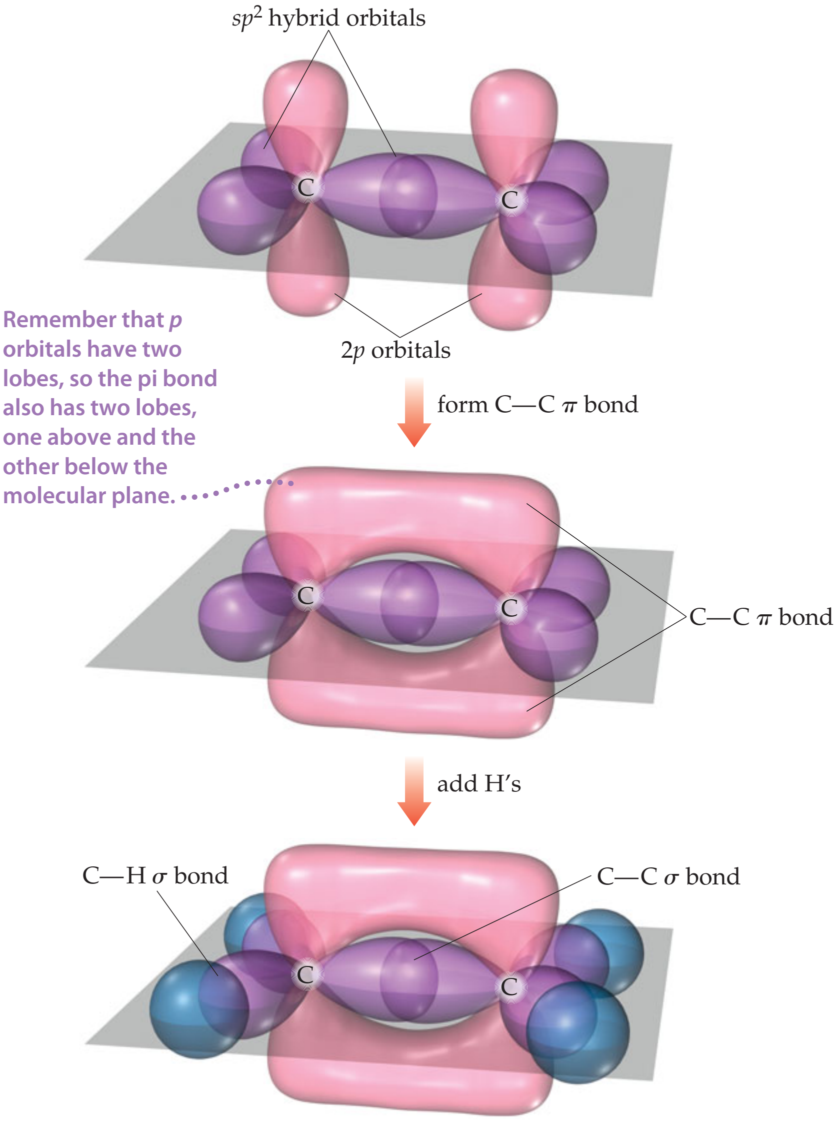
Each sp^2 hybrid orbital on a carbon atom contains one electron. ▶ **FIGURE 9.23** shows how the C—H σ bonds are formed by overlap of sp^2 hybrid orbitals on C with the 1*s* orbitals on each H atom. We use eight electrons to form these four C—H bonds. The C—C σ bond is formed by the overlap of two sp^2 hybrid orbitals, one on each carbon atom, and requires two more electrons. Thus, ten of the 12 valence electrons in the C_2H_4 molecule are used to form five σ bonds.

The remaining two valence electrons reside in the unhybridized 2*p* orbitals, one electron on each carbon. These two orbitals can overlap sideways with each other, as shown in Figure 9.23. The resultant electron density is concentrated above and below the C—C bond axis, which means this is a π bond (Figure 9.21). Thus, the C=C double bond in ethylene consists of one σ bond and one π bond. You should note one point about the carbon *p* orbitals that form the π bond. It appears from Figure 9.21 that the *p* orbitals on the two carbons don't overlap sufficiently to form a π bond. The problem is that we can't show the true extent of overlap in the drawing without obscuring other aspects of the figure. Although π bonding of the *p* orbitals does occur, as pointed out earlier, π bonds are generally weaker than σ bonds.

Although we cannot experimentally observe a π bond directly (all we can observe are the positions of the atoms), the structure of ethylene provides strong support for its presence. First, the C—C bond length in ethylene (1.34 Å) is much shorter than in compounds with C—C single bonds (1.54 Å), consistent with the presence of a stronger C=C double bond. Second, all six atoms in C_2H_4 lie in the same plane. The 2*p* orbitals that make up the π bond can achieve a good overlap only when the two CH_2

GO FIGURE

Why is it important that the *sp*^{2} hybrid orbitals of the two carbon atoms lie in the same plane?



◀ FIGURE 9.23 The orbital structure of ethylene.

fragments lie in the same plane. If the π bond were absent, there would be no reason for the two CH_2 fragments to lie in the same plane. Because π bonds require that portions of a molecule be planar, they can introduce rigidity into molecules.

GIVE IT SOME THOUGHT

The molecule called *diazine* has the formula N_2H_2 and the Lewis structure

$$H-\ddot{N}=\ddot{N}-H$$

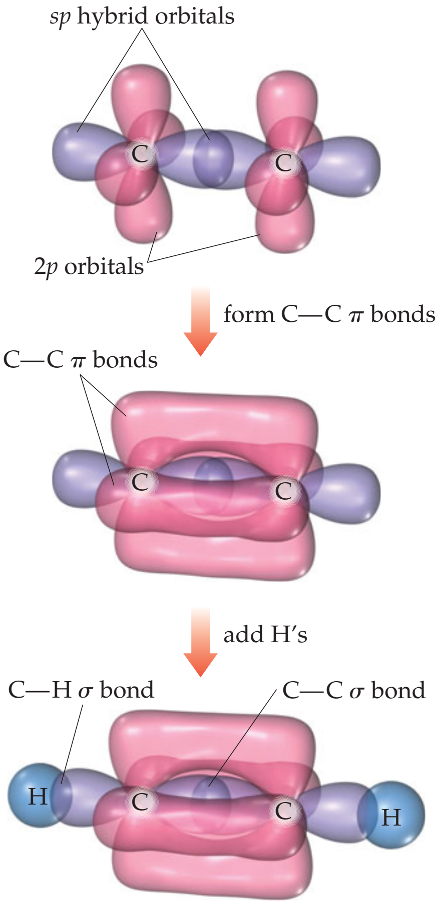
Do you expect diazine to be a linear molecule (all four atoms on the same line)? If not, do you expect the molecule to be planar (all four atoms in the same plane)?

Triple bonds can also be explained using hybrid orbitals. Acetylene (C_2H_2), for example, is a linear molecule containing a triple bond: $H-C\equiv C-H$. The linear geometry suggests that each carbon atom uses *sp* hybrid orbitals to form σ bonds with the other carbon and one hydrogen. Each carbon atom thus has two unhybridized $2p$ orbitals at right angles to each other and to the axis of the sp hybrid set (◀ **FIGURE 9.24**). These p orbitals overlap to form a pair of π bonds. Thus, the triple bond in acetylene consists of one σ bond and two π bonds.

Although it is possible to make π bonds from d orbitals, the only π bonds we will consider are those formed by the overlap of p orbitals. These π bonds can form only if unhybridized p orbitals are present on the bonded atoms. Therefore, only atoms having sp or sp^2 hybridization can form π bonds. Further, double and triple bonds (and hence π bonds) are more common in molecules made up of period 2 atoms, especially C, N, and O. Larger atoms, such as S, P, and Si, form π bonds less readily.

GO FIGURE

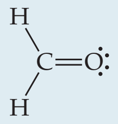
Based on the models of bonding in ethylene and acetylene, which molecule should have the higher carbon–carbon bond energy?



▲ **FIGURE 9.24 Formation of two π bonds in acetylene, C_2H_2.**

SAMPLE EXERCISE 9.6 Describing σ and π Bonds in a Molecule

Formaldehyde has the Lewis structure



Describe how the bonds in formaldehyde are formed in terms of overlaps of hybrid and unhybridized orbitals.

SOLUTION

Analyze We are asked to describe the bonding in formaldehyde in terms of hybrid orbitals.

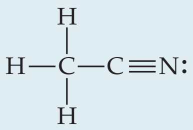
Plan Single bonds are σ bonds, and double bonds consist of one σ bond and one π bond. The ways in which these bonds form can be deduced from the molecular geometry, which we predict using the VSEPR model.

Solve The C atom has three electron domains around it, which suggests a trigonal-planar geometry with bond angles of about 120°. This geometry implies sp^2 hybrid orbitals on C (Table 9.4). These hybrids are used to make the two C—H and one C—O σ bonds to C. There remains an unhybridized $2p$ orbital on carbon, perpendicular to the plane of the three sp^2 hybrids.

The O atom also has three electron domains around it, and so we assume it has sp^2 hybridization as well. One of these hybrid orbitals participates in the C—O σ bond, while the other two hold the two nonbonding electron pairs of the O atom. Like the C atom, therefore, the O atom has an unhybridized $2p$ orbital that is perpendicular to the plane of the molecule. These two orbitals overlap to form a C—O π bond (▼ **FIGURE 9.25**).

PRACTICE EXERCISE

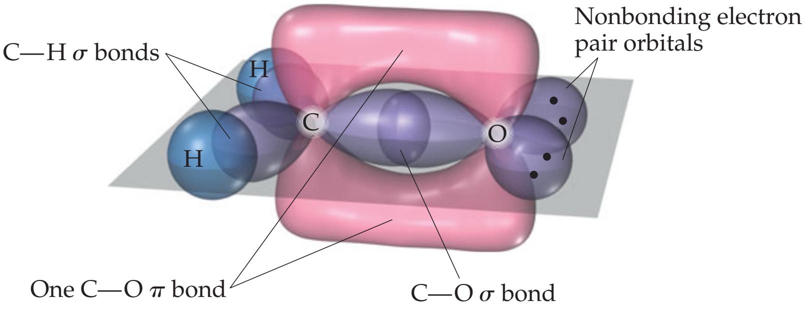
(a) Predict the bond angles around each carbon atom in acetonitrile:



$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H{-}\overset{}{C}{-}C{\equiv}N{:}}\\ |\\ \mathrm{H}\end{array}$$

(b) Describe the hybridization at each carbon atom, and **(c)** determine the number of σ and π bonds in the molecule.

Answers: **(a)** approximately 109° around the left C and 180° around the right C; **(b)** sp^3, sp; **(c)** five σ bonds and two π bonds

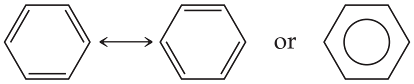


▶ **FIGURE 9.25 Formation of σ and π bonds in formaldehyde, H_2CO.**

Resonance Structures, Delocalization, and π Bonding

In the molecules we have discussed thus far in this section, the bonding electrons are *localized*. By this we mean that the σ and π electrons are associated totally with the two atoms that form the bond. In many molecules, however, we cannot adequately describe the bonding as being entirely localized. This situation arises particularly in molecules that have two or more resonance structures involving π bonds.

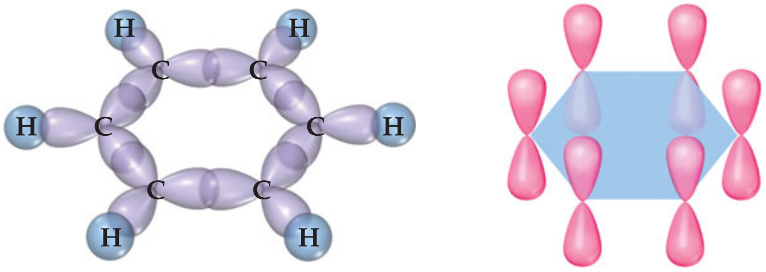
One molecule that cannot be described with localized π bonds is benzene (C_6H_6), which has two resonance structures: ∞ (Section 8.6)



To describe the bonding in benzene using hybrid orbitals, we first choose a hybridization scheme consistent with the geometry of the molecule. Because each carbon is surrounded by three atoms at 120° angles, the appropriate hybrid set is sp^2. Six localized C—C σ bonds and six localized C—H σ bonds are formed from the sp^2 hybrid orbitals, as shown in ▼ **FIGURE 9.26**(a). This leaves on each carbon a 2*p* orbital oriented perpendicular to the plane of the molecule. The situation is very much like that in ethylene except we now have six carbon 2*p* orbitals arranged in a ring [Figure 9.26(b)]. Each unhybridized 2*p* orbital is occupied by one electron, leaving six electrons to be accounted for by π bonding.

GO FIGURE

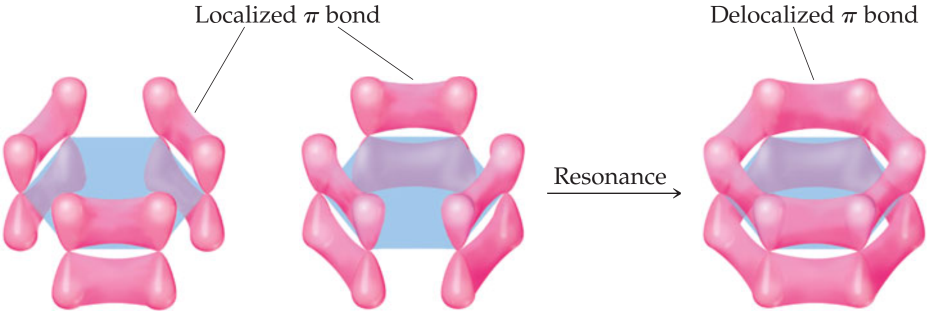
What are the two kinds of σ bonds found in benzene?



(a) σ bonds (b) 2*p* atomic orbitals

◀ **FIGURE 9.26** **σ and π bond networks in benzene, C_6H_6.** (a) The σ bond framework. (b) The π bonds are formed from overlap of the unhybridized 2*p* orbitals on the six carbon atoms.

We could envision using the unhybridized 2*p* orbitals to form three localized π bonds. As shown in ▼ **FIGURE 9.27**, there are two equivalent ways to make these localized bonds, each corresponding to one resonance structure. However, a representation that reflects *both* resonance structures has the six π electrons "smeared out" among all six carbon atoms, as shown on the right in Figure 9.27. Notice how this combined representation corresponds to the circle-in-a-hexagon drawing we often use to represent benzene. This model leads us to predict that all the carbon–carbon bond lengths will be identical, with a bond length between that of a C—C single bond (1.54 Å) and that of a C═C double bond (1.34 Å). This prediction is consistent with the observed carbon–carbon bond length in benzene (1.40 Å).



◀ **FIGURE 9.27** **Delocalized π bonds in benzene.**

Because we cannot describe the π bonds in benzene as individual bonds between neighboring atoms, we say that the π bonds are **delocalized** among the six carbon atoms. Delocalization of the electrons in its π bonds gives benzene a special stability. Delocalization of π bonds is also responsible for the color of many organic molecules. A final important point to remember about delocalized π bonds is the constraint they place on the geometry of a molecule. For optimal overlap of the unhybridized *p* orbitals, all the atoms involved in a delocalized π bonding network should lie in the same plane. This restriction imparts a certain rigidity to the molecule that is absent in molecules containing only σ bonds (see the "Chemistry and Life" box on vision).

If you take a course in organic chemistry, you will see many examples of how electron delocalization influences the properties of organic molecules.

SAMPLE EXERCISE 9.7 Delocalized Bonding

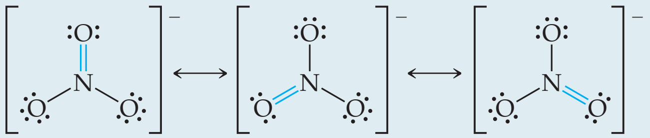
Describe the bonding in the nitrate ion, NO_3^-. Does this ion have delocalized π bonds?

SOLUTION

Analyze Given the chemical formula for a polyatomic anion, we are asked to describe the bonding and determine whether the ion has delocalized π bonds.

Plan Our first step is to draw Lewis structures. Multiple resonance structures involving the placement of the double bonds in different locations suggest that the π component of the double bonds is delocalized.

Solve In Section 8.6 we saw that NO_3^- has three resonance structures:



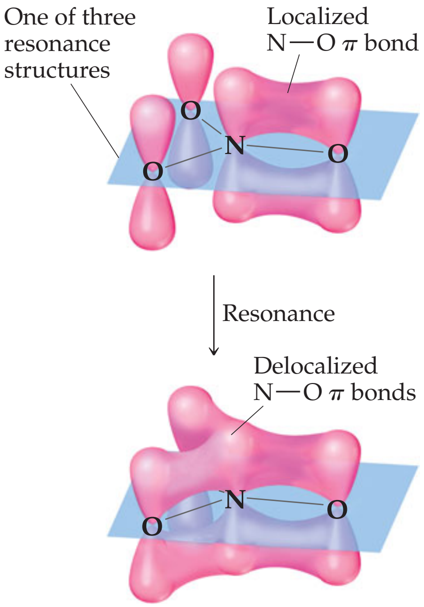
In each structure, the electron-domain geometry at nitrogen is trigonal planar, which implies sp^2 hybridization of the N atom. The sp^2 hybrid orbitals are used to construct the three N—O σ bonds present in each resonance structure.

The unhybridized 2*p* orbital on the N atom can be used to make π bonds. For any one of the three resonance structures shown, we might imagine a single localized N—O π bond formed by the overlap of the unhybridized 2*p* orbital on N and a 2*p* orbital on one of the O atoms, as shown in ◀ **FIGURE 9.28**. Because each resonance structure contributes equally to the observed structure of NO_3^-, however, we represent the π bonding as delocalized over the three N—O bonds, as shown in the figure.

PRACTICE EXERCISE

Which of these species have delocalized bonding: SO_3, SO_3^{2-}, H_2CO, O_3, NH_4^+?

Answer: SO_3 and O_3, as indicated by the presence of two or more resonance structures involving π bonding for each of these molecules



▲ **FIGURE 9.28 Localized and delocalized π bonds in NO_3^-.**

General Conclusions

On the basis of the examples we have seen, we can draw a few helpful conclusions for using hybrid orbitals to describe molecular structures:

1. Every pair of bonded atoms shares one or more pairs of electrons. The lines we draw in Lewis structures represent two electrons each. In every bond at least one pair of electrons is localized in the space between the atoms in a σ bond. The appropriate set of hybrid orbitals used to form the σ bonds between an atom and its neighbors is determined by the observed geometry of the molecule. The correlation between the set of hybrid orbitals and the geometry about an atom is given in Table 9.4.
2. The electrons in σ bonds are localized in the region between two bonded atoms and do not make a significant contribution to the bonding between any other two atoms.
3. When atoms share more than one pair of electrons, one pair is used to form a σ bond; the additional pairs form π bonds. The centers of charge density in a π bond lie above and below the internuclear axis.

4. Molecules with two or more resonance structures can have π bonds that extend over more than two bonded atoms. Electrons in π bonds that extend over more than two atoms are said to be "delocalized."

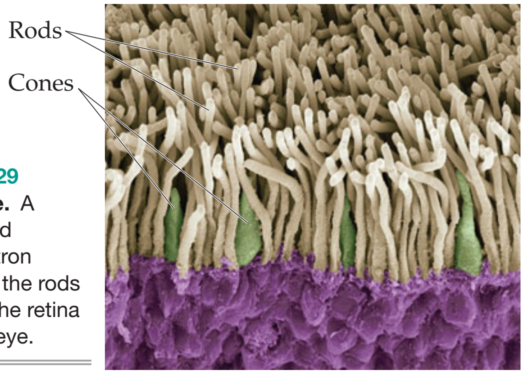
CHEMISTRY AND LIFE

THE CHEMISTRY OF VISION

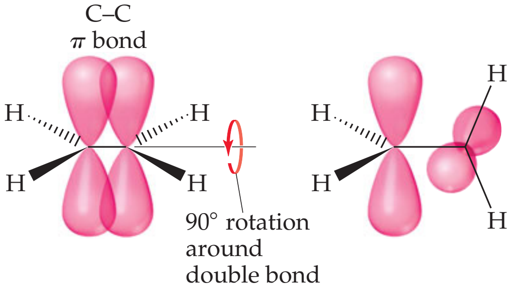
Vision begins when light is focused by the lens of the eye onto the retina, the layer of cells lining the interior of the eyeball. The retina contains *photoreceptor* cells called rods and cones (▼ **FIGURE 9.29**). The rods are sensitive to dim light and are used in night vision. The cones are sensitive to colors. The tops of the rods and cones contain a molecule called *rhodopsin,* which consists of a protein, *opsin,* bonded to a reddish purple pigment called *retinal.* Structural changes around a double bond in the retinal portion of the molecule trigger a series of chemical reactions that result in vision.

We know that a double bond between two atoms is stronger than a single bond between the same atom, but our recent discussions allow us to appreciate another aspect of double bonds: the rigidity they introduce into molecules.

Imagine rotating one —CH_2 group in ethylene relative to the other —CH_2 group, as in ▶ **FIGURE 9.30**. This rotation destroys the overlap of p orbitals, breaking the π bond, a process that requires considerable energy. Thus, the presence of a double bond restricts bond rotation in a molecule. In contrast, molecules can rotate almost freely around the bond axis in single (σ) bonds because this motion has no effect on the orbital overlap for a σ bond. This rotation allows molecules with single bonds to twist and fold almost as if their atoms were attached by hinges.



▶ **FIGURE 9.29** **Inside the eye.** A color-enhanced scanning electron micrograph of the rods and cones in the retina of the human eye.

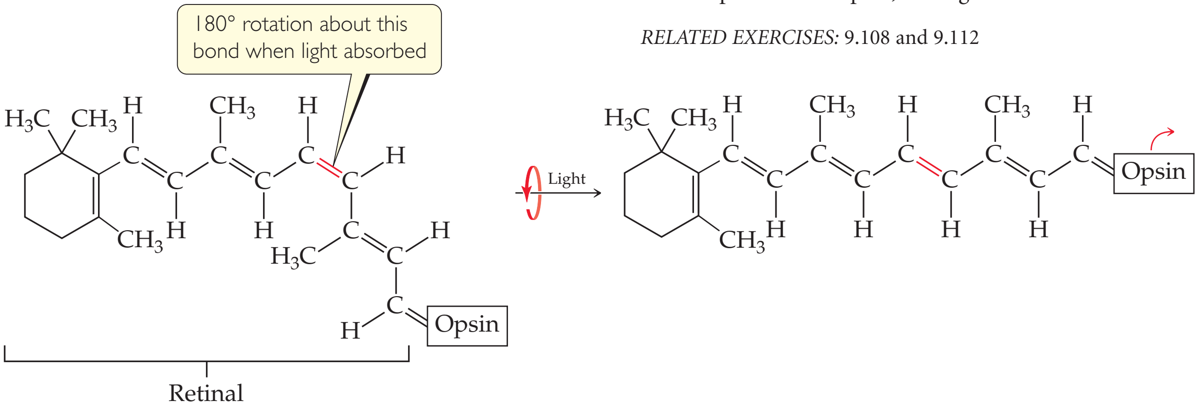


▲ **FIGURE 9.30** **Rotation about the carbon–carbon double bond in ethylene breaks the π bond.**

Our vision depends on the rigidity of double bonds in retinal. In its normal form, retinal is held rigid by its double bonds. Light entering the eye is absorbed by rhodopsin, and the energy is used to break the π-bond portion of the double bond shown in red in ▼ **FIGURE 9.31**. The molecule then rotates around this bond, changing its geometry. The retinal then separates from the opsin, triggering the reactions that produce a nerve impulse that the brain interprets as the sensation of vision. It takes as few as five closely spaced molecules reacting in this fashion to produce the sensation of vision. Thus, only five photons of light are necessary to stimulate the eye.

The retinal slowly reverts to its original form and reattaches to the opsin. The slowness of this process helps explain why intense bright light causes temporary blindness. The light causes all the retinal to separate from opsin, leaving no molecules to absorb light.

RELATED EXERCISES: 9.108 and 9.112



▲ **FIGURE 9.31** **The rhodopsin molecule, the chemical basis of vision.** When rhodopsin absorbs visible light, the π component of the double bond shown in red breaks, allowing rotation that produces a change in molecular geometry before the π bond re-forms.

GIVE IT SOME THOUGHT

When two atoms are bonded by a triple bond, what is the hybridization of the orbitals that make up the σ-bond component of the bond?

9.7 | MOLECULAR ORBITALS

Valence-bond theory and hybrid orbitals allow us to move in a straightforward way from Lewis structures to rationalizing the observed geometries of molecules in terms of atomic orbitals. The valence-bond model, however, does not explain all aspects of bonding. It is not successful, for example, in describing the excited states of molecules, which we must understand to explain how molecules absorb light, giving them color.

Some aspects of bonding are better explained by a more sophisticated model called **molecular orbital theory**. In Chapter 6 we saw that electrons in atoms can be described by wave functions, which we call atomic orbitals. In a similar way, molecular orbital theory describes the electrons in molecules by using specific wave functions called **molecular orbitals (MO)**.

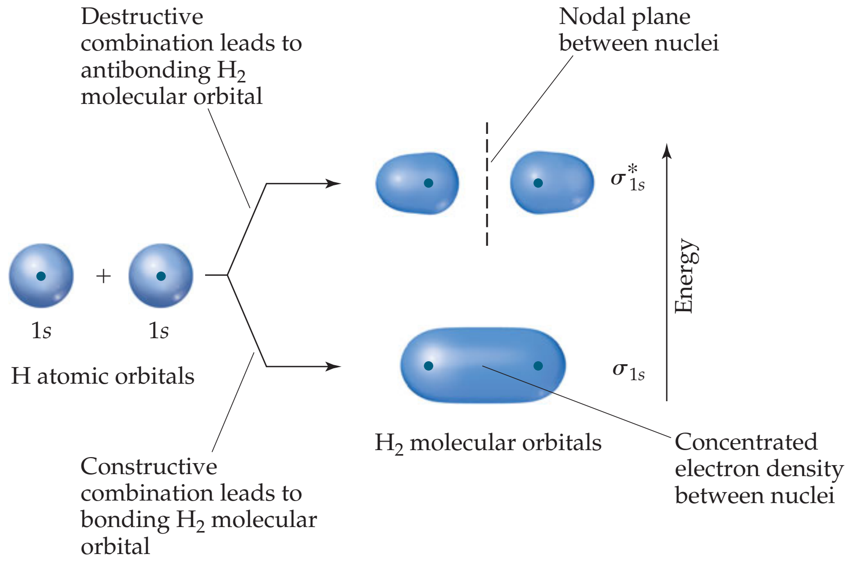
Molecular orbitals have many of the same characteristics as atomic orbitals. For example, an MO can hold a maximum of two electrons (with opposite spins), it has a definite energy, and we can visualize its electron-density distribution by using a contour representation, as we did with atomic orbitals. Unlike atomic orbitals, however, MOs are associated with an entire molecule, not with a single atom.

The Hydrogen Molecule

We begin our study of MO theory with the hydrogen molecule, H_2. *Whenever two atomic orbitals overlap, two molecular orbitals form*. Thus, the overlap of the 1*s* orbitals of two hydrogen atoms to form H_2 produces two MOs (▼ **FIGURE 9.32**). One MO is formed by adding the wave functions for the two 1*s* orbitals. We refer to this as *constructive combination*. The energy of the resulting MO is lower than the energy of the two atomic orbitals from which it was made. It is called the **bonding molecular orbital**.

The other MO is formed by combining the two atomic orbitals in a way that causes the electron density to be more or less canceled in the central region where the two overlap. We refer to this as *destructive combination*. The process is discussed more fully in the "Closer Look" box later in the chapter; we don't need to concern ourselves with it to understand molecular orbital bond formation. The energy of the resulting MO, referred to as the **antibonding molecular orbital**, is higher than the energy of the atomic orbitals.

As illustrated in Figure 9.32, in the bonding MO electron density is concentrated in the region between the two nuclei. This sausage-shaped MO results from summing the



► **FIGURE 9.32** **The two molecular orbitals of H_2, one a bonding MO and one an antibonding MO.**

two atomic orbitals so that the atomic orbital wave functions combine in the region between the two nuclei. Because an electron in this MO is attracted to both nuclei, the electron is more stable (it has lower energy) than it is in the 1*s* atomic orbital of an isolated hydrogen atom. Further, because this bonding MO concentrates electron density between the nuclei, it holds the atoms together in a covalent bond.

By contrast, the antibonding MO has very little electron density between the nuclei. Instead of combining in the region between the nuclei, the atomic orbital wave functions cancel each other in this region, leaving the greatest electron density on opposite sides of the two nuclei. Thus, this MO excludes electrons from the very region in which a bond must be formed. Antibonding orbitals invariably have a nodal plane in the region between the nuclei, where the electron density is zero. (The nodal plane is shown as a dashed line in Figure 9.32 and subsequent figures.) An electron in an antibonding MO is repelled from the bonding region and is therefore less stable (it has higher energy) than it is in the 1*s* atomic orbital of a hydrogen atom.

Notice from Figure 9.32 that the electron density in both the bonding MO and the antibonding MO of H_2 is centered about the internuclear axis. MOs of this type are called **sigma (σ) molecular orbitals** (by analogy to σ bonds). The bonding sigma MO of H_2 is labeled σ_{1s}; the subscript indicates that the MO is formed from two 1*s* orbitals. The antibonding sigma MO of H_2 is labeled $\sigma^{\star}_{1s}$ (read "sigma-star-one-*s*"); the asterisk denotes that the MO is antibonding.

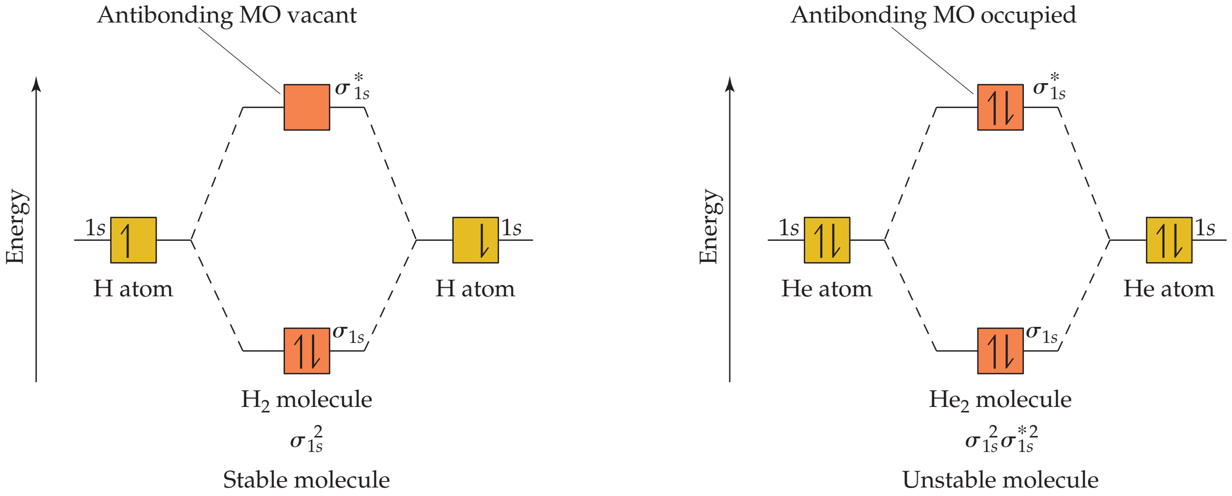
The relative energies of two 1*s* atomic orbitals and the molecular orbitals formed from them are represented by an **energy-level diagram** (also called a **molecular orbital diagram**). Such diagrams show the interacting atomic orbitals on the left and right and the MOs in the middle, as shown in ▼ **FIGURE 9.33**. Like atomic orbitals, each MO can accommodate two electrons with their spins paired (Pauli exclusion principle). (Section 6.7)

As the MO diagram for H_2 in Figure 9.33 shows, each H atom brings one electron to the molecule, so there are two electrons in H_2. These two electrons occupy the lower-energy bonding (σ_{1s}) MO, and their spins are paired. Electrons occupying a bonding molecular orbital are called *bonding electrons*. Because the σ_{1s} MO is lower in energy than the 1*s* atomic orbitals, the H_2 molecule is more stable than the two separate H atoms.

By analogy with atomic electron configurations, the electron configurations for molecules can be written with superscripts to indicate electron occupancy. The electron configuration for H_2, then, is σ_{1s}^2.

GO FIGURE

By referring to Figure 9.32, determine which molecular orbital in He_2 has a node between the nuclei.



▲ **FIGURE 9.33** **Energy-level diagrams and electron configurations for H_2 and He_2.**

Figure 9.33 also shows the energy-level diagram for the hypothetical He_2 molecule, which requires four electrons to fill its molecular orbitals. Because only two electrons can go in the σ_{1s} MO, the other two electrons must go in the $\sigma^{\star}_{1s}$ MO. The electron configuration of He_2 is thus $\sigma_{1s}{}^2\sigma^{\star}_{1s}{}^2$. The energy decrease realized in going from He atomic orbitals to the He bonding MO is offset by the energy increase realized in going from the atomic orbitals to the He antibonding MO.[†] Hence, He_2 is an unstable molecule. Molecular orbital theory correctly predicts that hydrogen forms diatomic molecules but helium does not.

Bond Order

In molecular orbital theory, the stability of a covalent bond is related to its **bond order**, defined as half the difference between the number of bonding electrons and the number of antibonding electrons:

$$\text{Bond order} = \tfrac{1}{2}\,(\text{no. of bonding electrons} - \text{no. of antibonding electrons}) \qquad [9.1]$$

We take half the difference because we are used to thinking of bonds as pairs of electrons. *A bond order of 1 represents a single bond, a bond order of 2 represents a double bond, and a bond order of 3 represents a triple bond.* Because MO theory also treats molecules containing an odd number of electrons, bond orders of 1/2 , 3/2, or 5/2 are possible.

Because, as Figure 9.33 shows, H_2 has two bonding electrons and zero antibonding electrons, it has a bond order of 1. Because He_2 has two bonding electrons and two antibonding electrons, it has a bond order of 0. A bond order of 0 means that no bond exists.

GIVE IT SOME THOUGHT

Suppose one electron in H_2 is excited from the σ_{1s} MO to the $\sigma^{\star}_{1s}$ MO. Would you expect the H atoms to remain bonded to each other, or would the molecule fall apart?

SAMPLE EXERCISE 9.8 Bond Order

What is the bond order of the $He_2{}^+$ ion? Would you expect this ion to be stable relative to the separated He atom and He^+ ion?

SOLUTION

Analyze We will determine the bond order for the $He_2{}^+$ ion and use it to predict whether the ion is stable.

Plan To determine the bond order, we must determine the number of electrons in the molecule and how these electrons populate the available MOs. The valence electrons of He are in the 1*s* orbital, and the 1*s* orbitals combine to give an MO diagram like that for H_2 or He_2 (Figure 9.33). If the bond order is greater than 0, we expect a bond to exist, and the ion is stable.

Solve The energy-level diagram for the $He_2{}^+$ ion is shown in ◀ **FIGURE 9.34**. This ion has three electrons. Two are placed in the bonding orbital and the third in the antibonding orbital. Thus, the bond order is

$$\text{Bond order} = \tfrac{1}{2}(2 - 1) = \tfrac{1}{2}$$

Because the bond order is greater than 0, we predict the $He_2{}^+$ ion to be stable relative to the separated He and He^+. Formation of $He_2{}^+$ in the gas phase has been demonstrated in laboratory experiments.

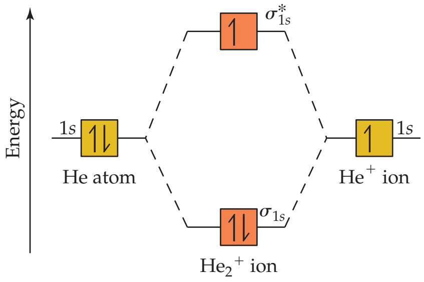
PRACTICE EXERCISE

Determine the bond order of the $H_2{}^-$ ion.

Answer: $\tfrac{1}{2}$

GO FIGURE

Which electrons in this diagram contribute to the stability of the $He_2{}^+$ ion?



▲ **FIGURE 9.34 Energy-level diagram for the $He_2{}^+$ ion.**

[†] Antibonding MOs are slightly more energetically unfavorable than bonding MOs are energetically favorable. Thus, whenever there is an equal number of electrons in bonding and antibonding orbitals, the energy of the molecule is slightly higher than that for the separated atoms. As a result, no bond is formed.

9.8 PERIOD 2 DIATOMIC MOLECULES

In considering the MO description of diatomic molecules other than H_2, we will initially restrict our discussion to *homonuclear* diatomic molecules (those composed of two identical atoms) of period 2 elements.

Period 2 atoms have valence 2*s* and 2*p* orbitals, and we need to consider how they interact to form MOs. The following rules summarize some of the guiding principles for the formation of MOs and for how they are populated by electrons:

1. The number of MOs formed equals the number of atomic orbitals combined.
2. Atomic orbitals combine most effectively with other atomic orbitals of similar energy.
3. The effectiveness with which two atomic orbitals combine is proportional to their overlap. That is, as the overlap increases, the energy of the bonding MO is lowered and the energy of the antibonding MO is raised.
4. Each MO can accommodate, at most, two electrons, with their spins paired (Pauli exclusion principle). (Section 6.7)
5. When MOs of the same energy are populated, one electron enters each orbital (with the same spin) before spin pairing occurs (Hund's rule). (Section 6.8)

Molecular Orbitals for Li_2 and Be_2

Lithium has the electron configuration $1s^22s^1$. When lithium metal is heated above its boiling point (1342 °C), Li_2 molecules are found in the vapor phase. The Lewis structure for Li_2 indicates a Li—Li single bond. We will now use MOs to describe the bonding in Li_2.

▶ **FIGURE 9.35** shows that the Li 1*s* and 2*s* atomic orbitals have substantially different energy levels. From this, we can assume that the 1*s* orbital on one Li atom interacts only with the 1*s* orbital on the other atom (rule 2), just as Figure 9.35 indicates. Likewise, the 2*s* orbitals interact only with each other. Notice that combining four atomic orbitals produces four MOs (rule 1).

The Li 1*s* orbitals combine to form σ_{1s} and σ^*_{1s} bonding and antibonding MOs, as they did for H_2. The 2*s* orbitals interact with one another in exactly the same way, producing bonding (σ_{2s}) and antibonding (σ^*_{2s}) MOs. In general, the separation between bonding and antibonding MOs depends on the extent to which the constituent atomic orbitals overlap. Because the Li 2*s* orbitals extend farther from the nucleus than the 1*s* orbitals do, the 2*s* orbitals overlap more effectively. As a result, the energy difference between the σ_{2s} and σ^*_{2s} orbitals is greater than the energy difference between the σ_{1s} and σ^*_{1s} orbitals. The 1*s* orbitals of Li are so much lower in energy than the 2*s* orbitals, however, that the energy of the σ^*_{1s} antibonding MO is much lower than the energy of σ_{2s} bonding MO.

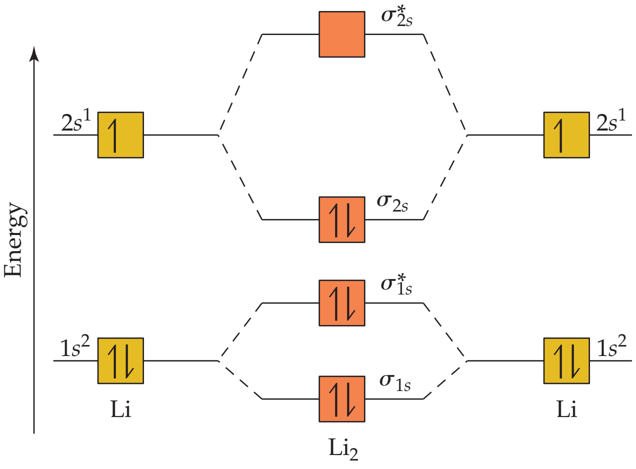
Each Li atom has three electrons, so six electrons must be placed in Li_2 MOs. As shown in Figure 9.35, these electrons occupy the σ_{1s}, σ^*_{1s}, and σ_{2s} MOs, each with two electrons. There are four electrons in bonding orbitals and two in antibonding orbitals, so the bond order is $\frac{1}{2}(4 - 2) = 1$. The molecule has a single bond, in agreement with its Lewis structure.

Because both the σ_{1s} and σ^*_{1s} MOs of Li_2 are completely filled, the 1*s* orbitals contribute almost nothing to the bonding. The single bond in Li_2 is due essentially to the interaction of the valence 2*s* orbitals on the Li atoms. This example illustrates the general rule that *core electrons usually do not contribute significantly to bonding in molecules*. The rule is equivalent to using only the valence electrons when drawing Lewis structures. Thus, we need not consider further the 1*s* orbitals while discussing the other period 2 diatomic molecules.

The MO description of Be_2 follows readily from the energy-level diagram for Li_2. Each Be atom has four electrons ($1s^22s^2$), so we must place eight electrons in molecular orbitals. Thus, we completely fill the

GO FIGURE

Why do the 1*s* orbitals of the Li atoms not contribute to the bonding in Li_2?



▲ **FIGURE 9.35 Energy-level diagram for the Li_2 molecule.**

σ_{1s}, σ^*_{1s}, σ_{2s}, and σ^*_{2s} MOs. With equal numbers of bonding and antibonding electrons, the bond order is zero; thus, Be_2 does not exist.

GIVE IT SOME THOUGHT

Would you expect Be_2^+ to be a stable ion?

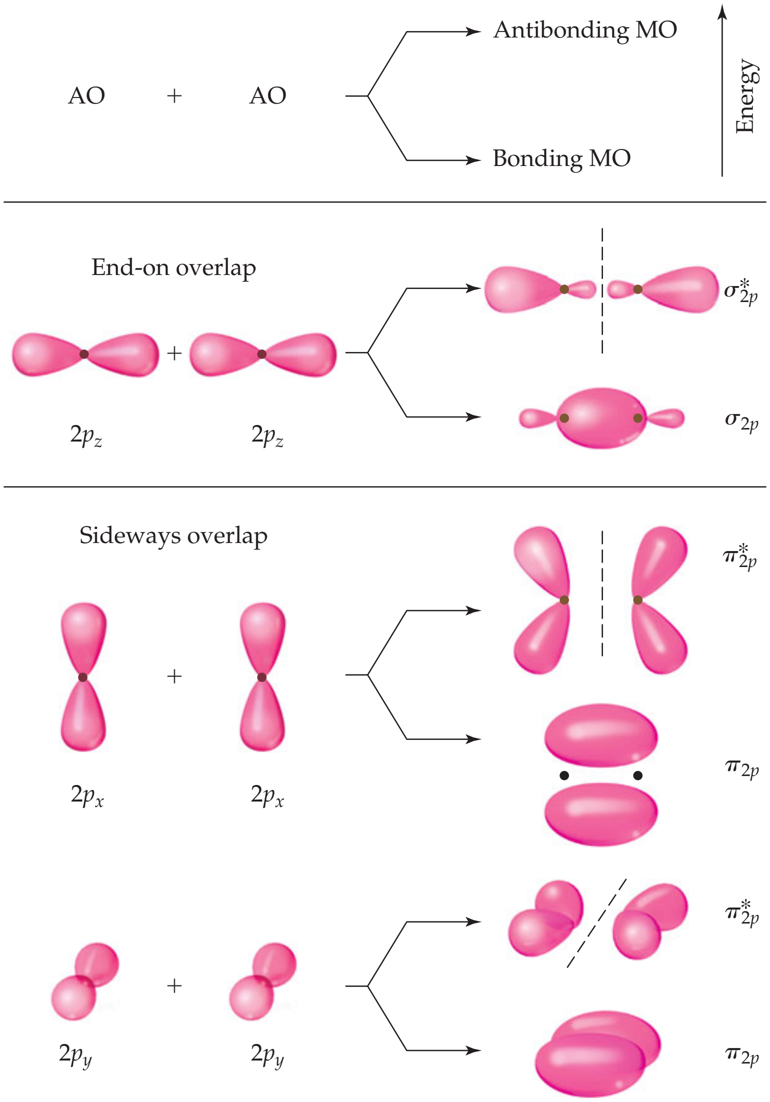
Molecular Orbitals from 2*p* Atomic Orbitals

Before we can consider the remaining period 2 diatomic molecules, we must look at the MOs that result from combining 2*p* atomic orbitals. The interactions between *p* orbitals are shown in ▼ **FIGURE 9.36**, where we have arbitrarily chosen the internuclear axis to be the *z*-axis. The $2p_z$ orbitals face each other head to head. Just as with *s* orbitals, we can combine $2p_z$ orbitals in two ways. One combination concentrates electron density between the nuclei and is, therefore, a bonding molecular orbital. The other combination excludes electron density from the bonding region and so is an antibonding molecular orbital. In both MOs the electron density lies along the internuclear axis, so they are σ molecular orbitals: σ_{2p} and σ^*_{2p}.

The other 2*p* orbitals overlap sideways and thus concentrate electron density above and below the internuclear axis. MOs of this type are called **pi (π) molecular orbitals** by

GO FIGURE

In what types of MOs do we find nodal planes?



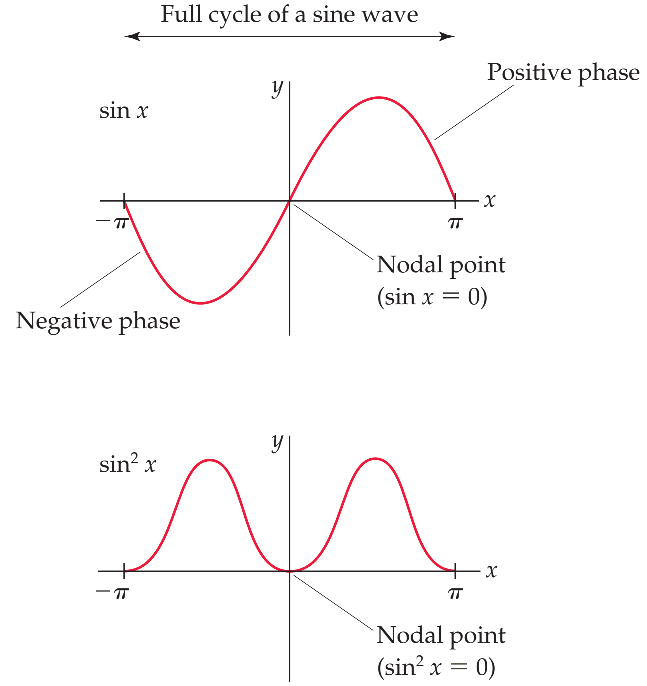
▶ **FIGURE 9.36 Contour representations of the molecular orbitals formed by 2*p* orbitals.**

A CLOSER LOOK

PHASES IN ATOMIC AND MOLECULAR ORBITALS

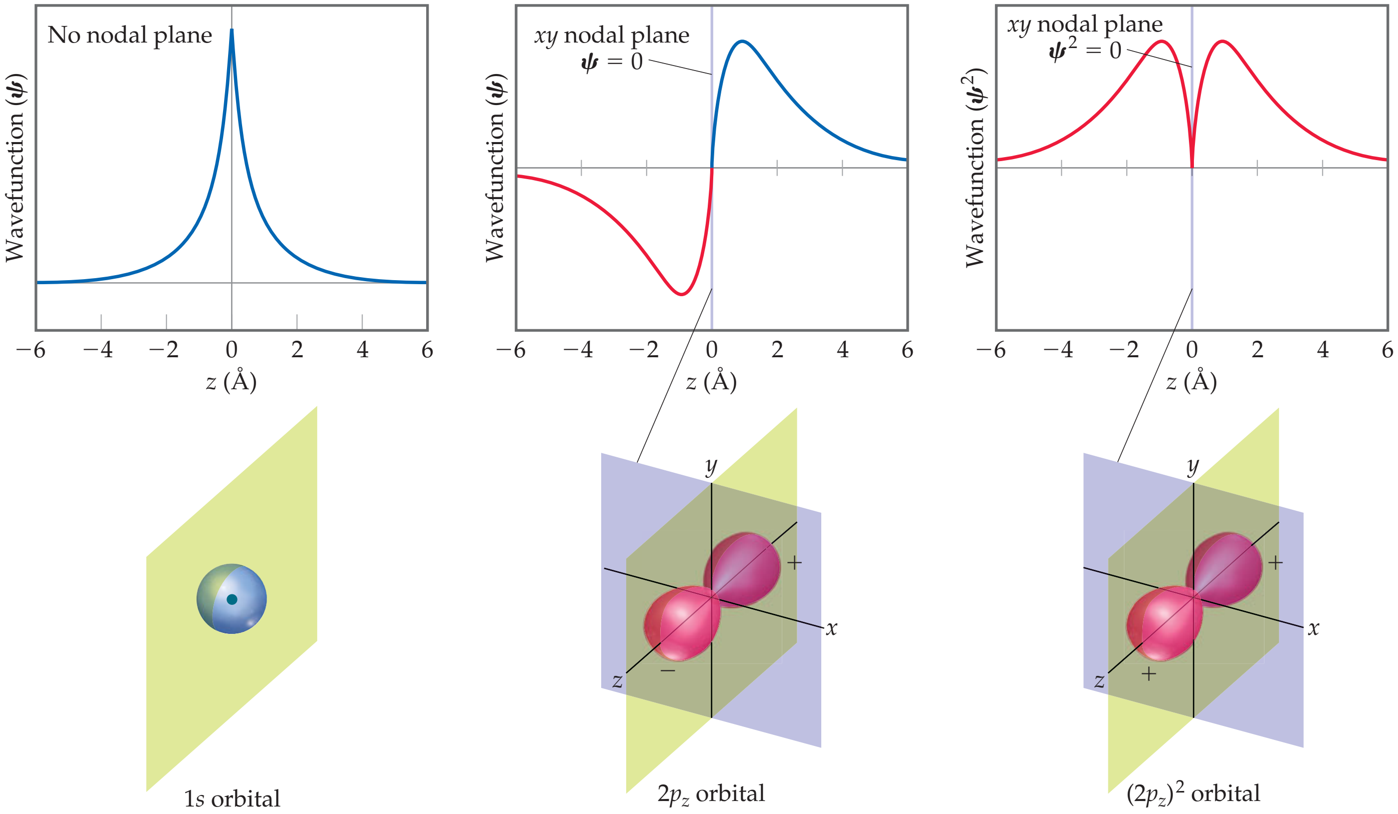
Our discussion of atomic orbitals in Chapter 6 and molecular orbitals in this chapter highlights some of the most important applications of quantum mechanics in chemistry. In the quantum mechanical treatment of electrons in atoms and molecules, we are mainly interested in determining two characteristics of the electrons—their energies and their distribution in space. Recall that solving Schrödinger's wave equation yields the electron's energy, *E*, and wave function, ψ, but that ψ does not have a direct physical meaning. (Section 6.5) The contour representations of atomic and molecular orbitals we have presented thus far are based on ψ^2 (the *probability density*), which gives the probability of finding the electron at a given point in space.

Because probability densities are squares of functions, their values must be nonnegative (zero or positive) at all points in space. However, the functions themselves can have negative values. Consider, for example, the sine function plotted in ▶ **FIGURE 9.37**. In the top graph, the sine function is negative for x between 0 and $-\pi$ and positive for x between 0 and $+\pi$. We say that the *phase* of the sine function is negative between 0 and $-\pi$ and positive between 0 and $+\pi$. If we square the sine function (bottom graph), we get two peaks that are symmetrical about the origin. Both peaks are positive because squaring a negative number produces a positive number. In other words, *we lose the phase information of the function upon squaring it.*



▲ **FIGURE 9.37 Graphs for a sine function and the same function squared.**

Like the sine function, the more complicated wave functions for atomic orbitals can also have phases. Consider, for example, the representations of the 1*s* orbital in ▼ **FIGURE 9.38**. Note that here we plot this orbital a bit differently from what is shown in Section 6.6. The origin is the point where the nucleus resides, and the wave function for



▲ **FIGURE 9.38 Phases in wave functions of *s* and *p* atomic orbitals.**

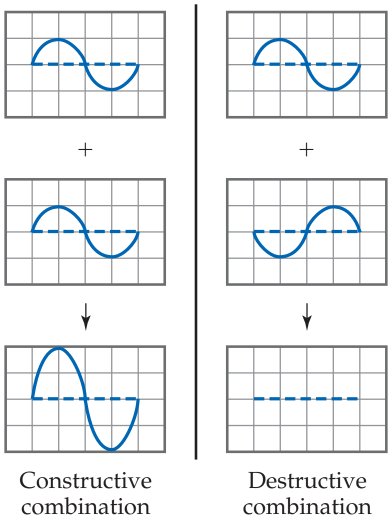
the 1*s* orbital extends from the origin out into space. The plot shows the value of ψ for a slice taken along the *z*-axis. Below the plot is a contour representation of the 1*s* orbital. Notice that the value of the 1*s* wave function is always a positive number. Thus, it has only one phase. Notice also that the wave function approaches zero only at a long distance from the nucleus. It therefore has no nodes, as we saw in Figure 6.21.

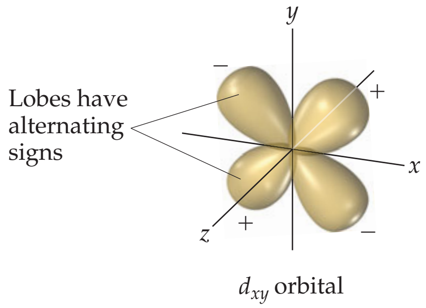
In the Figure 9.38 graph for the $2p_z$ orbital, the wave function changes sign when it passes through $z = 0$. Notice that the two halves of the wave have the same shape except that one has positive values and the other negative values. Analogously to the sine function, the wave function changes phase when it passes through the origin. Mathematically the $2p_z$ wave function is equal to zero whenever $z = 0$. This corresponds to any point on the *xy* plane, so we say that the *xy* plane is a *nodal plane* of the $2p_z$ orbital. The wave function for a *p* orbital is much like a sine function because it has two equal parts that have opposite phases. Figure 9.38 gives a typical representation used by chemists of the wave function for a p_z orbital.* The plus and minus signs indicate the phases of the orbital. As with the sine function, the origin is a node.

The third graph in Figure 9.38 shows that when we square the wave function of the $2p_z$ orbital, we get two peaks that are symmetrical about the origin. Both peaks are positive because squaring a negative number produces a positive number. Thus, *we lose the phase information of the function upon squaring it* just as we did for the sine function. When we square the wave function for the p_z orbital, we get the probability density for the orbital, which is given as a contour representation in Figure 9.38. This is what we saw in the earlier presentation of *p* orbitals. (Section 6.6) For this squared wave function, both lobes have the same phase and therefore the same sign. We use this representation throughout most of this book because it has a simple physical interpretation: The square of the wave function at any point in space represents the electron density at that point.

The lobes of the wave functions for the *d* orbitals also have different phases. For example, the wave function for a d_{xy} orbital has four lobes, with the phase of each lobe opposite the phase of its nearest neighbors (▶ **FIGURE 9.39**). The wave functions for the other *d* orbitals likewise have lobes in which the phase in one lobe is opposite that in an adjacent lobe.

Why do we need to consider the complexity introduced by considering the phase of the wave function? While it is true that the phase is not necessary to visualize the shape of an atomic orbital in an isolated atom, it does become important when we consider overlap of orbitals in molecular orbital theory. Let's use the sine function as an example again. If you add two sine functions having the same phase, they add *constructively*, resulting in increased amplitude: but if you add two sine functions having opposite phases, they add *destructively* and cancel each other.



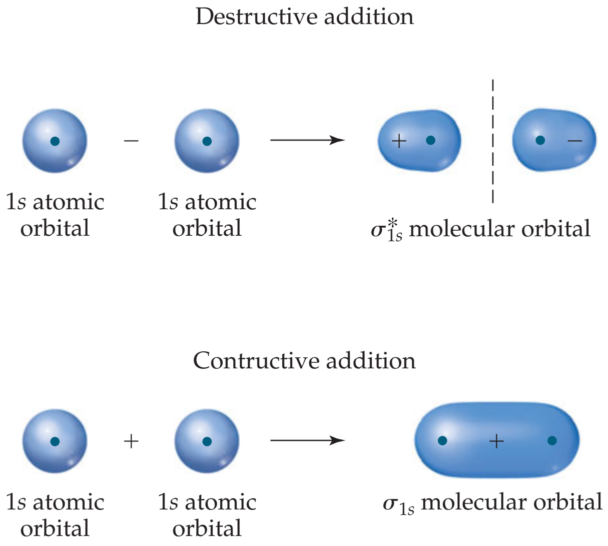


▲ **FIGURE 9.39 Phases in *d* orbitals.**

The idea of constructive and destructive interactions of wave functions is key to understanding the origin of bonding and antibonding molecular orbitals. For example, the wave function of the σ_{1s} MO of H_2 is generated by adding the wave function for the 1*s* orbital on one atom to the wave function for the 1*s* orbital on the other atom, with both orbitals having the same phase. The atomic wave functions overlap *constructively* in this case to increase the electron density between the two atoms (▼ **FIGURE 9.40**). The wave function of the σ^*_{1s} MO of H_2 is generated by subtracting the wave function for a 1*s* orbital on one atom from the wave function for a 1*s* orbital on the other atom. The result is that the atomic orbital wave functions overlap *destructively* to create a region of zero electron density between the two atoms—a node. Notice the similarity between this figure and Figure 9.32. In Figure 9.40 we use plus and minus signs to denote positive and negative phases in the H atomic orbitals. However, chemists may alternatively draw contour representations in different colors to denote the two phases.

When we square the wave function of the σ^*_{1s} MO, we get the electron density representation which we saw earlier, in Figure 9.32. Notice once again that we lose the phase information when we look at the electron density.

RELATED EXERCISES: 9.103, 9.115, 9.117



▲ **FIGURE 9.40 Molecular orbitals from atomic orbital wave functions.**

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*The mathematical development of this three-dimensional function (and its square) is beyond the scope of this book and, as is typically done by chemists, we have used lobes that are the same shape as in Figure 6.22.

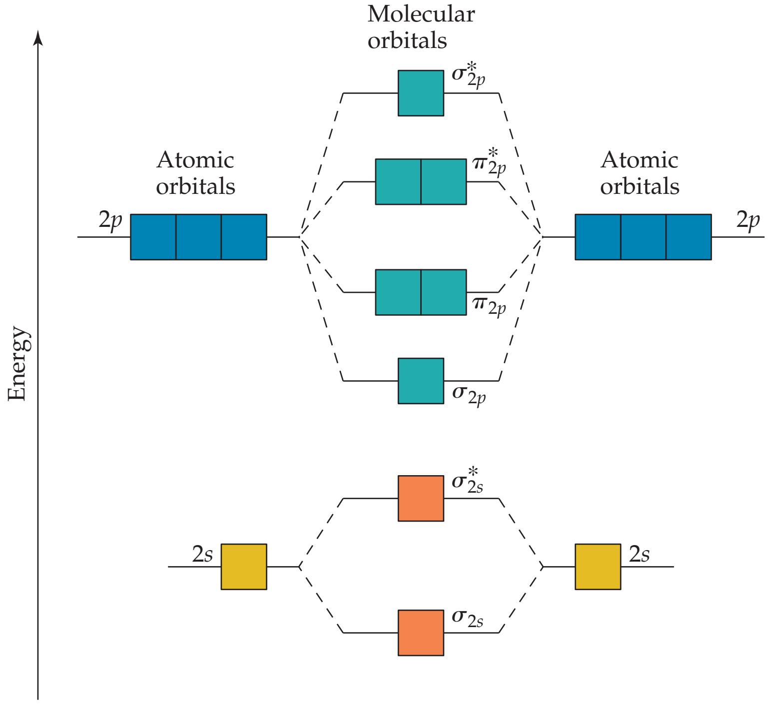
analogy to π bonds. We get one π bonding MO by combining the $2p_x$ atomic orbitals and another from the $2p_y$ atomic orbitals. These two π_{2p} molecular orbitals have the same energy; in other words, they are degenerate. Likewise, we get two degenerate π^*_{2p} antibonding MOs that are perpendicular to each other like the $2p$ orbitals from which they were made. These π^*_{2p} orbitals have four lobes, pointing away from the two nuclei, as shown in Figure 9.36. The $2p_z$ orbitals on two atoms point directly at each other. Hence, the overlap of two $2p_z$ orbitals is greater than that of two $2p_x$ or $2p_y$ orbitals. From rule 3 we therefore expect the σ_{2p} MO to be lower in energy (more stable) than the π_{2p} MOs. Similarly, the σ^*_{2p} MO should be higher in energy (less stable) than the π^*_{2p} MOs.

Electron Configurations for B_2 through Ne_2

We can combine our analyses of MOs formed from *s* orbitals (Figure 9.32) and from *p* orbitals (Figure 9.36) to construct an energy-level diagram (▼ **FIGURE 9.41**) for homonuclear diatomic molecules of the elements boron through neon, all of which have valence 2*s* and 2*p* atomic orbitals. The following features of the diagram are notable:

1. The 2*s* atomic orbitals are substantially lower in energy than the 2*p* atomic orbitals. ∞ (Section 6.7) Consequently, both MOs formed from the 2*s* orbitals are lower in energy than the lowest-energy MO derived from the 2*p* atomic orbitals.
2. The overlap of the two $2p_z$ orbitals is greater than that of the two $2p_x$ or $2p_y$ orbitals. As a result, the bonding σ_{2p} MO is lower in energy than the π_{2p} MOs, and the antibonding σ^*_{2p} MO is higher in energy than the π^*_{2p} MOs.
3. Both the π_{2p} and π^*_{2p} MOs are *doubly degenerate*; that is, there are two degenerate MOs of each type.

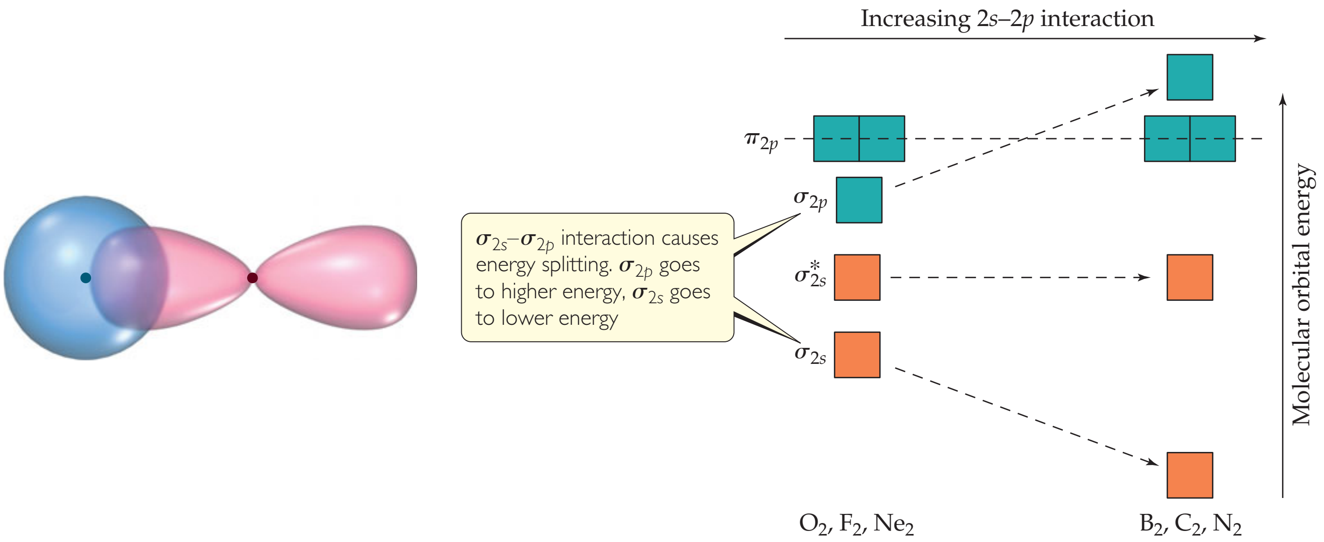
Before we can add electrons to Figure 9.41, we must consider one more effect. We have constructed the diagram assuming no interaction between the 2*s* orbital on one atom and the 2*p* orbitals on the other. In fact, such interactions can and do take place. ► **FIGURE 9.42** shows the overlap of a 2*s* orbital on one of the atoms with a 2*p* orbital on the other. These interactions increase the energy difference between the σ_{2s} and σ_{2p} MOs, with the σ_{2s} energy decreasing and the σ_{2p} energy increasing (Figure 9.42). These 2*s*–2*p* interactions can be strong enough that the energetic ordering of the MOs can be altered: For B_2, C_2, and N_2, the σ_{2p} MO is above the π_{2p} MOs in energy. For O_2, F_2, and Ne_2, the σ_{2p} MO is below the π_{2p} MOs .



◄ **FIGURE 9.41 Energy-level diagram for MOs of period 2 homonuclear diatomic molecules.** The diagram assumes no interaction between the 2*s* atomic orbital on one atom and the 2*p* atomic orbitals on the other atom, and experiment shows that it fits only for O_2, F_2, and Ne_2.

GO FIGURE

Which molecular orbitals have switched relative energy in the group on the right as compared with the group on the left?



▲ **FIGURE 9.42** **The effect of interactions between 2*s* and 2*p* atomic orbitals.**

Given the energy ordering of the molecular orbitals, it is a simple matter to determine the electron configurations for the diatomic molecules B_2 through Ne_2. For example, a boron atom has three valence electrons. (Remember that we are ignoring the 1*s* electrons.) Thus, for B_2 we must place six electrons in MOs. Four of them fill the σ_{2s} and σ^*_{2s} MOs, leading to no net bonding. The fifth electron goes in one π_{2p} MO, and the sixth goes in the other π_{2p} MO, with the two electrons having the same spin. Therefore, B_2 has a bond order of 1.

Each time we move one element to the right in period 2, two more electrons must be placed in the diagram of Figure 9.41. For example, on moving to C_2, we have two more electrons than in B_2, and these electrons are placed in the π_{2p} MOs, completely filling them. The electron configurations and bond orders for B_2 through Ne_2 are given in ▶ **FIGURE 9.43**.

Electron Configurations and Molecular Properties

The way a substance behaves in a magnetic field can in some cases provide insight into the arrangements of its electrons. Molecules with one or more unpaired electrons are attracted to a magnetic field. The more unpaired electrons in a species, the stronger the attractive force. This type of magnetic behavior is called **paramagnetism**.

Substances with no unpaired electrons are weakly repelled by a magnetic field. This property is called **diamagnetism**. The distinction between paramagnetism and diamagnetism is nicely illustrated in an older method for measuring magnetic properties (▶ **FIGURE 9.44**). It involves weighing the substance in the presence and absence of a magnetic field. A paramagnetic substance appears to weigh more in the magnetic field; a diamagnetic substance appears to weigh less. The magnetic behaviors observed for the period 2 diatomic molecules agree with the electron configurations shown in Figure 9.43.

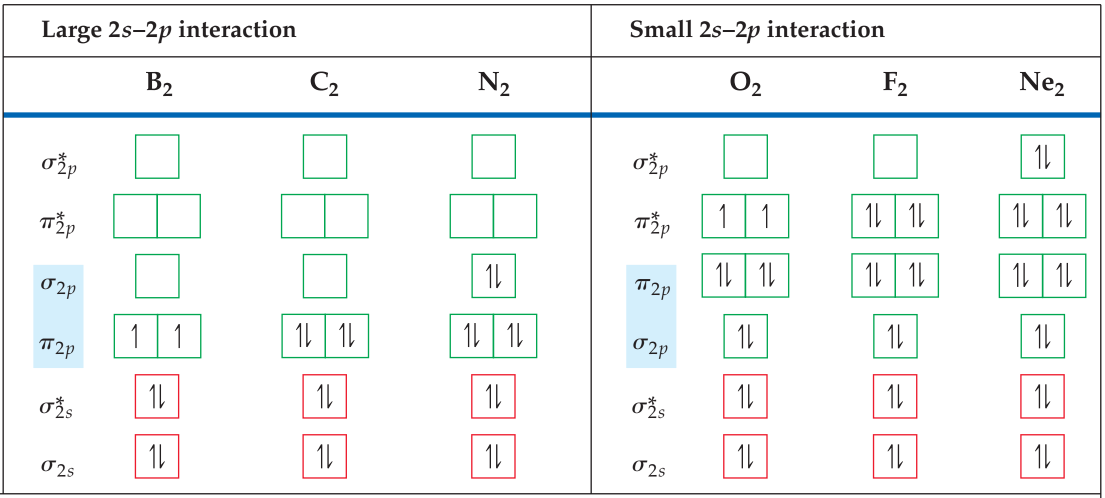
GIVE IT SOME THOUGHT

Figure 9.43 indicates that C_2 is diamagnetic. Would that be expected if the σ_{2p} MO were lower in energy than the π_{2p} MOs?

Electron configurations in molecules can also be related to bond distances and bond enthalpies. ∞ (Section 8.8) As bond order increases, bond distances decrease

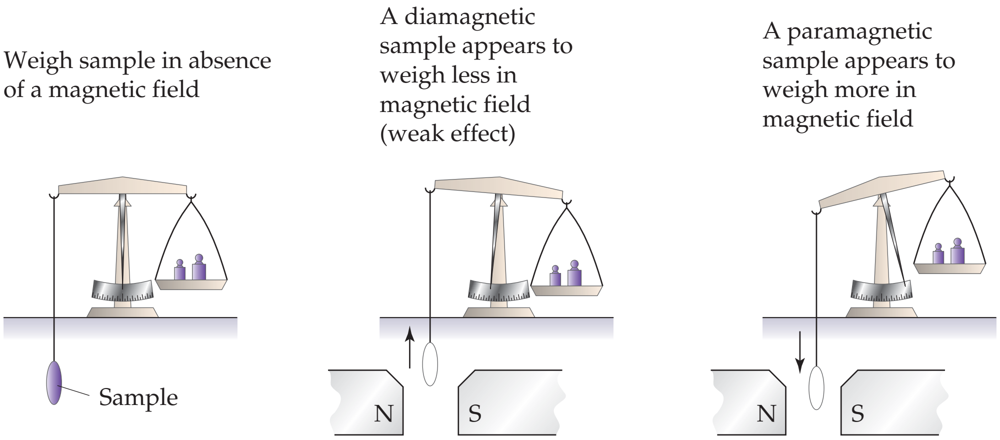
GO FIGURE

What difference in electron configuration accounts for most of the difference between the bond enthalpy of N_2 and that of F_2?



	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

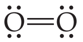
▲ **FIGURE 9.43 Molecular orbital electron configurations and some experimental data for period 2 diatomic molecules.**



◀ **FIGURE 9.44 Determining the magnetic properties of a sample.**

and bond enthalpies increase. N_2, for example, whose bond order is 3, has a short bond distance and a large bond enthalpy. The N_2 molecule does not react readily with other substances to form nitrogen compounds. The relatively high bond order of the molecule helps explain its exceptional stability. We should also note, however, that molecules with the same bond orders do *not* have the same bond distances and bond enthalpies. Bond order is only one factor influencing these properties. Other factors include nuclear charge and extent of orbital overlap.

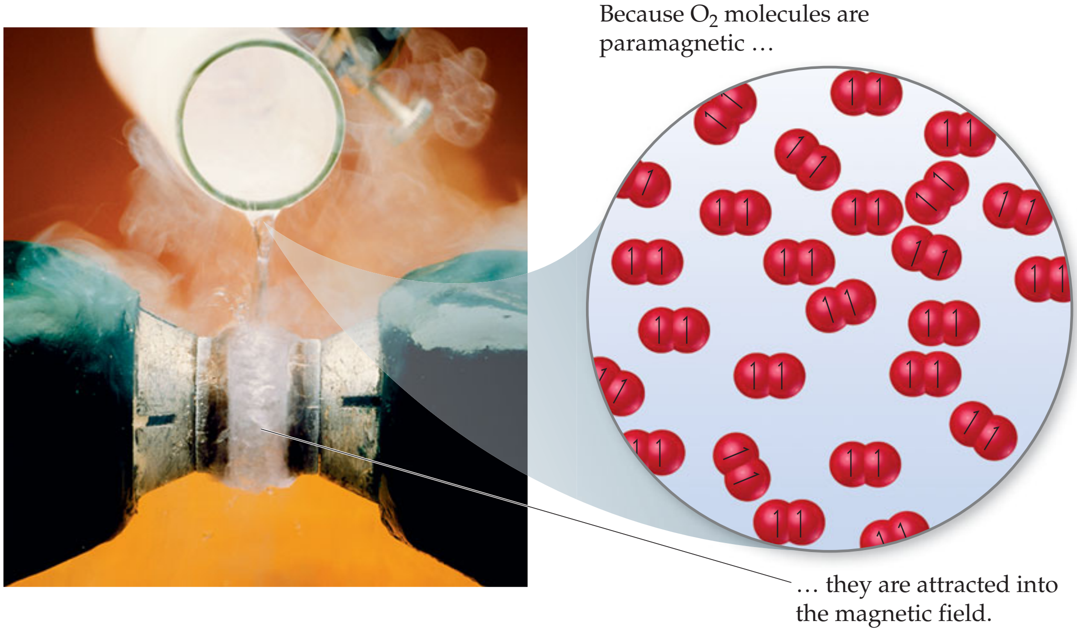
Bonding in O_2 provides an interesting test case for molecular orbital theory. The Lewis structure for this molecule shows a double bond and complete pairing of electrons:


$$\underset{\cdot\cdot}{\ddot{\mathrm{O}}}=\underset{\cdot\cdot}{\ddot{\mathrm{O}}}$$

The short O—O bond distance (1.21 Å) and relatively high bond enthalpy (495 kJ/mol) are in agreement with the presence of a double bond. However, Figure 9.43 tells us that

GO FIGURE

What would you expect to see if liquid nitrogen were poured between the poles of the magnet?



▲ **FIGURE 9.45** **Paramagnetism of O_2.**

the molecule contains two unpaired electrons, a detail not discernible in the Lewis structure. Unpaired electrons mean paramagnetism, and the paramagnetism of O_2 is demonstrated in ▲ **FIGURE 9.45**. The Lewis structure fails to account for this paramagnetism, but molecular orbital theory correctly predicts two unpaired electrons in the π^{*}_{2p} orbital. The MO description also correctly indicates a bond order of 2.

Going from O_2 to F_2, we add two electrons, completely filling the π^{*}_{2p} MOs. Thus, F_2 is expected to be diamagnetic and have an F—F single bond, in accord with its Lewis structure. Finally, the addition of two more electrons to make Ne_2 fills all the bonding and antibonding MOs. Therefore, the bond order of Ne_2 is zero, and the molecule is not expected to exist.

SAMPLE EXERCISE 9.9 Molecular Orbitals of a Period 2 Diatomic Ion

For the O_2^{+} ion, predict (**a**) number of unpaired electrons, (**b**) bond order, (**c**) bond enthalpy and bond length.

SOLUTION

Analyze Our task is to predict several properties of the cation O_2^{+}.

Plan We will use the MO description of O_2^{+} to determine the desired properties. We must first determine the number of electrons in O_2^{+} and then draw its MO energy diagram. The unpaired electrons are those without a partner of opposite spin. The bond order is one-half the difference between the number of bonding and antibonding electrons. After calculating the bond order, we can use Figure 9.43 to estimate the bond enthalpy and bond length.

Solve

(**a**) The O_2^{+} ion has 11 valence electrons, one fewer than O_2. The electron removed from O_2 to form O_2^{+} is one of the two unpaired π^{*}_{2p} electrons (see Figure 9.43). Therefore, O_2^{+} has one unpaired electron.

(b) The molecule has eight bonding electrons (the same as O_2) and three antibonding electrons (one fewer than O_2). Thus, its bond order is

$$\frac{1}{2}(8 - 3) = 2\frac{1}{2}$$

(c) The bond order of O_2^+ is between that for O_2 (bond order 2) and N_2 (bond order 3). Thus, the bond enthalpy and bond length should be about midway between those for O_2 and N_2, approximately 700 kJ/mol and 1.15 Å. (The experimentally measured values are 625 kJ/mol and 1.123 Å.)

PRACTICE EXERCISE

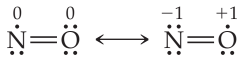
Predict the magnetic properties and bond orders of **(a)** the peroxide ion, O_2^{2-}; **(b)** the acetylide ion, C_2^{2-}.

Answers: **(a)** diamagnetic, 1; **(b)** diamagnetic, 3

Heteronuclear Diatomic Molecules

The principles we have used in developing an MO description of homonuclear diatomic molecules can be extended to *heteronuclear* diatomic molecules—those in which the two atoms in the molecule are not the same—and we conclude this section with a fascinating heteronuclear diatomic molecule—nitric oxide, NO.

The NO molecule controls several important human physiological functions. Our bodies use it, for example, to relax muscles, kill foreign cells, and reinforce memory. The 1998 Nobel Prize in Physiology or Medicine was awarded to three scientists for their research that uncovered the importance of NO as a "signaling" molecule in the cardiovascular system. NO also functions as a neurotransmitter and is implicated in many other biological pathways. That NO plays such an important role in human metabolism was unsuspected before 1987 because NO has an odd number of electrons and is highly reactive. The molecule has 11 valence electrons, and two possible Lewis structures can be drawn. The Lewis structure with the lower formal charges places the odd electron on the N atom:



$$\overset{0}{\dot{N}}{=}\overset{0}{O} \longleftrightarrow \overset{-1}{N}{=}\overset{+1}{O}$$

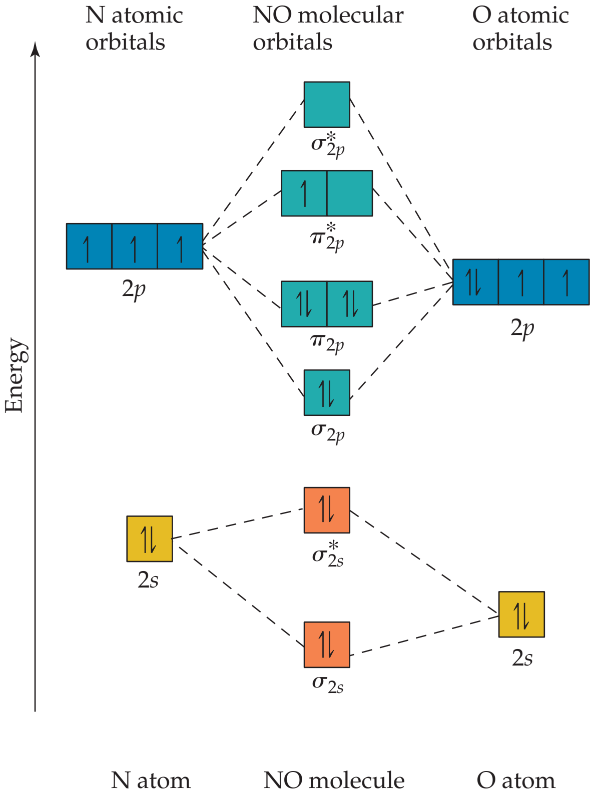
Both structures indicate the presence of a double bond, but when compared with the molecules in Figure 9.43, the experimental bond length of NO (1.15 Å) suggests a bond order greater than 2. How do we treat NO using the MO model?

If the atoms in a heteronuclear diatomic molecule do not differ too greatly in electronegativities, their MOs resemble those in homonuclear diatomics, with one important modification: The energy of the atomic orbitals of the more electronegative atom is lower than that of the atomic orbitals of the less electronegative element. In ▶ **FIGURE 9.46**, you see that the 2*s* and 2*p* atomic orbitals of oxygen are slightly lower than those of nitrogen because oxygen is more electronegative than nitrogen. The MO energy-level diagram for NO is much like that of a homonuclear diatomic molecule—because the 2*s* and 2*p* orbitals on the two atoms interact, the same types of MOs are produced.

There is one other important difference in the MOs of heteronuclear molecules. The MOs are still a mix of atomic orbitals from both atoms, but in general *an MO in a heteronuclear diatomic molecule has a greater contribution from the atomic orbital to which it is closer in energy*. In the case of NO, for example, the σ_{2s} bonding MO is closer in energy to the O 2*s* atomic orbital than to the N 2*s* atomic orbital. As a result, the σ_{2s} MO has a slightly greater contribution from O than from N—the orbital is no longer an equal mixture of the two atoms, as was the case for the homonuclear diatomic molecules. Similarly, the $\sigma^{\star}_{2s}$ antibonding MO is weighted more heavily toward the N atom because that MO is closest in energy to the N 2*s* atomic orbital.

GO FIGURE

How many valence-shell electrons are there in NO?



▲ **FIGURE 9.46 The energy-level diagram for atomic and molecular orbitals in NO.**

CHEMISTRY PUT TO WORK

Orbitals and Energy

Asked to identify the major technological challenge for the twenty-first century, you might say "energy," reasoning that development of sustainable energy sources is crucial to meet the needs of future generations of people on our planet. Currently, the majority of the world, in one way or another, relies on exothermic combustion reactions of oil, coal, or natural gas to provide heat and power. These are all *fossil fuels*—carbon-containing compounds that are the long-term decomposition products of ancient plants and animals.

Fossil fuels are not renewable in the several-hundred-year timeframe in which we need them, but every day our planet receives plenty of energy from the Sun to easily power the world for millions of years. Whereas combustion of fossil fuels releases CO_2 into the atmosphere, solar energy represents a renewable energy source that is potentially less harmful to the environment. One way to utilize solar energy is to convert it into electrical energy via photovoltaic solar cells. The problem with this alternative is that the current efficiency of solar-cell devices is low; only about 10–15% of sunlight is converted into useful energy. Furthermore, the cost of manufacturing solar cells is relatively high.

How does solar energy conversion work? Fundamentally, we need to be able to use photons from the Sun to excite electrons in molecules and materials to different energy levels. The brilliant colors around you—those of your clothes, the photographs in this book, the foods you eat—are due to the selective absorption of light by chemicals. Light excites electrons in molecules. In a molecular orbital picture, we can envision light exciting an electron from a filled molecular orbital to an empty one at higher energy. Because the MOs have definite energies, only light of the proper wavelengths can excite electrons. The situation is analogous to that of atomic line spectra. ∞ (Section 6.3) If the appropriate wavelength for exciting electrons is in the visible portion of the electromagnetic spectrum, the substance appears colored: Certain wavelengths of white light are absorbed; others are not. A green leaf appears green because green light is most strongly reflected by the leaf while other wavelengths of visible light are absorbed.

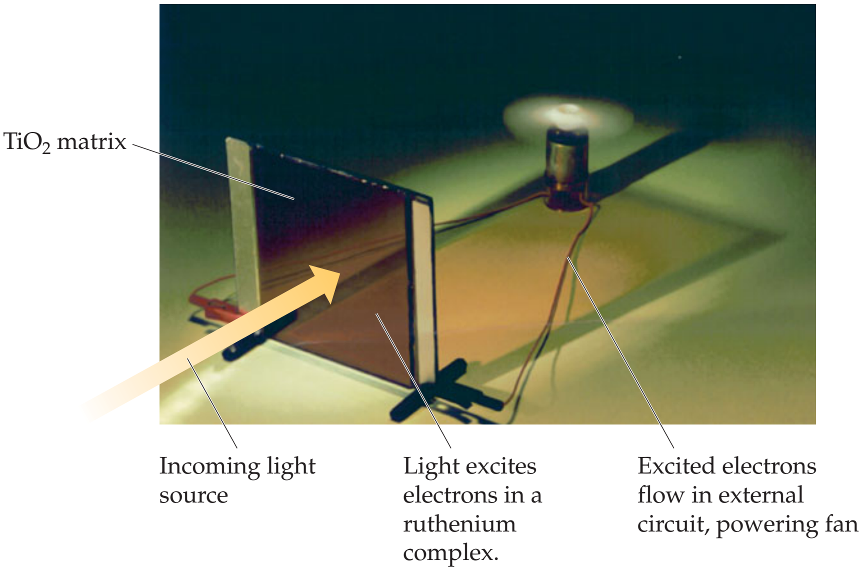
In discussing light absorption by molecules, we can focus on two MOs. The *highest occupied molecular orbital* (HOMO) is the MO of highest energy that has electrons in it. The *lowest unoccupied molecular orbital* (LUMO) is the MO of lowest energy that does not have electrons in it. In N_2, for example, the HOMO is the σ_{2p} MO and the LUMO is the $\pi^{\star}_{2p}$ MO (Figure 9.43).

The energy difference between the HOMO and the LUMO—known as the HOMO–LUMO gap—is related to the minimum energy needed to excite an electron in the molecule. Colorless or white substances usually have such a large HOMO–LUMO gap that visible light is not energetic enough to excite an electron to the higher level. The minimum energy needed to excite an electron from the HOMO to the LUMO in N_2 corresponds to light with a wavelength of less than 200 nm, which is far into the ultraviolet part of the spectrum. ∞ (Figure 6.4) As a result, N_2 cannot absorb visible light and is therefore colorless.

The magnitude of the energy gap between filled and empty electronic states is critical for solar energy conversion. Ideally, we want a substance that absorbs as many solar photons as possible and then converts the energy of those photons into a useful form of energy. Titanium dioxide is a readily available material that can be reasonably efficient at converting light directly into electricity. However, TiO_2 is white and absorbs only a small amount of the Sun's radiant energy. Scientists are working to make solar cells in which TiO_2 is mixed with highly colored molecules, whose HOMO–LUMO gaps correspond to visible and near-infrared light. That way, the molecules can absorb more of the solar spectrum. The molecule's HOMO must also be higher in energy than the TiO_2's HOMO so that the excited electrons can flow from the molecules into the TiO_2, thereby generating electricity when the device is illuminated with light and connected to an external circuit.

▼ **FIGURE 9.47** shows a solar cell made from ruthenium-containing molecules, which appear red, mixed with TiO_2 in a paste that is sandwiched between two glass plates. Incoming light excites electrons on the ruthenium-containing molecules from occupied MOs to empty MOs. The electrons are then transferred into the TiO_2 and move through the external circuit, generating enough current to run the small fan.

RELATED EXERCISES: 9.105, 9.116



▲ **FIGURE 9.47** **Light into electricity.**

We complete the MO diagram for NO by filling the MOs in Figure 9.46 with the 11 valence electrons. Eight bonding and three antibonding electrons give a bond order of $\frac{1}{2}(8 - 3) = 2\frac{1}{2}$, which agrees better with experiment than the Lewis structures do. The unpaired electron resides in one of the $\pi^{\star}_{2p}$ MOs, which are more heavily weighted toward the N atom. (We could have placed this electron in either the left or right $\pi^{\star}_{2p}$ MO.) Thus, the Lewis structure that places the unpaired electron on nitrogen (the one preferred on the basis of formal charge) is the more accurate description of the true electron distribution in the molecule.

SAMPLE INTEGRATIVE EXERCISE Putting Concepts Together

Elemental sulfur is a yellow solid that consists of S_8 molecules. The structure of the S_8 molecule is a puckered, eight-membered ring (see Figure 7.26). Heating elemental sulfur to high temperatures produces gaseous S_2 molecules:

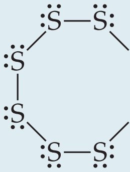
$$S_8(s) \longrightarrow 4\, S_2(g)$$

(a) The electron configuration of which period 2 element is most similar to that of sulfur? **(b)** Use the VSEPR model to predict the S—S—S bond angles in S_8 and the hybridization at S in S_8. **(c)** Use MO theory to predict the sulfur–sulfur bond order in S_2. Do you expect this molecule to be diamagnetic or paramagnetic? **(d)** Use average bond enthalpies (Table 8.4) to estimate the enthalpy change for this reaction. Is the reaction exothermic or endothermic?

SOLUTION

(a) Sulfur is a group 6A element with an $[\mathrm{Ne}]3s^23p^4$ electron configuration. It is expected to be most similar electronically to oxygen (electron configuration, $[\mathrm{He}]2s^22p^4$), which is immediately above it in the periodic table.

(b) The Lewis structure of S_8 is



There is a single bond between each pair of S atoms and two nonbonding electron pairs on each S atom. Thus, we see four electron domains around each S atom and expect a tetrahedral electron-domain geometry corresponding to sp^3 hybridization. Because of the nonbonding pairs, we expect the S—S—S angles to be somewhat less than 109.5°, the tetrahedral angle. Experimentally, the S—S—S angle in S_8 is 108°, in good agreement with this prediction. Interestingly, if S_8 were a planar ring, it would have S—S—S angles of 135°. Instead, the S_8 ring puckers to accommodate the smaller angles dictated by sp^3 hybridization.

(c) The MOs of S_2 are analogous to those of O_2, although the MOs for S_2 are constructed from the 3s and 3p atomic orbitals of sulfur. Further, S_2 has the same number of valence electrons as O_2. Thus, by analogy with O_2, we expect S_2 to have a bond order of 2 (a double bond) and to be paramagnetic with two unpaired electrons in the $\pi^{\star}_{3p}$ molecular orbitals of S_2.

(d) We are considering the reaction in which an S_8 molecule falls apart into four S_2 molecules. From parts (b) and (c), we see that S_8 has S—S single bonds and S_2 has S═S double bonds. During the reaction, therefore, we are breaking eight S—S single bonds and forming four S═S double bonds. We can estimate the enthalpy of the reaction by using Equation 8.12 and the average bond enthalpies in Table 8.4:

$$\Delta H_{\mathrm{rxn}} = 8\,D(\mathrm{S{-}S}) - 4\,D(\mathrm{S{=}S}) = 8(266\ \mathrm{kJ}) - 4(418\ \mathrm{kJ}) = +456\ \mathrm{kJ}$$

Recall that $D(\mathrm{X{-}Y})$ represents the X—Y bond enthalpy. Because $\Delta H_{\mathrm{rxn}} > 0$, the reaction is endothermic. (Section 5.4) The very positive value of ΔH_{rxn} suggests that high temperatures are required to cause the reaction to occur.

CHAPTER SUMMARY AND KEY TERMS

INTRODUCTION AND SECTION 9.1 The three-dimensional shapes and sizes of molecules are determined by their **bond angles** and bond lengths. Molecules with a central atom A surrounded by n atoms B, denoted AB_n, adopt a number of different geometric shapes, depending on the value of n and on the particular atoms involved. In the overwhelming majority of cases, these geometries are related to five basic shapes (linear, trigonal pyramidal, tetrahedral, trigonal bipyramidal, and octahedral).

SECTION 9.2 The **valence-shell electron-pair repulsion (VSEPR) model** rationalizes molecular geometries based on the repulsions between **electron domains**, which are regions about a central atom in which electrons are likely to be found. **Bonding pairs** of electrons, which are those involved in making bonds, and **nonbonding pairs** of electrons, also called **lone pairs**, both create electron domains around an atom. According to the VSEPR model, electron domains orient themselves to minimize electrostatic repulsions; that is, they remain as far apart as possible. Electron domains from nonbonding pairs exert slightly greater repulsions than those from bonding pairs, which leads to certain preferred positions for nonbonding pairs and to the departure of bond angles from idealized values. Electron domains from multiple bonds exert slightly greater repulsions than those from single bonds. The arrangement of electron domains around a central atom is called the **electron-domain geometry**; the arrangement of atoms is called the **molecular geometry**.

SECTION 9.3 The dipole moment of a polyatomic molecule depends on the vector sum of the dipole moments associated with the individual bonds, called the **bond dipoles**. Certain molecular shapes, such as linear AB_2 and trigonal planar AB_3, assure that the bond dipoles cancel, producing a nonpolar molecule, which is one whose dipole moment is zero. In other shapes, such as bent AB_2 and trigonal pyramidal AB_3, the bond dipoles do not cancel and the molecule will be polar (that is, it will have a nonzero dipole moment).

SECTION 9.4 **Valence-bond theory** is an extension of Lewis's notion of electron-pair bonds. In valence-bond theory, covalent bonds are formed when atomic orbitals on neighboring atoms overlap one another. The overlap region is one of low energy, or greater stability, for the two electrons because of their simultaneous attraction to two nuclei. The greater the overlap between two orbitals, the stronger will be the bond that is formed.

SECTION 9.5 To extend the ideas of valence-bond theory to polyatomic molecules, we must envision mixing *s, p,* and sometimes *d* orbitals to form **hybrid orbitals**. The process of **hybridization** leads to hybrid atomic orbitals that have a large lobe directed to overlap with orbitals on another atom to make a bond. Hybrid orbitals can also accommodate nonbonding pairs. A particular mode of hybridization can be associated with each of three common electron-domain geometries (linear = sp; trigonal planar = sp^2; tetrahedral = sp^3).

SECTION 9.6 Covalent bonds in which the electron density lies along the line connecting the atoms (the internuclear axis) are called **sigma (σ) bonds**. Bonds can also be formed from the sideways overlap of p orbitals. Such a bond is called a **pi (π) bond**. A double bond, such as that in C_2H_4, consists of one σ bond and one π bond; a triple bond, such as that in C_2H_2, consists of one σ and two π bonds. The formation of a π bond requires that molecules adopt a specific orientation; the two CH_2 groups in C_2H_4, for example, must lie in the same plane. As a result, the presence of π bonds introduces rigidity into molecules. In molecules that have multiple bonds and more than one resonance structure, such as C_6H_6, the π bonds are **delocalized**; that is, the π bonds are spread among several atoms.

SECTION 9.7 **Molecular orbital theory** is another model used to describe the bonding in molecules. In this model the electrons exist in allowed energy states called **molecular orbitals (MOs)**. An MO can extend over all the atoms of a molecule. Like an atomic orbital, a molecular orbital has a definite energy and can hold two electrons of opposite spin. We can think of molecular orbitals as built up by combining atomic orbitals on different atomic centers. In the simplest case, the combination of two atomic orbitals leads to the formation of two MOs, one at lower energy and one at higher energy relative to the energy of the atomic orbitals. The lower-energy MO concentrates charge density in the region between the nuclei and is called a **bonding molecular orbital**. The higher-energy MO excludes electrons from the region between the nuclei and is called an **antibonding molecular orbital**. Occupation of bonding MOs favors bond formation, whereas occupation of antibonding MOs is unfavorable. The bonding and antibonding MOs formed by the combination of s orbitals are **sigma (σ) molecular orbitals**; they lie on the internuclear axis.

The combination of atomic orbitals and the relative energies of the molecular orbitals are shown by an **energy-level** (or **molecular orbital**) **diagram**. When the appropriate number of electrons are put into the MOs, we can calculate the **bond order** of a bond, which is half the difference between the number of electrons in bonding MOs and the number of electrons in antibonding MOs. A bond order of 1 corresponds to a single bond, and so forth. Bond orders can be fractional numbers.

SECTION 9.8 Electrons in core orbitals do not contribute to the bonding between atoms, so a molecular orbital description usually needs to consider only electrons in the outermost electron subshells. In order to describe the MOs of period 2 homonuclear diatomic molecules, we need to consider the MOs that can form by the combination of p orbitals. The p orbitals that point directly at one another can form σ bonding and σ^* antibonding MOs. The p orbitals that are oriented perpendicular to the internuclear axis combine to form **pi (π) molecular orbitals**. In diatomic molecules the π molecular orbitals occur as a pair of degenerate (same energy) bonding MOs and a pair of degenerate antibonding MOs. The σ_{2p} bonding MO is expected to be lower in energy than the π_{2p} bonding MOs because of larger orbital overlap of the p orbitals directed along the internuclear axis. However, this ordering is reversed in B_2, C_2, and N_2 because of interaction between the $2s$ and $2p$ atomic orbitals of different atoms.

The molecular orbital description of period 2 diatomic molecules leads to bond orders in accord with the Lewis structures of these molecules. Further, the model predicts correctly that O_2 should exhibit **paramagnetism**, which leads to attraction of a molecule into a magnetic field due to the influence of unpaired electrons. Molecules in which all the electrons are paired exhibit **diamagnetism**, which leads to weak repulsion from a magnetic field.

KEY SKILLS

- Be able to describe the three-dimensional shapes of molecules using the VSEPR model. (Section 9.2)
- Determine whether a molecule is polar or nonpolar based on its geometry and the individual bond dipole moments. (Section 9.3)
- Be able to explain the role of orbital overlap in the formation of covalent bonds. (Section 9.4)
- Be able to specify the hybridization state of atoms in molecules based on observed molecular structures. (Section 9.5)
- Be able to sketch how orbitals overlap to form sigma (σ) and pi (π) bonds. (Section 9.6)
- Be able to explain the existence of delocalized π bonds in molecules such as benzene. (Section 9.6)
- Be able to explain the concept of bonding and antibonding orbitals. (Section 9.7)
- Be able to draw molecular orbital energy-level diagrams and place electrons into them to obtain the bond orders and electron configurations of diatomic molecules using molecular orbital theory. (Sections 9.7 and 9.8)
- Understand the relationships among bond order, bond strength (bond enthalpy), and bond length. (Section 9.8)

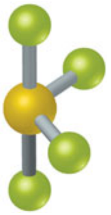
KEY EQUATION

- Bond order $= \frac{1}{2}$ (no. of bonding electrons $-$ no. of antibonding electrons) [9.1]

EXERCISES

VISUALIZING CONCEPTS

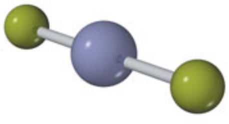
9.1 A certain AB_4 molecule has a "seesaw" shape:



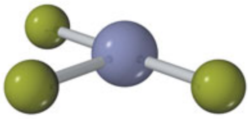
From which of the fundamental geometries shown in Figure 9.3 could you remove one or more atoms to create a molecule having this seesaw shape? [Section 9.1]

9.2 (**a**) If these three balloons are all the same size, what angle is formed between the red one and the green one? (**b**) If additional air is added to the blue balloon so that it gets larger, what happens to the angle between the red and green balloons? (**c**) What aspect of the VSEPR model is illustrated by part (b)? [Section 9.2]

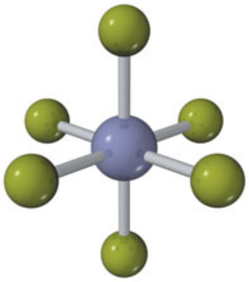
9.3 For each molecule (a)-(f), indicate how many different electron-domain geometries are consistent with the molecular geometry shown. [Section 9.2]



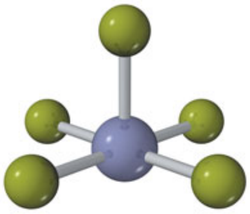
(a)



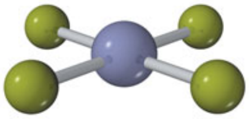
(b)



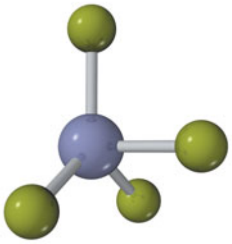
(c)



(d)

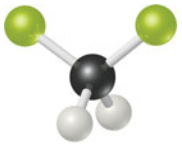


(e)

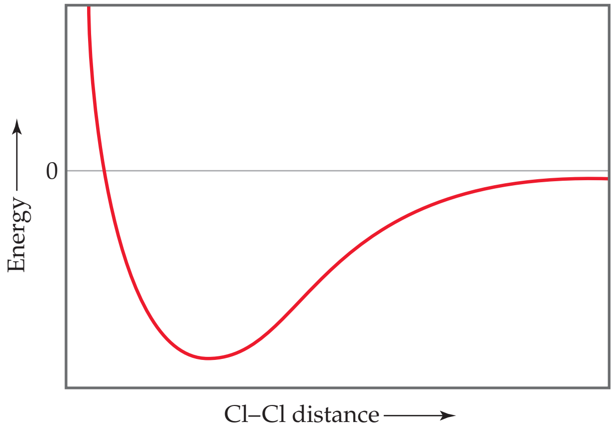


(f)

9.4 The molecule shown here is *difluoromethane* (CH_2F_2), which is used as a refrigerant called R-32. (**a**) Based on the structure, how many electron domains surround the C atom in this molecule? (**b**) Would the molecule have a nonzero dipole moment? (**c**) If the molecule is polar, in what direction will the overall dipole moment vector point in the molecule? [Sections 9.2 and 9.3]

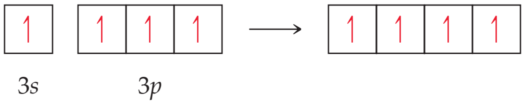


9.5 The following plot shows the potential energy of two Cl atoms as a function of the distance between them. (**a**) To what does an energy of zero correspond in this diagram? (**b**) According to the valence-bond model, why does the energy decrease as the Cl atoms move from a large separation to a smaller one? (**c**) What is the significance of the Cl—Cl distance at the minimum point in the plot? (**d**) Why does the energy rise at Cl—Cl distances less than that at the minimum point in the plot? (**e**) How can you estimate the bond strength of the Cl—Cl bond from the plot? [Section 9.4]

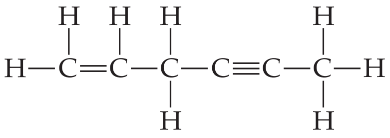


9.6 In the series SiF_4, PF_3, and SF_2, estimate the F—X—F bond angle in each case and explain your rationale. [Section 9.2]

9.7 The orbital diagram that follows presents the final step in the formation of hybrid orbitals by a silicon atom. What type of hybrid orbital is produced in this hybridization? [Section 9.5]



9.8 In the hydrocarbon

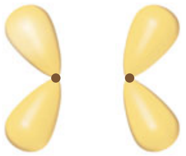

$H_2C{=}CH{-}CH_2{-}C{\equiv}C{-}CH_3$

(**a**) What is the hybridization at each carbon atom in the molecule? (**b**) How many σ bonds are there in the molecule? (**c**) How many π bonds? (d) Identify all the 120° bond angles in the molecule. [Section 9.6]

9.9 For each of these contour representations of molecular orbitals, identify (**a**) the atomic orbitals (*s* or *p*) used to construct the MO (**b**) the type of MO (σ or π), (**c**) whether the MO is bonding or antibonding, and (**d**) the locations of nodal planes. [Sections 9.7 and 9.8]

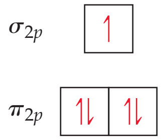
(i)

(ii)



(iii)

9.10 The diagram that follows shows the highest-energy occupied MOs of a neutral molecule CX, where element X is in the same row of the periodic table as C. (**a**) Based on the number of electrons, can you determine the identity of X? (**b**) Would the molecule be diamagnetic or paramagnetic? (**c**) Consider the π_{2p} MOs of the molecule. Would you expect them to have a greater atomic orbital contribution from C, have a greater atomic orbital contribution from X, or be an equal mixture of atomic orbitals from the two atoms? [Section 9.8]



MOLECULAR SHAPES; THE VSEPR MODEL (sections 9.1 and 9.2)

9.11 An AB_2 molecule is described as linear, and the A—B bond length is known. (**a**) Does this information completely describe the geometry of the molecule? (**b**) Can you tell how many nonbonding pairs of electrons are around the A atom from this information?

9.12 (**a**) Methane (CH_4) and the perchlorate ion (ClO_4^-) are both described as tetrahedral. What does this indicate about their bond angles? (**b**) The NH_3 molecule is trigonal pyramidal, while BF_3 is trigonal planar. Which of these molecules is flat?

9.13 How does a trigonal pyramid differ from a tetrahedron so far as molecular geometry is concerned?

9.14 Describe the bond angles to be found in each of the following molecular structures: (**a**) planar trigonal, (**b**) tetrahedral, (**c**) octahedral, (**d**) linear.

9.15 (**a**) What is meant by the term *electron domain*? (**b**) Explain in what way electron domains behave like the balloons in Figure 9.5. Why do they do so?

9.16 What property of the electron causes electron domains to have an effect on molecular shapes?

9.17 (**a**) How does one determine the number of electron domains in a molecule or ion? (**b**) What is the difference between a *bonding electron domain* and a *nonbonding electron domain*?

9.18 Would you expect the nonbonding electron-pair domain in NH_3 to be greater or less in size than for the corresponding one in PH_3? Explain.

9.19 In which of these molecules or ions does the presence of nonbonding electron pairs produce an effect on molecular shape, assuming they are all in the gaseous state? (**a**) SiH_4, (**b**) PF_3, (**c**) HBr, (**d**) HCN, (**e**) SO_2.

9.20 In which of the following molecules can you confidently predict the bond angles about the central atom, and for which would you be a bit uncertain? Explain in each case. (**a**) H_2S, (**b**) BCl_3, (**c**) CH_3I, (**d**) CBr_4, (**e**) $TeBr_4$.

9.21 How many nonbonding electron pairs are there in each of the following molecules: **(a)** $(CH_3)_2S$, **(b)** HCN, **(c)** H_2C_2, **(d)** CH_3F?

9.22 Describe the characteristic electron-domain geometry of each of the following numbers of electron domains about a central atom: **(a)** 3, **(b)** 4, **(c)** 5, **(d)** 6.

9.23 What is the difference between the electron-domain geometry and the molecular geometry of a molecule? Use the water molecule as an example in your discussion. Why do we need to make this distinction?

9.24 An AB_3 molecule is described as having a trigonal-bipyramidal electron-domain geometry. How many nonbonding domains are on atom A? Explain.

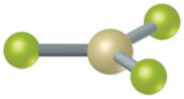
9.25 Give the electron-domain and molecular geometries of a molecule that has the following electron domains on its central atom: **(a)** four bonding domains and no nonbonding domains, **(b)** three bonding domains and two nonbonding domains, **(c)** five bonding domains and one nonbonding domain, **(d)** four bonding domains and two nonbonding domains.

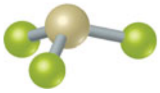
9.26 What are the electron-domain and molecular geometries of a molecule that has the following electron domains on its central atom? **(a)** three bonding domains and no nonbonding domains, **(b)** three bonding domains and one nonbonding domain, **(c)** two bonding domains and two nonbonding domains.

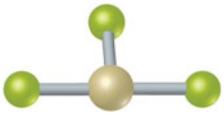
9.27 Give the electron-domain and molecular geometries for the following molecules and ions: **(a)** HCN, **(b)** SO_3^{2-}, **(c)** SF_4, **(d)** PF_6^-, **(e)** NH_3Cl^+, **(f)** N_3^-.

9.28 Draw the Lewis structure for each of the following molecules or ions, and predict their electron-domain and molecular geometries: **(a)** AsF_3, **(b)** CH_3^+, **(c)** BrF_3, **(d)** ClO_3^-, **(e)** XeF_2, **(f)** BrO_2^-.

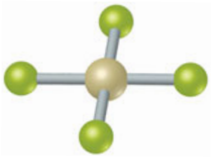
9.29 The figure that follows shows ball-and-stick drawings of three possible shapes of an AF_3 molecule. **(a)** For each shape, give the electron-domain geometry on which the molecular geometry is based. **(b)** For each shape, how many nonbonding electron domains are there on atom A? **(c)** Which of the following elements will lead to an AF_3 molecule with the shape in (ii): Li, B, N, Al, P, Cl? **(d)** Name an element A that is expected to lead to the AF_3 structure shown in (iii). Explain your reasoning.

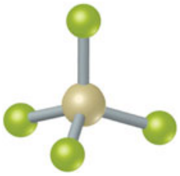

(i)


(ii)


(iii)

9.30 The figure that follows contains ball-and-stick drawings of three possible shapes of an AF_4 molecule. **(a)** For each shape, give the electron-domain geometry on which the molecular geometry is based. **(b)** For each shape, how many nonbonding electron domains are there on atom A? **(c)** Which of the following elements will lead to an AF_4 molecule with the shape in (iii): Be, C, S, Se, Si, Xe? **(d)** Name an element A that is expected to lead to the AF_4 structure shown in (i).


(i)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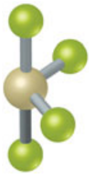
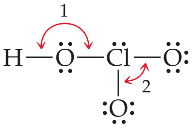
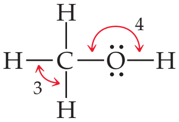
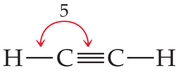
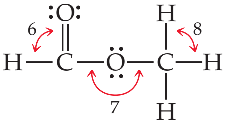

(iii)

9.31 Give the approximate values for the indicated bond angles in the following molecules:

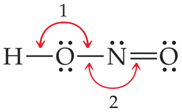
(a)


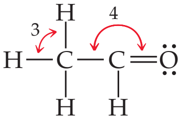
(b)


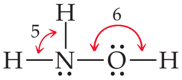
(c)


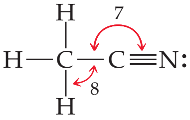
(d)


9.32 Give approximate values for the indicated bond angles in the following molecules:

(a)


(b)


(c)


(d)


9.33 In which of the following AF_n molecules or ions is there more than one F—A—F bond angle: SiF_4, PF_5, SF_4, AsF_3?

9.34 The three species NH_2^-, NH_3, and NH_4^+ have H—N—H bond angles of 105°, 107°, and 109°, respectively. Explain this variation in bond angles.

9.35 **(a)** Explain why BrF_4^- is square planar, whereas BF_4^- is tetrahedral. **(b)** How would you expect the H—X—H bond angle to vary in the series H_2O, H_2S, H_2Se? Explain. (*Hint:* The size of an electron pair domain depends in part on the electronegativity of the central atom.)

9.36 **(a)** Explain why the following ions have different bond angles: ClO_2^- and NO_2^-. Predict the bond angle in each case. **(b)** Explain why the XeF_2 molecule is linear.

SHAPES AND POLARITY OF POLYATOMIC MOLECULES (section 9.3)

9.37 What is the distinction between a bond dipole and a molecular dipole moment?

9.38 Consider a molecule with formula AX_3. Supposing the A—X bond is polar, how would you expect the dipole moment of the AX_3 molecule to change as the X—A—X bond angle increases from 100° to 120°?

9.39 **(a)** Does SCl_2 have a dipole moment? If so, in which direction does the net dipole point? **(b)** Does $BeCl_2$ have a dipole moment? If so, in which direction does the net dipole point?

9.40 **(a)** The PH_3 molecule is polar. Does this offer experimental proof that the molecule cannot be planar? Explain. **(b)** It turns out that ozone, O_3, has a small dipole moment. How is this possible, given that all the atoms are the same?

9.41 **(a)** Consider the AF_3 molecules in Exercise 9.29. Which of these will have a nonzero dipole moment? Explain. **(b)** Which of the AF_4 molecules in Exercise 9.30 will have a zero dipole moment?

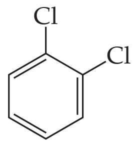
9.42 **(a)** What conditions must be met if a molecule with polar bonds is nonpolar? **(b)** What geometries will signify nonpolar molecules for AB_2, AB_3, and AB_4 geometries?

9.43 Predict whether each of the following molecules is polar or nonpolar: **(a)** IF, **(b)** CS_2, **(c)** SO_3, **(d)** PCl_3, **(e)** SF_6, **(f)** IF_5.

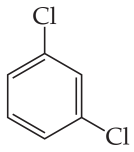
9.44 Predict whether each of the following molecules is polar or nonpolar: **(a)** CCl_4, **(b)** NH_3, **(c)** SF_4, **(d)** XeF_4, **(e)** CH_3Br, **(f)** GaH_3.

9.45 Dichloroethylene ($C_2H_2Cl_2$) has three forms (isomers), each of which is a different substance. **(a)** Draw Lewis structures of the three isomers, all of which have a carbon–carbon double bond. **(b)** Which of these isomers has a zero dipole moment? **(c)** How many isomeric forms can chloroethylene, C_2H_3Cl, have? Would they be expected to have dipole moments?

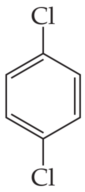
9.46 Dichlorobenzene, $C_6H_4Cl_2$, exists in three forms (isomers) called *ortho*, *meta*, and *para*:



ortho



meta



para

Which of these has a nonzero dipole moment? Explain.

ORBITAL OVERLAP; HYBRID ORBITALS (sections 9.4 and 9.5)

9.47 **(a)** What is meant by the term *orbital overlap*? **(b)** Describe what a chemical bond is in terms of electron density between two atoms.

9.48 Draw sketches illustrating the overlap between the following orbitals on two atoms: **(a)** the 2*s* orbital on each atom, **(b)** the $2p_z$ orbital on each atom (assume both atoms are on the *z*-axis), **(c)** the 2*s* orbital on one atom and the $2p_z$ orbital on the other atom.

9.49 Consider the bonding in an MgH_2 molecule. **(a)** Draw a Lewis structure for the molecule, and predict its molecular geometry. **(b)** What hybridization scheme is used in MgH_2? **(c)** Sketch one of the two-electron bonds between an Mg hybrid orbital and an H 1*s* atomic orbital.

9.50 How would you expect the extent of overlap of the bonding atomic orbitals to vary in the series IF, ICl, IBr, and I_2? Explain your answer.

9.51 Fill in the blank spaces in the following chart. If the molecule column is blank, find an example that fulfills the conditions of the rest of the row.

Molecule	Electron-Domain Geometry	Hybridization of Central Atom	Dipole Moment? Yes or No
CO_2			
		sp^3	Yes
		sp^3	No
	Trigonal planar		No
SF_4			
	Octahedral		No
		sp^2	Yes
	Trigonal bipyramidal		No
XeF_2			

9.52 Why are there no sp^4 or sp^5 hybrid orbitals?

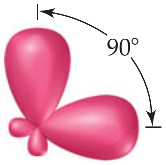
9.53 **(a)** Starting with the orbital diagram of a boron atom, describe the steps needed to construct hybrid orbitals appropriate to describe the bonding in BF_3. **(b)** What is the name given to the hybrid orbitals constructed in (a)? **(c)** Sketch the large lobes of the hybrid orbitals constructed in part (a). **(d)** Are any valence atomic orbitals of B left unhybridized? If so, how are they oriented relative to the hybrid orbitals?

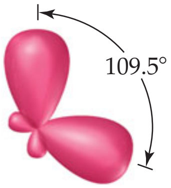
9.54 **(a)** Starting with the orbital diagram of a sulfur atom, describe the steps needed to construct hybrid orbitals appropriate to describe the bonding in SF_2. **(b)** What is the name given to the hybrid orbitals constructed in (a)? **(c)** Sketch the large lobes of these hybrid orbitals. **(d)** Would the hybridization scheme in part (a) be appropriate for SF_4? Explain.

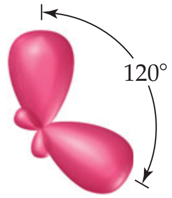
9.55 Indicate the hybridization of the central atom in **(a)** BCl_3, **(b)** $AlCl_4^-$, **(c)** CS_2, **(d)** GeH_4.

9.56 What is the hybridization of the central atom in **(a)** $SiCl_4$, **(b)** HCN, **(c)** SO_3, **(d)** $TeCl_2$.

9.57 Shown here are three pairs of hybrid orbitals, with each set at a characteristic angle. For each pair, determine the type of hybridization, if any, that could lead to hybrid orbitals at the specified angle.







9.58 **(a)** Which geometry and central atom hybridization would you expect in the series BH_4^-, CH_4, NH_4^+? **(b)** What would you expect for the magnitude and direction of the bond dipoles in this series? **(c)** Write the formulas for the analogous species of the elements of period 3; would you expect them to have the same hybridization at the central atom?

MULTIPLE BONDS (section 9.6)

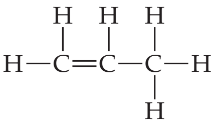
9.59 (**a**) Draw a picture showing how two *p* orbitals on two different atoms can be combined to make a sigma bond. (**b**) Sketch a π bond that is constructed from *p* orbitals. (**c**) Which is generally stronger, a σ bond or a π bond? Explain. (**d**) Can two *s* orbitals combine to form a π bond? Explain.

9.60 (**a**) If the valence atomic orbitals of an atom are *sp* hybridized, how many unhybridized *p* orbitals remain in the valence shell? How many π bonds can the atom form? (**b**) Imagine that you could hold two atoms that are bonded together, twist them, and not change the bond length. Would it be easier to twist (rotate) around a single σ bond or around a double (σ plus π) bond, or would they be the same? Explain.

9.61 (**a**) Draw Lewis structures for ethane (C_2H_6), ethylene (C_2H_4), and acetylene (C_2H_2). (**b**) What is the hybridization of the carbon atoms in each molecule? (**c**) Predict which molecules, if any, are planar. (**d**) How many σ and π bonds are there in each molecule? (**e**) Suppose that silicon could form molecules that are precisely the analogs of ethane, ethylene, and acetylene. How would you describe the bonding about Si in terms of hydrid orbitals? Silicon does not readily form some of the analogous compounds containing π bonds. Why might this be the case?

9.62 The nitrogen atoms in N_2 participate in multiple bonding, whereas those in hydrazine, N_2H_4, do not. (**a**) Draw Lewis structures for both molecules. (**b**) What is the hybridization of the nitrogen atoms in each molecule? (**c**) Which molecule has the stronger N—N bond?

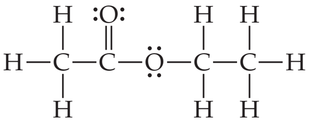
9.63 Propylene, C_3H_6, is a gas that is used to form the important polymer called polypropylene. Its Lewis structure is



$$H-\overset{H}{C}=\overset{H}{C}-\underset{H}{\overset{H}{C}}-H$$

(**a**) What is the total number of valence electrons in the propylene molecule? (**b**) How many valence electrons are used to make σ bonds in the molecule? (**c**) How many valence electrons are used to make π bonds in the molecule? (**d**) How many valence electrons remain in nonbonding pairs in the molecule? (**e**) What is the hybridization at each carbon atom in the molecule?

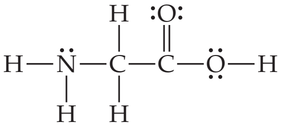
9.64 Ethyl acetate, $C_4H_8O_2$, is a fragrant substance used both as a solvent and as an aroma enhancer. Its Lewis structure is



$$H-\underset{H}{\overset{H}{C}}-\overset{:O:}{\overset{\|}{C}}-\ddot{\underset{..}{O}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

(**a**) What is the hybridization at each of the carbon atoms of the molecule? (**b**) What is the total number of valence electrons in ethyl acetate? (**c**) How many of the valence electrons are used to make σ bonds in the molecule? (**d**) How many valence electrons are used to make π bonds? (**e**) How many valence electrons remain in nonbonding pairs in the molecule?

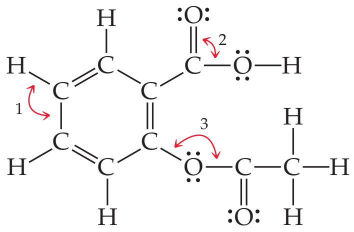
9.65 Consider the Lewis structure for glycine, the simplest amino acid:



$$H-\underset{H}{\ddot{N}}-\underset{H}{\overset{H}{C}}-\overset{:O:}{\overset{\|}{C}}-\ddot{\underset{..}{O}}-H$$

(**a**) What are the approximate bond angles about each of the two carbon atoms, and what are the hybridizations of the orbitals on each of them? (**b**) What are the hybridizations of the orbitals on the two oxygens and the nitrogen atom, and what are the approximate bond angles at the nitrogen? (**c**) What is the total number of σ bonds in the entire molecule, and what is the total number of π bonds?

9.66 Acetylsalicylic acid, better known as aspirin, has the Lewis structure



(**a**) What are the approximate values of the bond angles labeled 1, 2, and 3? (**b**) What hybrid orbitals are used about the central atom of each of these angles? (**c**) How many σ bonds are in the molecule?

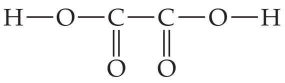
9.67 (**a**) What is the difference between a localized π bond and a delocalized one? (**b**) How can you determine whether a molecule or ion will exhibit delocalized π bonding? (**c**) Is the π bond in NO_2^- localized or delocalized?

9.68 (**a**) Write a single Lewis structure for SO_3, and determine the hybridization at the S atom. (**b**) Are there other equivalent Lewis structures for the molecule? (**c**) Would you expect SO_3 to exhibit delocalized π bonding? Explain.

9.69 Predict the molecular geometry of each of the following molecules:

(**a**) $H-C\equiv C-C\equiv C-C\equiv N$

(**b**)



$$H-O-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-O-H$$

(**c**) $H-N=N-H$

9.70 What hybridization do you expect for the atom indicated in red in each of the following species?

(**a**) $CH_3CO_2^-$; (**b**) PH_4^+; (**c**) AlF_3; (**d**) $H_2C=CH-CH_2^+$

MOLECULAR ORBITALS AND SECOND-ROW DIATOMIC MOLECULES (sections 9.7 and 9.8)

9.71 (**a**) What is the difference between hybrid orbitals and molecular orbitals? (**b**) How many electrons can be placed into each MO of a molecule? (**c**) Can antibonding molecular orbitals have electrons in them?

9.72 (**a**) If you combine two atomic orbitals on two different atoms to make a new orbital, is this a hybrid orbital or a molecular orbital? (**b**) If you combine two atomic orbitals on *one* atom to make a new orbital, is this a hybrid orbital or a molecular orbital? (**c**) Does the Pauli exclusion principle (Section 6.7) apply to MOs? Explain.

9.73 Consider the H_2^+ ion. (**a**) Sketch the molecular orbitals of the ion and draw its energy-level diagram. (**b**) How many electrons are there in the H_2^+ ion? (**c**) Draw the electron configuration of the ion in terms of its MOs. (**d**) What is the bond order in H_2^+? (**e**) Suppose that the ion is excited by light so that an electron moves from a lower-energy to a higher-energy MO. Would you expect the excited-state H_2^+ ion to be stable or to fall apart? Explain.

9.74 (**a**) Sketch the molecular orbitals of the H_2^- ion and draw its energy-level diagram. (**b**) Write the electron configuration of the ion in terms of its MOs. (**c**) Calculate the bond order in H_2^-. (**d**) Suppose that the ion is excited by light, so that an electron moves from a lower-energy to a higher-energy molecular orbital. Would you expect the excited-state H_2^- ion to be stable? Explain.

9.75 Draw a picture that shows all three $2p$ orbitals on one atom and all three $2p$ orbitals on another atom. (**a**) Imagine the atoms coming close together to bond. How many σ bonds can the two sets of $2p$ orbitals make with each other? (**b**) How many π bonds can the two sets of $2p$ orbitals make with each other? (**c**) How many antibonding orbitals, and of what type, can be made from the two sets of $2p$ orbitals?

9.76 (**a**) What is the probability of finding an electron on the internuclear axis if the electron occupies a π molecular orbital? (**b**) For a homonuclear diatomic molecule, what similarities and differences are there between the π_{2p} MO made from the $2p_x$ atomic orbitals and the π_{2p} MO made from the $2p_y$ atomic orbitals? (**c**) How do the π^*_{2p} MOs formed from the $2p_x$ and $2p_y$ atomic orbitals differ from the π_{2p} MOs in terms of energies and electron distributions?

9.77 (**a**) What are the relationships among bond order, bond length, and bond energy? (**b**) According to molecular orbital theory, would either Be_2 or Be_2^+ be expected to exist? Explain.

9.78 Explain the following: (**a**) The *peroxide* ion, O_2^{2-}, has a longer bond length than the *superoxide* ion, O_2^-. (**b**) The magnetic properties of B_2 are consistent with the π_{2p} MOs being lower in energy than the σ_{2p} MO. (**c**) The O_2^{2+} ion has a stronger O—O bond than O_2 itself.

9.79 (**a**) What does the term *diamagnetism* mean? (**b**) How does a diamagnetic substance respond to a magnetic field? (**c**) Which of the following ions would you expect to be diamagnetic: N_2^{2-}, O_2^{2-}, Be_2^{2+}, C_2^-?

9.80 (**a**) What does the term *paramagnetism* mean? (**b**) How can one determine experimentally whether a substance is paramagnetic? (**c**) Which of the following ions would you expect to be paramagnetic: O_2^+, N_2^{2-}, Li_2^+, O_2^{2-}? For those ions that are paramagnetic, determine the number of unpaired electrons.

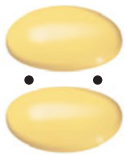
9.81 Using Figures 9.35 and 9.43 as guides, draw the molecular orbital electron configuration for (**a**) B_2^+, (**b**) Li_2^+, (**c**) N_2^+, (**d**) Ne_2^{2+}. In each case indicate whether the addition of an electron to the ion would increase or decrease the bond order of the species.

9.82 If we assume that the energy-level diagrams for homonuclear diatomic molecules shown in Figure 9.43 can be applied to heteronuclear diatomic molecules and ions, predict the bond order and magnetic behavior of (**a**) CO^+, (**b**) NO^-, (**c**) OF^+, (**d**) NeF^+.

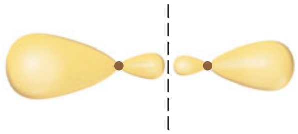
9.83 Determine the electron configurations for CN^+, CN, and CN^-. (**a**) Which species has the strongest C—N bond? (**b**) Which species, if any, has unpaired electrons?

9.84 (**a**) The nitric oxide molecule, NO, readily loses one electron to form the NO^+ ion. Why is this consistent with the electronic structure of NO? (**b**) Predict the order of the N—O bond strengths in NO, NO^+, and NO^-, and describe the magnetic properties of each. (**c**) With what neutral homonuclear diatomic molecules are the NO^+ and NO^- ions isoelectronic (same number of electrons)?

[9.85] Consider the molecular orbitals of the P_2 molecule. Assume that the MOs of diatomics from the third row of the periodic table are analogous to those from the second row. (**a**) Which valence atomic orbitals of P are used to construct the MOs of P_2? (**b**) The figure that follows shows a sketch of one of the MOs for P_2. What is the label for this MO? (**c**) For the P_2 molecule, how many electrons occupy the MO in the figure? (**d**) Is P_2 expected to be diamagnetic or paramagnetic? Explain.



[9.86] The iodine bromide molecule, IBr, is an *interhalogen compound*. Assume that the molecular orbitals of IBr are analogous to the homonuclear diatomic molecule F_2. (**a**) Which valence atomic orbitals of I and of Br are used to construct the MOs of IBr? (**b**) What is the bond order of the IBr molecule? (**c**) One of the valence MOs of IBr is sketched here. Why are the atomic orbital contributions to this MO different in size? (**d**) What is the label for the MO? (**e**) For the IBr molecule, how many electrons occupy the MO?



ADDITIONAL EXERCISES

9.87 (**a**) What is the physical basis for the VSEPR model? (**b**) When applying the VSEPR model, we count a double or triple bond as a single electron domain. Why is this justified?

9.88 What is the fundamental basis on which we assign electrons to electron domains in pairs and with their spins paired?

9.89 The molecules SiF_4, SF_4, and XeF_4 have molecular formulas of the type AF_4, but the molecules have different molecular geometries. Predict the shape of each molecule, and explain why the shapes differ.

9.90 Consider the molecule PF_4Cl. (**a**) Draw a Lewis structure for the molecule, and predict its electron-domain geometry. (**b**) Which would you expect to take up more space, a P—F bond or a P—Cl bond? Explain. (**c**) Predict the molecular geometry of PF_4Cl. How did your answer for part (b) influence your answer here in part (c)? (**d**) Would you expect the molecule to distort from its ideal electron-domain geometry? If so, how would it distort?

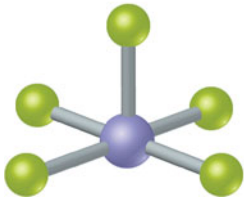
[9.91] The vertices of a tetrahedron correspond to four alternating corners of a cube. By using analytical geometry, demonstrate that the angle made by connecting two of the vertices to a point at the center of the cube is 109.5°, the characteristic angle for tetrahedral molecules.

9.92 From their Lewis structures, determine the number of σ and π bonds in each of the following molecules or ions: (**a**) CO_2; (**b**) cyanogen, $(CN)_2$; (**c**) formaldehyde, H_2CO; (**d**) formic acid, HCOOH, which has one H and two O atoms attached to C.

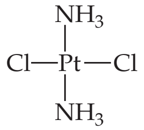
9.93 The lactic acid molecule, $CH_3CH(OH)COOH$, gives sour milk its unpleasant, sour taste. (**a**) Draw the Lewis structure for the molecule, assuming that carbon always forms four bonds in its stable compounds. (**b**) How many π and how many σ bonds are in the molecule? (**c**) Which CO bond is shortest in the molecule? (**d**) What is the hybridization of atomic orbitals around the carbon atom associated with that short bond? (**e**) What are the approximate bond angles around each carbon atom in the molecule?

9.94 The PF_3 molecule has a dipole moment of 1.03 D, but BF_3 has a dipole moment of zero. How can you explain the difference?

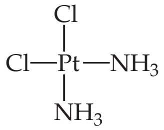
9.95 An AB_5 molecule adopts the geometry shown here. (**a**) What is the name of this geometry? (**b**) Do you think there are any nonbonding electron pairs on atom A? Why or why not? (**c**) Suppose the atoms B are halogen atoms. Can you determine uniquely to which group in the periodic table atom A belongs?



9.96 There are two compounds of the formula $Pt(NH_3)_2Cl_2$:



$$Cl{-}\overset{NH_3}{\underset{NH_3}{Pt}}{-}Cl$$



$$Cl{-}\overset{Cl}{\underset{NH_3}{Pt}}{-}NH_3$$

The compound on the right, *cisplatin,* is used in cancer therapy. The compound on the left, *transplatin,* is ineffective for cancer therapy. Both compounds have a square-planar geometry. (**a**) Which compound has a nonzero dipole moment? (**b**) The reason cisplatin is a good anticancer drug is that it binds tightly to DNA. Cancer cells are rapidly dividing, producing a lot of DNA. Consequently, cisplatin kills cancer cells at a faster rate than normal cells. However, since normal cells also are making DNA, cisplatin also attacks healthy cells, which leads to unpleasant side effects. The way both molecules bind to DNA involves the Cl^- ions leaving the Pt ion, to be replaced by two nitrogens in DNA. Draw a picture in which a long vertical line represents a piece of DNA. Draw the $Pt(NH_3)_2$ fragments of cisplatin and transplatin with the proper shape. Also draw them attaching to your DNA line. Can you explain from your drawing why the shape of the cisplatin causes it to bind to DNA more effectively than transplatin?

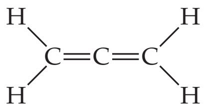
[9.97] The O—H bond lengths in the water molecule (H_2O) are 0.96 Å, and the H—O—H angle is 104.5°. The dipole moment of the water molecule is 1.85 D. (**a**) In what directions do the bond dipoles of the O—H bonds point? In what direction does the dipole moment vector of the water molecule point? (**b**) Calculate the magnitude of the bond dipole of the O—H bonds. (*Note:* You will need to use vector addition to do this.) (**c**) Compare your answer from part (b) to the dipole moments of the hydrogen halides (Table 8.3). Is your answer in accord with the relative electronegativity of oxygen?

[9.98] The reaction of three molecules of fluorine gas with a Xe atom produces the substance xenon hexafluoride, XeF_6:

$$Xe(g) + 3\,F_2(g) \longrightarrow XeF_6(s)$$

(**a**) Draw a Lewis structure for XeF_6. (**b**) If you try to use the VSEPR model to predict the molecular geometry of XeF_6, you run into a problem. What is it? (**c**) What could you do to resolve the difficulty in part (b)? (**d**) The molecule IF_7 has a pentagonal-bipyramidal structure (five equatorial fluorine atoms at the vertices of a regular pentagon and two axial fluorine atoms). Based on the structure of IF_7, suggest a structure for XeF_6.

[9.99] The Lewis structure for allene is

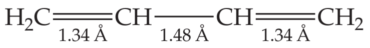


Make a sketch of the structure of this molecule that is analogous to Figure 9.25. In addition, answer the following three questions: (**a**) Is the molecule planar? (**b**) Does it have a nonzero dipole moment? (**c**) Would the bonding in allene be described as delocalized? Explain.

[9.100] The azide ion, N_3^-, is linear with two N—N bonds of equal length, 1.16 Å. (**a**) Draw a Lewis structure for the azide ion. (**b**) With reference to Table 8.5, is the observed N—N bond length consistent with your Lewis structure? (**c**) What hybridization scheme would you expect at each of the nitrogen atoms in N_3^-? (**d**) Show which hybridized and unhybridized orbitals are involved in the formation of σ and π bonds in N_3^-. (**e**) It is often observed that σ bonds that involve an *sp* hybrid orbital are shorter than those that involve only sp^2 or sp^3 hybrid orbitals. Can you propose a reason for this? Is this observation applicable to the observed bond lengths in N_3^-?

[9.101] In ozone, O_3, the two oxygen atoms on the ends of the molecule are equivalent to one another. (**a**) What is the best choice of hybridization scheme for the atoms of ozone? (**b**) For one of the resonance forms of ozone, which of the orbitals are used to make bonds and which are used to hold nonbonding pairs of electrons? (**c**) Which of the orbitals can be used to delocalize the π electrons? (**d**) How many electrons are delocalized in the π system of ozone?

9.102 Butadiene, C_4H_6, is a planar molecule that has the following carbon–carbon bond lengths:

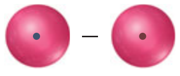


$$H_2C\underset{1.34\,Å}{=\!=\!=}CH\underset{1.48\,Å}{-\!-\!-}CH\underset{1.34\,Å}{=\!=\!=}CH_2$$

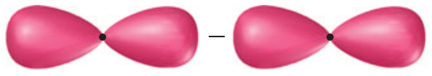
(**a**) Predict the bond angles around each of the carbon atoms and sketch the molecule.

(**b**) Compare the bond lengths to the average bond lengths listed in Table 8.5. Can you explain any differences?

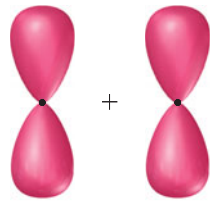
[9.103] The following sketches show the atomic orbital wave functions (with phases) used to construct some of the MOs of a homonuclear diatomic molecule. For each sketch, determine the type of MO that will result from mixing the atomic orbital wave functions as drawn. Use the same labels for the MOs as in the "Closer Look" box on phases.



(a)



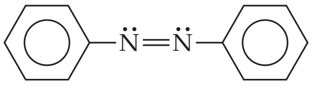
(b)



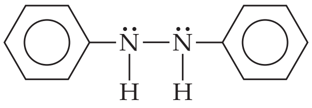
(c)

9.104 Write the electron configuration for the first excited state for N_2 —that is, the state with the highest-energy electron moved to the next available energy level. (**a**) Is the nitrogen in its first excited state diamagnetic or paramagnetic? (**b**) Is the N—N bond strength in the first excited state stronger or weaker compared to that in the ground state? Explain.

9.105 *Azo dyes* are organic dyes that are used for many applications, such as the coloring of fabrics. Many azo dyes are derivatives of the organic substance *azobenzene*, $C_{12}H_{10}N_2$. A closely related substance is *hydrazobenzene*, $C_{12}H_{12}N_2$. The Lewis structures of these two substances are



Azobenzene



Hydrazobenzene

(Recall the shorthand notation used for benzene.) (**a**) What is the hybridization at the N atom in each of the substances? (**b**) How many unhybridized atomic orbitals are there on the N and the C atoms in each of the substances? (**c**) Predict the N—N—C angles in each of the substances. (**d**) Azobenzene is said to have greater delocalization of its π electrons than hydrazobenzene. Discuss this statement in light of your answers to (a) and (b). (**e**) All the atoms of azobenzene lie in one plane, whereas those of hydrazobenzene do not. Is this observation consistent with the statement in part (d)? (**f**) Azobenzene is an intense red-orange color, whereas hydrazobenzene is nearly colorless. Which molecule would be a better one to use in a solar energy conversion device? (See the "Chemistry Put to Work" box for more information about solar cells.)

[9.106] (**a**) Using only the valence atomic orbitals of a hydrogen atom and a fluorine atom, and following the model of Figure 9.46, how many MOs would you expect for the HF molecule? (**b**) How many of the MOs from part (a) would be occupied by electrons? (**c**) It turns out that the difference in energies between the valence atomic orbitals of H and F are sufficiently different that we can neglect the interaction of the 1*s* orbital of hydrogen with the 2*s* orbital of fluorine. The 1*s* orbital of hydrogen will mix only with one 2*p* orbital of fluorine. Draw pictures showing the proper orientation of all three 2*p* orbitals on F interacting with a 1*s* orbital on H. Which of the 2*p* orbitals can actually make a bond with a 1*s* orbital, assuming that the atoms lie on the *z*-axis? (**d**) In the most accepted picture of HF, all the other atomic orbitals on fluorine move over at the same energy into the molecular orbital energy-level diagram for HF. These are called "nonbonding orbitals." Sketch the energy-level diagram for HF using this information and calculate the bond order. (Nonbonding electrons do not contribute to bond order.) (**e**) Look at the Lewis structure for HF. Where are the nonbonding electrons?

[9.107] Carbon monoxide, CO, is isoelectronic to N_2. (**a**) Draw a Lewis structure for CO that satisfies the octet rule. (**b**) Assume that the diagram in Figure 9.46 can be used to describe the MOs of CO. What is the predicted bond order for CO? Is this answer in accord with the Lewis structure you drew in part (a)? (**c**) Experimentally, it is found that the highest-energy electrons in CO reside in a σ-type MO. Is that observation consistent with Figure 9.46? If not, what modification needs to be made to the diagram? How does this modification relate to Figure 9.43? (**d**) Would you expect the π_{2p} MOs of CO to have equal atomic orbital contributions from the C and O atoms? If not, which atom would have the greater contribution?

9.108 The energy-level diagram in Figure 9.36 shows that the sideways overlap of a pair of *p* orbitals produces two molecular orbitals, one bonding and one antibonding. In ethylene there is a pair of electrons in the bonding π orbital between the two carbons. Absorption of a photon of the appropriate wavelength can result in promotion of one of the bonding electrons from the π_{2p} to the π^*_{2p} molecular orbital. (**a**) What would you expect this electronic transition to do to the carbon–carbon bond order in ethylene? (**b**) How does this relate to the fact that absorption of a photon of appropriate wavelength can cause ready rotation about the carbon–carbon bond, as described in the "Chemistry and Life" box and shown in Figure 9.30?

INTEGRATIVE EXERCISES

9.109 A compound composed of 2.1% H, 29.8% N, and 68.1% O has a molar mass of approximately 50 g/mol. (**a**) What is the molecular formula of the compound? (**b**) What is its Lewis structure if H is bonded to O? (**c**) What is the geometry of the molecule? (**d**) What is the hybridization of the orbitals around the N atom? (**e**) How many σ and how many π bonds are there in the molecule?

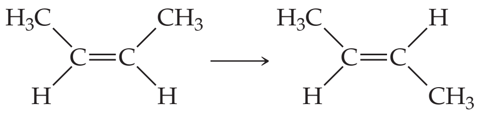
9.110 Sulfur tetrafluoride (SF_4) reacts slowly with O_2 to form sulfur tetrafluoride monoxide (OSF_4) according to the following unbalanced reaction:

$$SF_4(g) + O_2(g) \longrightarrow OSF_4(g)$$

The O atom and the four F atoms in OSF_4 are bonded to a central S atom. (**a**) Balance the equation. (**b**) Write a Lewis structure of OSF_4 in which the formal charges of all atoms are zero. (**c**) Use average bond enthalpies (Table 8.4) to estimate the enthalpy of the reaction. Is it endothermic or exothermic? (**d**) Determine the electron-domain geometry of OSF_4, and write two possible molecular geometries for the molecule based on this electron-domain geometry. (**e**) Which of the molecular geometries in part (d) is more likely to be observed for the molecule? Explain.

[9.111] The phosphorus trihalides (PX_3) show the following variation in the bond angle X—P—X: PF_3, 96.3°; PCl_3, 100.3°; PBr_3, 101.0°; PI_3, 102.0°. The trend is generally attributed to the change in the electronegativity of the halogen. (**a**) Assuming that all electron domains are the same size, what value of the X—P—X angle is predicted by the VSEPR model? (**b**) What is the general trend in the X—P—X angle as the halide electronegativity increases? (**c**) Using the VSEPR model, explain the observed trend in X—P—X angle as the electronegativity of X changes. (**d**) Based on your answer to part (c), predict the structure of $PBrCl_4$.

[9.112] The molecule 2-butene, C_4H_8, can undergo a geometric change called *cis-trans isomerization*:



cis-2-butene *trans*-2-butene

As discussed in the "Chemistry and Life" box on the chemistry of vision, such transformations can be induced by light and are the key to human vision. (**a**) What is the hybridization at the two central carbon atoms of 2-butene? (**b**) The isomerization occurs by rotation about the central C—C bond. With reference to Figure 9.30, explain why the π bond between the two central carbon atoms is destroyed halfway through the rotation from *cis*- to *trans*-2-butene. (**c**) Based on average bond enthalpies (Table 8.4), how much energy per molecule must be supplied to break the C—C π bond? (**d**) What is the longest wavelength of light that will provide photons of sufficient energy to break the C—C π bond and cause the isomerization? (**e**) Is the wavelength in your answer to part (d) in the visible portion of the electromagnetic spectrum? Comment on the importance of this result for human vision.

9.113 (**a**) Compare the bond enthalpies (Table 8.4) of the carbon–carbon single, double, and triple bonds to deduce an average π-bond contribution to the enthalpy. What fraction of a single bond does this quantity represent? (**b**) Make a similar comparison of nitrogen–nitrogen bonds. What do you observe? (**c**) Write Lewis structures of N_2H_4, N_2H_2, and N_2, and determine the hybridization around nitrogen in each case. (**d**) Propose a reason for the large difference in your observations of parts (a) and (b).

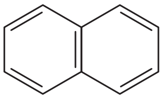
9.114 Use average bond enthalpies (Table 8.4) to estimate ΔH for the atomization of benzene, C_6H_6:

$$C_6H_6(g) \longrightarrow 6\,C(g) + 6\,H(g)$$

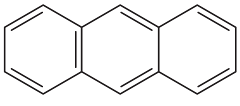
Compare the value to that obtained by using ΔH_f° data given in Appendix C and Hess's law. To what do you attribute the large discrepancy in the two values?

[9.115] Many compounds of the transition-metal elements contain direct bonds between metal atoms. We will assume that the *z*-axis is defined as the metal–metal bond axis. (**a**) Which of the 3*d* orbitals (Figure 6.23) can be used to make a σ bond between metal atoms? (**b**) Sketch the σ_{3d} bonding and σ^*_{3d} antibonding MOs. (**c**) With reference to the "Closer Look" box on the phases of orbitals, explain why a node is generated in the σ^*_{3d} MO. (**d**) Sketch the energy-level diagram for the Sc_2 molecule, assuming that only the 3*d* orbital from part (a) is important. (**e**) What is the bond order in Sc_2?

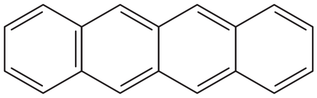
[9.116] The organic molecules shown here are derivatives of benzene in which six-membered rings are "fused" at the edges of the hexagons.



Naphthalene



Anthracene



Tetracene

(**a**) Determine the empirical formula of benzene and of these three compounds. (**b**) Suppose you are given a sample of one of the compounds. Could combustion analysis be used to determine unambiguously which of the three it is? (**c**) Naphthalene, the active ingredient in mothballs, is a white solid. Write a balanced equation for the combustion of naphthalene to $CO_2(g)$ and $H_2O(g)$. (**d**) Using the Lewis structure for naphthalene and the average bond enthalpies in Table 8.4, estimate the heat of combustion of naphthalene in kJ/mol. (**e**) Would you expect naphthalene, anthracene, and tetracene to have multiple resonance structures? If so, draw the additional resonance structures for naphthalene. (**f**) Benzene, naphthalene, and anthracene are colorless, but tetracene is orange. What does this imply about the relative HOMO–LUMO energy gaps in these molecules? See the "Chemistry Put to Work" box on orbitals and energy.

[9.117] Antibonding molecular orbitals can be used to make bonds to other atoms in a molecule. For example, metal atoms can use appropriate *d* orbitals to overlap with the π^*_{2p} orbitals of the carbon monoxide molecule. This is called *d*–π backbonding. (**a**) Draw a coordinate axis system in which the *y*-axis is vertical in the plane of the paper and the *x*-axis horizontal. Write "M" at the origin to denote a metal atom. (**b**) Now, on the *x*-axis to the right of M, draw the Lewis structure of a CO molecule, with the carbon nearest the M. The CO bond axis should be on the *x*-axis. (**c**) Draw the CO π^*_{2p} orbital, with phases (see the "Closer Look" box on phases) in the plane of the paper. Two lobes should be pointing toward M. (**d**) Now draw the d_{xy} orbital of M, with phases. Can you see how they will overlap with the π^*_{2p} orbital of CO? (**e**) What kind of bond is being made with the orbitals between M and C, σ or π ? (**f**) Predict what will happen to the strength of the CO bond in a metal–CO complex compared to CO alone.

9.118 Methyl isocyanate, CH_3NCO, was made infamous in 1984 when an accidental leakage of this compound from a storage tank in Bhopal, India, resulted in the deaths of about 3,800 people and severe and lasting injury to many thousands more. (**a**) Draw a Lewis structure for methyl isocyanate. (**b**) Draw a ball-and-stick model of the structure, including estimates of all the bond angles in the compound. (**c**) Predict all the bond distances in the molecule. (**d**) Do you predict that the molecule will have a dipole moment? Explain.

WHAT’S AHEAD

3.1 CHEMICAL EQUATIONS

We begin by considering how we can use chemical formulas to write equations representing chemical reactions.

3.2 SOME SIMPLE PATTERNS OF CHEMICAL REACTIVITY

We then examine some simple chemical reactions: *combination reactions, decomposition reactions,* and *combustion reactions.*

3.3 FORMULA WEIGHTS

We see how to obtain quantitative information from chemical formulas by using *formula weights*.

3.4 AVOGADRO’S NUMBER AND THE MOLE

We use chemical formulas to relate the masses of substances to the numbers of atoms, molecules, or ions contained in the substances, a relationship that leads to the crucially important concept of the *mole,* defined as 6.022×10^{23} objects (atoms, molecules, ions, etc.).

3.5 EMPIRICAL FORMULAS FROM ANALYSES

We apply the mole concept to determine chemical formulas from the masses of each element in a given quantity of a compound.

3

A BURNING MATCH. The heat and flame are visible evidence of a chemical reaction. Combustion reactions were among the first systematically studied chemical reactions.

3.6 QUANTITATIVE INFORMATION FROM BALANCED EQUATIONS

We use the quantitative information inherent in chemical formulas and equations together with the mole concept to predict the amounts of substances consumed or produced in chemical reactions.

3.7 LIMITING REACTANTS

We recognize that one reactant may be used up before others in a chemical reaction. This is the *limiting reactant*. The reaction stops, leaving some excess starting material.

STOICHIOMETRY: CALCULATIONS WITH CHEMICAL FORMULAS AND EQUATIONS

YOU POUR VINEGAR INTO a glass of water containing baking soda and bubbles form. You strike a match and use the flame to light a candle. You heat sugar in a pan and it turns brown. The bubbles, flame, and color change are visual evidence that something is happening.

To an experienced eye, these visual changes indicate a chemical change, or chemical reaction. Some chemical changes are simple; others are complex. Some are dramatic; some are very subtle. Even as you sit reading this chapter, chemical changes are occurring in your body. Those occurring in your eyes and brain, for example, allow you to see these words and think about them. Although not as obvious as those we see in the laboratory, the chemical changes taking place in our bodies are nevertheless remarkable for how they allow us to function.

In this chapter we explore some important aspects of chemical change. Our focus will be both on the use of chemical formulas to represent reactions and on the quantitative information we can obtain about the amounts of substances involved in reactions. **Stoichiometry** (pronounced stoy-key-OM-uh-tree) is the area of study that examines the quantities of substances consumed and produced in chemical reactions. Stoichiometry (Greek *stoicheion*, "element," and *metron*, "measure") provides an essential set of tools widely used in chemistry, including such diverse applications as measuring ozone concentrations in the atmosphere and assessing different processes for converting coal into gaseous fuels.

Stoichiometry is built on an understanding of atomic masses (Section 2.4), chemical formulas, and the law of conservation of mass. (Section 2.1) The French nobleman and scientist Antoine Lavoisier (◀ **FIGURE 3.1**) discovered this important chemical law during the late 1700s. Lavoisier stated the law in this eloquent way: "We may lay it down as an incontestable axiom that, in all the operations of art and nature, nothing is created; an equal quantity of matter exists both before and after the experiment. Upon this principle, the whole art of performing chemical experiments depends." With the advent of Dalton's atomic theory, chemists came to understand the basis for this law: *Atoms are neither created nor destroyed during a chemical reaction.* The changes that occur during any reaction merely rearrange the atoms. The same collection of atoms is present both before and after the reaction.

▲ **FIGURE 3.1 Antoine Lavoisier (1734–1794).** The science career of Lavoisier, who conducted many important studies on combustion reactions, was cut short by the French Revolution. Guillotined in 1794 during the Reign of Terror, he is generally considered the father of modern chemistry because he conducted carefully controlled experiments and used quantitative measurements.

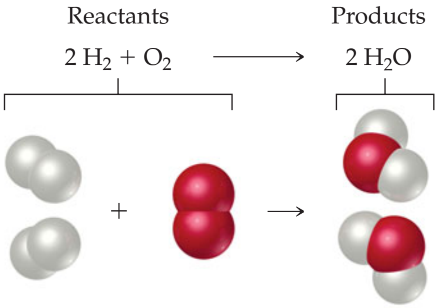
3.1 CHEMICAL EQUATIONS

We represent chemical reactions by **chemical equations**. When the gas hydrogen (H_2) burns, for example, it reacts with oxygen (O_2) in the air to form water (H_2O). We write the chemical equation for this reaction as

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O \qquad [3.1]$$

We read the + sign as "reacts with" and the arrow as "produces." The chemical formulas to the left of the arrow represent the starting substances, called **reactants**. The chemical formulas to the right of the arrow represent substances produced in the reaction, called **products**. The numbers in front of the formulas, called *coefficients*, indicate the relative numbers of molecules of each kind involved in the reaction. (As in algebraic equations, *the coefficient 1 is usually not written*.)

Because atoms are neither created nor destroyed in any reaction, a chemical equation must have an equal number of atoms of each element on each side of the arrow. When this condition is met, the equation is *balanced*. On the right side of Equation 3.1, for example, there are two molecules of H_2O, each composed of two atoms of hydrogen and one atom of oxygen (◀ **FIGURE 3.2**). Thus, $2\,H_2O$ (read "two molecules of water") contains $2 \times 2 = 4$ H atoms and $2 \times 1 = 2$ O atoms. Notice that *the number of atoms is obtained by multiplying each subscript in a chemical formula by the coefficient for the formula.* Because there are four H atoms and two O atoms on each side of the equation, the equation is balanced.



▲ **FIGURE 3.2 A balanced chemical equation.**

GIVE IT SOME THOUGHT

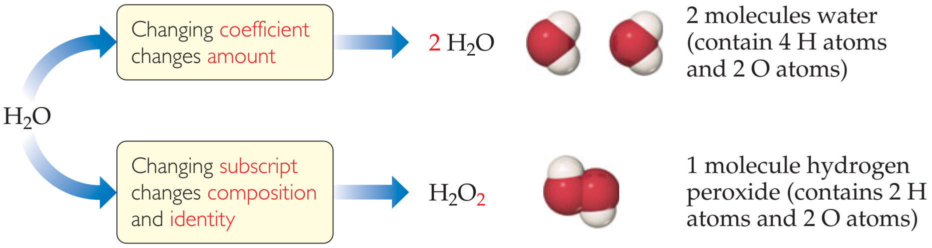
How many atoms of Mg, O, and H are represented by the notation $3\,Mg(OH)_2$?

Balancing Equations

Once we know the formulas of the reactants and products in a reaction, we can write an unbalanced equation. We then balance the equation by determining the coefficients that provide equal numbers of each type of atom on the two sides of the equation. For most purposes, a balanced equation should contain the smallest possible whole-number coefficients.

GO FIGURE

What is the difference in atom count between the notation CO_2 and the notation 2 CO?



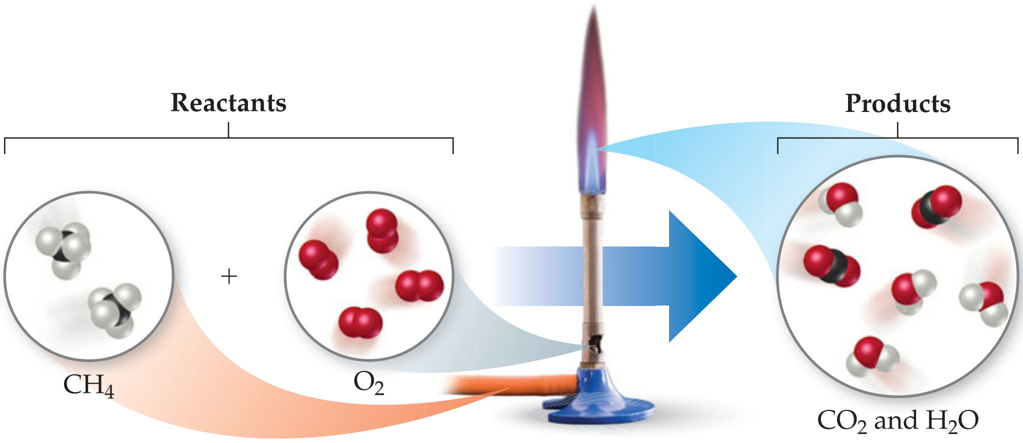
▲ **FIGURE 3.3 The difference between changing subscripts and changing coefficients in chemical equations.**

In balancing an equation, you need to understand the difference between coefficients and subscripts. As ▲ **FIGURE 3.3** illustrates, changing a subscript in a formula—from H_2O to H_2O_2, for example—changes the identity of the substance. The substance H_2O_2, hydrogen peroxide, is quite different from the substance H_2O, water. *Never change subscripts when balancing an equation*. In contrast, placing a coefficient in front of a formula changes only the *amount* of the substance and not its *identity*. Thus, 2 H_2O means two molecules of water, 3 H_2O means three molecules of water, and so forth.

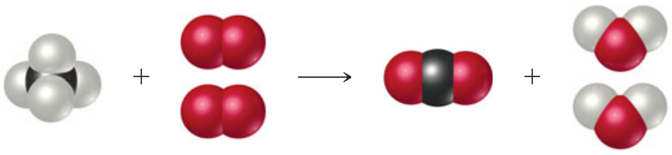
To illustrate the process of balancing an equation, consider the reaction that occurs when methane (CH_4), the principal component of natural gas, burns in air to produce carbon dioxide gas (CO_2) and water vapor (H_2O) (▼ **FIGURE 3.4**). Both products contain oxygen atoms that come from O_2 in the air. Thus, O_2 is a reactant, and the unbalanced equation is

$$CH_4 + O_2 \longrightarrow CO_2 + H_2O \quad \text{(unbalanced)} \qquad [3.2]$$

It is usually best to balance first those elements that occur in the fewest chemical formulas in the equation. In our example, C appears in only one reactant (CH_4) and one product (CO_2). The same is true for H (CH_4 and H_2O). Notice, however, that O appears in one reactant (O_2) and two products (CO_2 and H_2O). So, let's begin with C. Because one molecule of CH_4 contains the same number of C atoms (one) as one molecule of CO_2 the coefficients for these substances *must* be the same in the balanced equation. Therefore, we start by choosing the coefficient 1 (unwritten) for both CH_4 and CO_2.



▲ **FIGURE 3.4 Methane reacts with oxygen in a Bunsen burner.**



$$\underbrace{CH_4 + 2\,O_2}_{1\,C,\,4\,H,\;4\,O} \longrightarrow \underbrace{CO_2 + 2\,H_2O}_{1\,C,\,4\,H,\;4\,O}$$

▲ **FIGURE 3.5** **Balanced chemical equation for the combustion of CH_4.**

Next we focus on H. Because CH_4 contains four H atoms and H_2O contains two H atoms, we balance the H atoms by placing the coefficient 2 in front of H_2O. There are then four H atoms on each side of the equation:

$$CH_4 + O_2 \longrightarrow CO_2 + 2\,H_2O \quad \text{(unbalanced)} \qquad [3.3]$$

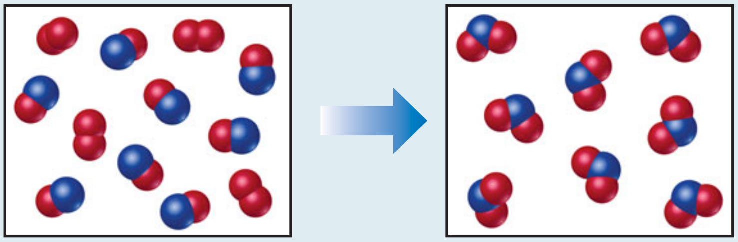
Finally, a coefficient 2 in front of O_2 balances the equation by giving four O atoms on each side (2×2 left, $2 + 2 \times 1$ right):

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O \quad \text{(balanced)} \qquad [3.4]$$

The molecular view of the balanced equation is shown in ◀ **FIGURE 3.5**.

SAMPLE EXERCISE 3.1 Interpreting and Balancing Chemical Equations

The following diagram represents a chemical reaction in which the red spheres are oxygen atoms and the blue spheres are nitrogen atoms. (**a**) Write the chemical formulas for the reactants and products. (**b**) Write a balanced equation for the reaction. (**c**) Is the diagram consistent with the law of conservation of mass?



SOLUTION

(**a**) The left box, which represents reactants, contains two kinds of molecules, those composed of two oxygen atoms (O_2) and those composed of one nitrogen atom and one oxygen atom (NO). The right box, which represents products, contains only molecules composed of one nitrogen atom and two oxygen atoms (NO_2).

(**b**) The unbalanced chemical equation is

$$O_2 + NO \longrightarrow NO_2 \quad \text{(unbalanced)}$$

An inventory of atoms on each side of the equation shows that there are one N and three O on the left side of the arrow and one N and two O on the right. To balance O we must increase the number of O atoms on the right while keeping the coefficients for NO and NO_2 equal. Sometimes we need to go back and forth several times from one side of an equation to the other, changing coefficients first on one side of the equation and then the other until it is balanced. In our present case, we can increase the number of O atoms by placing the coefficient 2 in front of NO_2:

$$O_2 + NO \longrightarrow 2\,NO_2 \quad \text{(unbalanced)}$$

That gives two N atoms and four O atoms on the right, so we go back to the left side. Placing the coefficient 2 in front of NO balances both N and O:

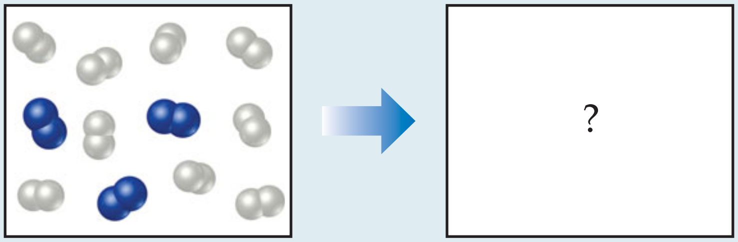
$$\underbrace{O_2 + 2\,NO}_{2\,N,\,4\,O} \longrightarrow \underbrace{2\,NO_2}_{2\,N,\,4\,O} \text{ (balanced)}$$

(**c**) The reactants box contains four O_2 and eight NO. Thus, the molecular ratio is one O_2 for each two NO, as required by the balanced equation. The products box contains eight NO_2, which means the number of NO_2 product molecules equals the number of NO reactant molecules, as the balanced equation requires.

There are eight N atoms in the eight NO molecules in the reactants box. There are also $4 \times 2 = 8$ O atoms in the O_2 molecules and eight O atoms in the NO molecules, giving a total of 16 O atoms. In the products box, we find eight N atoms and $8 \times 2 = 16$ O atoms in the eight NO_2 molecules. Because there are equal numbers of N and O atoms in the two boxes, the drawing is consistent with the law of conservation of mass.

PRACTICE EXERCISE

In the following diagram, the white spheres represent hydrogen atoms and the blue spheres represent nitrogen atoms.



To be consistent with the law of conservation of mass, how many NH_3 molecules should be shown in the right (products) box?

Answer: Six NH_3 molecules

Indicating the States of Reactants and Products

Symbols indicating the physical state of each reactant and product are often shown in chemical equations. We use the symbols (*g*), (*l*), (*s*), and (*aq*) for gas, liquid, solid, and aqueous (water) solution, respectively. Thus, Equation 3.4 can be written

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g) \qquad [3.5]$$

Sometimes the conditions under which the reaction proceeds appear above or below the reaction arrow. The symbol **Δ** (Greek uppercase delta) above the arrow indicates addition of heat.

SAMPLE EXERCISE 3.2 Balancing Chemical Equations

Balance the equation

$$Na(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$$

SOLUTION

Begin by counting each kind of atom on the two sides of the arrow. There are one Na, one O, and two H on the left side, and one Na, one O, and three H on the right. To increase the number of H atoms on the left, let's try placing the coefficient 2 in front of H_2O:

$$Na(s) + 2\,H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$$

Although beginning this way does not balance H, it does increase the number of reactant H atoms, which we need to do. (Also, adding the coefficient 2 on H_2O unbalances O, but we will take care of that after we balance H.) Now that we have 2 H_2O on the left, we balance H by putting the coefficient 2 in front of NaOH:

$$Na(s) + 2\,H_2O(l) \longrightarrow 2\,NaOH(aq) + H_2(g)$$

Balancing H in this way brings O into balance, but now Na is unbalanced, with one Na on the left and two on the right. To rebalance Na, we put the coefficient 2 in front of the reactant:

$$2\,Na(s) + 2\,H_2O(l) \longrightarrow 2\,NaOH(aq) + H_2(g)$$

We now have two Na atoms, four H atoms, and two O atoms on each side. The equation is balanced.

Comment Notice that we moved back and forth, placing a coefficient in front of H_2O, then NaOH, and finally Na. In balancing equations, we often find ourselves following this pattern of moving back and forth from one side of the arrow to the other, placing coefficients first in front of a formula on one side and then in front of a formula on the other side until the equation is balanced. You can always tell if you have balanced your equation correctly by checking that the number of atoms of each element is the same on the two sides of the arrow.

PRACTICE EXERCISE

Balance these equations by providing the missing coefficients:

(a) $\_\_\,Fe(s) + \_\_\,O_2(g) \longrightarrow \_\_\,Fe_2O_3(s)$

(b) $\_\_\,C_2H_4(g) + \_\_\,O_2(g) \longrightarrow \_\_\,CO_2(g) + \_\_\,H_2O(g)$

(c) $\_\_\,Al(s) + \_\_\,HCl(aq) \longrightarrow \_\_\,AlCl_3(aq) + \_\_\,H_2(g)$

Answers: **(a)** 4, 3, 2; **(b)** 1, 3, 2, 2; **(c)** 2, 6, 2, 3

3.2 SOME SIMPLE PATTERNS OF CHEMICAL REACTIVITY

In this section we examine three types of reactions that we see frequently throughout this chapter: combination reactions, decomposition reactions, and combustion reactions. Our first reason for examining these reactions is to become better acquainted with chemical reactions and their balanced equations. Our second reason is to consider how we might predict the products of some of these reactions knowing only their reactants. The key to predicting the products formed by a given combination of reactants is recognizing general patterns of chemical reactivity. Recognizing a pattern of reactivity for a class of substances gives you a broader understanding than merely memorizing a large number of unrelated reactions.

Combination and Decomposition Reactions

In **combination reactions** two or more substances react to form one product (▼ TABLE 3.1). For example, magnesium metal burns brilliantly in air to produce magnesium oxide (▼ FIGURE 3.6):

$$2\ \mathrm{Mg}(s) + \mathrm{O_2}(g) \longrightarrow 2\ \mathrm{MgO}(s) \qquad [3.6]$$

This reaction is used to produce the bright flame generated by flares and some fireworks.

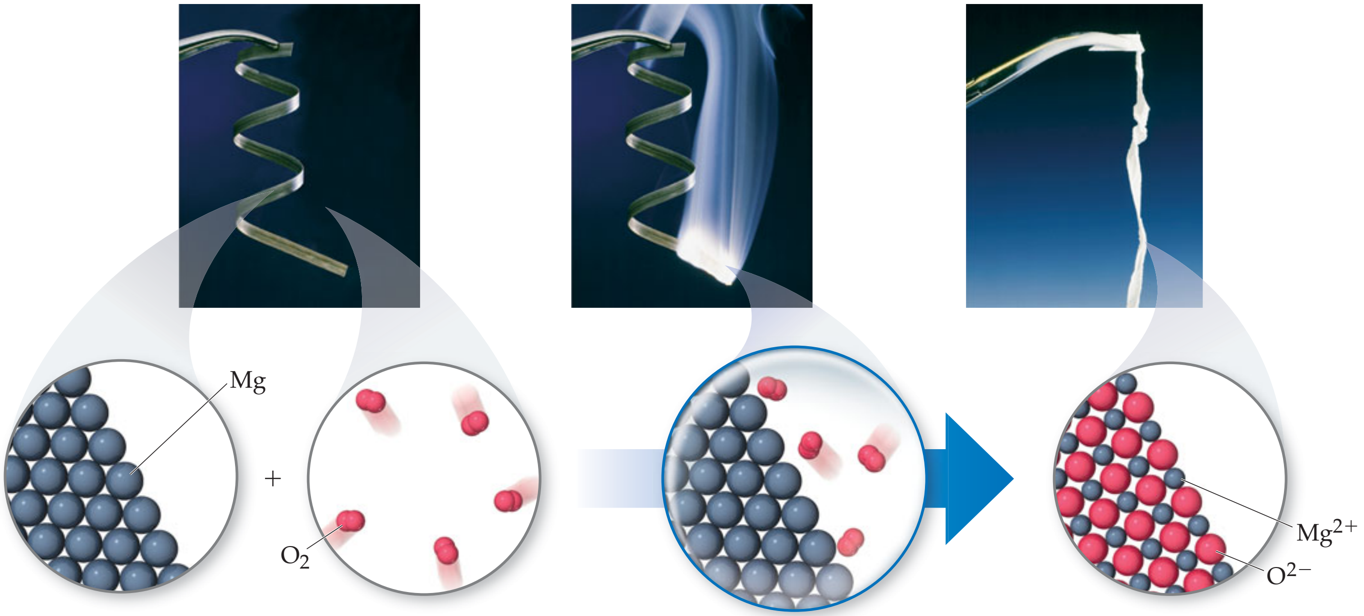
A combination reaction between a metal and a nonmetal, as in Equation 3.6, produces an ionic solid. Recall that the formula of an ionic compound can be determined from the charges of its ions. (Section 2.7) When magnesium reacts with oxygen, the magnesium loses electrons and forms the magnesium ion, Mg^{2+}. The oxygen gains electrons and forms the oxide ion, O^{2-}. Thus, the reaction product is MgO.

You should be able to recognize when a reaction is a combination reaction and to predict the products when the reactants are a metal and a nonmetal.

TABLE 3.1 • Combination and Decomposition Reactions

Combination Reactions	
$A + B \longrightarrow C$ $C(s) + O_2(g) \longrightarrow CO_2(g)$ $N_2(g) + 3\ H_2(g) \longrightarrow 2\ NH_3(g)$ $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$	Two or more reactants combine to form a single product. Many elements react with one another in this fashion to form compounds.
Decomposition Reactions	
$C \longrightarrow A + B$ $2\ KClO_3(s) \longrightarrow 2\ KCl(s) + 3\ O_2(g)$ $PbCO_3(s) \longrightarrow PbO(s) + CO_2(g)$ $Cu(OH)_2(s) \longrightarrow CuO(s) + H_2O(l)$	A single reactant breaks apart to form two or more substances. Many compounds react this way when heated.

▼ **FIGURE 3.6 Combustion of magnesium metal in air, a combination reaction.**



The ribbon of magnesium metal is surrounded by oxygen gas in the air.

An intense flame is produced as the Mg atoms react with O_2.

The reaction forms MgO, a white, ionic solid.

Reactants — *Products*

$$2\ \mathrm{Mg}(s) + \mathrm{O_2}(g) \longrightarrow 2\ \mathrm{MgO}(s)$$

GIVE IT SOME THOUGHT

When Na and S undergo a combination reaction, what is the chemical formula of the product?

In a **decomposition reaction** one substance undergoes a reaction to produce two or more other substances (Table 3.1). For example, many metal carbonates decompose to form metal oxides and carbon dioxide when heated:

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g) \qquad [3.7]$$

Decomposition of $CaCO_3$ is an important commercial process. Limestone or seashells, which are both primarily $CaCO_3$, are heated to prepare CaO, known as lime or quicklime. About 2×10^{10} kg (20 million tons) of CaO is used in the United States each year, principally in making glass, in obtaining iron from its ores, and in making mortar to bind bricks.

The decomposition of sodium azide (NaN_3) rapidly releases $N_2(g)$, so this reaction is used to inflate safety air bags in automobiles (▶ **FIGURE 3.7**):

$$2\,NaN_3(s) \longrightarrow 2\,Na(s) + 3\,N_2(g) \qquad [3.8]$$

The system is designed so that an impact ignites a detonator cap, which in turn causes NaN_3 to decompose explosively. A small quantity of NaN_3 (about 100 g) forms a large quantity of gas (about 50 L).

▲ **FIGURE 3.7 Decomposition of sodium azide, $NaN_3(s)$, is used to inflate automobile air bags.**

SAMPLE EXERCISE 3.3 Writing Balanced Equations for Combination and Decomposition Reactions

Write a balanced equation for **(a)** the combination reaction between lithium metal and fluorine gas and **(b)** the decomposition reaction that occurs when solid barium carbonate is heated (two products form, a solid and a gas).

SOLUTION

(a) With the exception of mercury, all metals are solids at room temperature. Fluorine occurs as a diatomic molecule. Thus, the reactants are Li(*s*) and $F_2(g)$. The product will be composed of a metal and a nonmetal, so we expect it to be an ionic solid. Lithium ions have a 1+ charge, Li^+, whereas fluoride ions have a 1– charge, F^-. Thus, the chemical formula for the product is LiF. The balanced chemical equation is

$$2\,Li(s) + F_2(g) \longrightarrow 2\,LiF(s)$$

(b) The chemical formula for barium carbonate is $BaCO_3$. As noted in the text, many metal carbonates decompose to metal oxides and carbon dioxide when heated. In Equation 3.7, for example, $CaCO_3$ decomposes to form CaO and CO_2. Thus, we expect $BaCO_3$ to decompose to BaO and CO_2. Barium and calcium are both in group 2A in the periodic table, which further suggests they react in the same way:

$$BaCO_3(s) \longrightarrow BaO(s) + CO_2(g)$$

PRACTICE EXERCISE

Write a balanced equation for **(a)** solid mercury(II) sulfide decomposing into its component elements when heated and **(b)** aluminum metal combining with oxygen in the air.

Answers: **(a)** $HgS(s) \longrightarrow Hg(l) + S(s)$, **(b)** $4\,Al(s) + 3\,O_2(g) \longrightarrow 2\,Al_2O_3(s)$

Combustion Reactions

Combustion reactions are rapid reactions that produce a flame. Most combustion reactions we observe involve O_2 from air as a reactant. Equation 3.5 illustrates a general class of reactions involving the burning, or combustion, of hydrocarbons (compounds that contain only carbon and hydrogen, such as CH_4 and C_2H_4). ∞ (Section 2.9)

Hydrocarbons combusted in air react with O_2 to form CO_2 and H_2O.* The number of molecules of O_2 required and the number of molecules of CO_2 and H_2O formed

---

*When there is an insufficient quantity of O_2 present, carbon monoxide (CO) is produced along with CO_2; this is called incomplete combustion. If the O_2 quantity is severely restricted, the fine particles of carbon we call soot are produced. Complete combustion produces only CO_2 and H_2O. Unless stated to the contrary, we will always take combustion to mean complete combustion.

GO FIGURE

In what ways are the reactions depicted in Figures 3.4 and 3.8 alike?

▲ **FIGURE 3.8** **Propane burning in air.** Liquid propane in the tank, C_3H_8, vaporizes and mixes with air as it escapes through the nozzle. The combustion reaction of C_3H_8 and O_2 produces a blue flame.

depend on the composition of the hydrocarbon, which acts as the fuel in the reaction. For example, the combustion of propane (C_3H_8, ◀ **FIGURE 3.8**), a gas used for cooking and home heating, is described by the equation

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(g) \qquad [3.9]$$

The state of the water in this reaction, $H_2O(g)$ or $H_2O(l)$, depends on the reaction conditions. Water vapor, $H_2O(g)$, is formed at high temperature in an open container.

Combustion of oxygen-containing derivatives of hydrocarbons, such as CH_3OH, also produces CO_2 and H_2O. The rule that hydrocarbons and their oxygen-containing derivatives form CO_2 and H_2O when they burn in air summarizes the behavior of about 3 million compounds. Many substances that our bodies use as energy sources, such as the sugar glucose ($C_6H_{12}O_6$), react with O_2 to form CO_2 and H_2O. In our bodies, however, the reactions take place in a series of intermediate steps that occur at body temperature. These reactions that involve intermediate steps are described as *oxidation reactions* instead of combustion reactions.

SAMPLE EXERCISE 3.4 Writing Balanced Equations for Combustion Reactions

Write the balanced equation for the reaction that occurs when methanol, $CH_3OH(l)$, is burned in air.

SOLUTION

When any compound containing C, H, and O is combusted, it reacts with the $O_2(g)$ in air to produce $CO_2(g)$ and $H_2O(g)$. Thus, the unbalanced equation is

$$CH_3OH(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$$

The C atoms are balanced, one on each side of the arrow. Because CH_3OH has four H atoms, we place the coefficient 2 in front of H_2O to balance the H atoms:

$$CH_3OH(l) + O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$$

Adding this coefficient balances H but gives four O atoms in the products. Because there are only three O atoms in the reactants, we are not finished. We can place the coefficient $\frac{3}{2}$ in front of O_2 to give four O atoms in the reactants ($\frac{3}{2} \times 2 = 3$ O atoms in $\frac{3}{2}\,O_2$):

$$CH_3OH(l) + \tfrac{3}{2}\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$$

Although this equation is balanced, it is not in its most conventional form because it contains a fractional coefficient. However, multiplying through by 2 removes the fraction and keeps the equation balanced:

$$2\,CH_3OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 4\,H_2O(g)$$

PRACTICE EXERCISE

Write the balanced equation for the reaction that occurs when ethanol, $C_2H_5OH(l)$, burns in air.

Answer: $C_2H_5OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(g)$

3.3 FORMULA WEIGHTS

Chemical formulas and chemical equations both have a *quantitative* significance in that the subscripts in formulas and the coefficients in equations represent precise quantities. The formula H_2O indicates that a molecule of this substance (water) contains exactly two atoms of hydrogen and one atom of oxygen. Similarly, the coefficients in a balanced chemical equation indicate the relative quantities of reactants and products. But how do we relate the numbers of atoms or molecules to the amounts we measure in the laboratory? Although we cannot directly count atoms or molecules, we can indirectly determine their numbers if we know their masses. Therefore, before we can pursue the quantitative aspects of chemical formulas and equations, we must examine the masses of atoms and molecules.

Formula and Molecular Weights

The **formula weight** of a substance is the sum of the atomic weights of the atoms in the chemical formula of the substance. Using atomic weights, we find, for example, that the formula weight of sulfuric acid (H_2SO_4) is 98.1 amu:*

$$\begin{aligned} \text{FW of } H_2SO_4 &= 2(\text{AW of H}) + (\text{AW of S}) + 4(\text{AW of O}) \\ &= 2(1.0\text{ amu}) + 32.1\text{ amu} + 4(16.0\text{ amu}) \\ &= 98.1\text{ amu} \end{aligned}$$

For convenience, we have rounded off the atomic weights to one decimal place, a practice we will follow in most calculations in this book.

If the chemical formula is the chemical symbol of an element, such as Na, the formula weight equals the atomic weight of the element, in this case 23.0 amu. If the chemical formula is that of a molecule, the formula weight is also called the **molecular weight**. The molecular weight of glucose ($C_6H_{12}O_6$), for example, is

$$\text{MW of } C_6H_{12}O_6 = 6(12.0\text{ amu}) + 12(1.0\text{ amu}) + 6(16.0\text{ amu}) = 180.0\text{ amu}$$

Because ionic substances exist as three-dimensional arrays of ions (see Figure 2.21), it is inappropriate to speak of molecules of these substances. Instead, we speak of *formula units*. The formula unit of NaCl, for instance, consists of one Na^+ ion and one Cl^- ion. Thus, the formula weight of NaCl is defined as the mass of one formula unit:

$$\text{FW of NaCl} = 23.0\text{ amu} + 35.5\text{ amu} = 58.5\text{ amu}$$

SAMPLE EXERCISE 3.5 Calculating Formula Weights

Calculate the formula weight of **(a)** sucrose, $C_{12}H_{22}O_{11}$ (table sugar), and **(b)** calcium nitrate, $Ca(NO_3)_2$.

SOLUTION

(a) By adding the atomic weights of the atoms in sucrose, we find the formula weight to be 342.0 amu:

$$\begin{aligned} 12\text{ C atoms} &= 12(12.0\text{ amu}) = 144.0\text{ amu} \\ 22\text{ H atoms} &= 22(1.0\text{ amu}) = 22.0\text{ amu} \\ 11\text{ O atoms} &= 11(16.0\text{ amu}) = \underline{176.0\text{ amu}} \\ & \qquad\qquad\qquad\quad 342.0\text{ amu} \end{aligned}$$

(b) If a chemical formula has parentheses, the subscript outside the parentheses is a multiplier for all atoms inside. Thus, for $Ca(NO_3)_2$ we have

$$\begin{aligned} 1\text{ Ca atom} &= 1(40.1\text{ amu}) = 40.1\text{ amu} \\ 2\text{ N atoms} &= 2(14.0\text{ amu}) = 28.0\text{ amu} \\ 6\text{ O atoms} &= 6(16.0\text{ amu}) = \underline{96.0\text{ amu}} \\ & \qquad\qquad\qquad\quad 164.1\text{ amu} \end{aligned}$$

PRACTICE EXERCISE

Calculate the formula weight of **(a)** $Al(OH)_3$ and **(b)** CH_3OH.

Answers: **(a)** 78.0 amu, **(b)** 32.0 amu

Percentage Composition from Chemical Formulas

Chemists must sometimes calculate the *percentage composition* of a compound—that is, the percentage by mass contributed by each element in the substance. Forensic chemists, for example, will measure the percentage composition of an unknown powder and compare it with the percentage compositions for sugar, salt, or cocaine to identify the powder.

Calculating the percentage composition of any element in a substance is straightforward if the chemical formula is known. The calculation depends on the formula weight of the substance, the atomic weight of the element of interest, and the number of atoms of that element in the chemical formula:

$$\%\text{ composition of element} = \frac{\begin{pmatrix}\text{number of atoms}\\ \text{of element}\end{pmatrix}\begin{pmatrix}\text{atomic weight}\\ \text{of element}\end{pmatrix}}{\text{formula weight of substance}} \times 100\% \qquad [3.10]$$

---

*The abbreviation AW is used for atomic weight, FW for formula weight, and MW for molecular weight.

SAMPLE EXERCISE 3.6 Calculating Percentage Composition

Calculate the percentage of carbon, hydrogen, and oxygen (by mass) in $C_{12}H_{22}O_{11}$.

SOLUTION

Let's examine this question using the problem-solving steps in the accompanying "Strategies in Chemistry: Problem Solving" essay.

Analyze We are given a chemical formula and asked to calculate the percentage by mass of each element.

Plan We use Equation 3.10, obtaining our atomic weights from a periodic table. We know the denominator in Equation 3.10, the formula weight of $C_{12}H_{22}O_{11}$, from Sample Exercise 3.5. We must use that value in three calculations, one for each element.

Solve

$$\%\text{C} = \frac{(12)(12.0\text{ amu})}{342.0\text{ amu}} \times 100\% = 42.1\%$$

$$\%\text{H} = \frac{(22)(1.0\text{ amu})}{342.0\text{ amu}} \times 100\% = 6.4\%$$

$$\%\text{O} = \frac{(11)(16.0\text{ amu})}{342.0\text{ amu}} \times 100\% = 51.5\%$$

Check Our calculated percentages must add up to 100%, which they do. We could have used more significant figures for our atomic weights, giving more significant figures for our percentage composition, but we have adhered to our suggested guideline of rounding atomic weights to one digit beyond the decimal point.

PRACTICE EXERCISE

Calculate the percentage of nitrogen, by mass, in $Ca(NO_3)_2$.

Answer: 17.1%

3.4 AVOGADRO'S NUMBER AND THE MOLE

Even the smallest samples we deal with in the laboratory contain enormous numbers of atoms, ions, or molecules. For example, a teaspoon of water (about 5 mL) contains 2×10^{23} water molecules, a number so large it almost defies comprehension. Chemists therefore have devised a counting unit for describing such large numbers of atoms or molecules.

In everyday life we use such familiar counting units as dozen (12 objects) and gross (144 objects). In chemistry the counting unit for numbers of atoms, ions, or molecules in a laboratory-size sample is the **mole**, abbreviated mol.* One mole is the amount of matter that contains as many objects (atoms, molecules, or whatever other objects we are considering) as the number of atoms in exactly 12 g of isotopically pure ^{12}C. From experiments, scientists have determined this number to be 6.0221421×10^{23}, which we will usually round to 6.02×10^{23}. Scientists call this value **Avogadro's number**, N_A, in honor

STRATEGIES IN CHEMISTRY

PROBLEM SOLVING

Practice is the key to success in solving problems. As you practice, you can improve your skills by following these steps:

Step 1: Analyze the problem. Read the problem carefully. What does it say? Draw a picture or diagram that will help you to visualize the problem. Write down both the data you are given and the quantity you need to obtain (the unknown).

Step 2: Develop a plan for solving the problem. Consider a possible path between the given information and the unknown. What principles or equations relate the known data to the unknown? Recognize that some data may not be given explicitly in the problem; you may be expected to know certain quantities (such as Avogadro's number) or look them up in tables (such as atomic weights). Recognize also that your plan may involve either a single step or a series of steps with intermediate answers.

Step 3: Solve the problem. Use the known information and suitable equations or relationships to solve for the unknown. Dimensional analysis (Section 1.6) is a useful tool for solving a great number of problems. Be careful with significant figures, signs, and units.

Step 4: Check the solution. Read the problem again to make sure you have found all the solutions asked for in the problem. Does your answer make sense? That is, is the answer outrageously large or small or is it in the ballpark? Finally, are the units and significant figures correct?

---

*The term *mole* comes from the Latin word *moles,* meaning "a mass." The term *molecule* is the diminutive of this word and means "a small mass."

of the Italian scientist Amedeo Avogadro (1776–1856), and it is often cited with units of reciprocal moles, $6.02 \times 10^{23}\ \text{mol}^{-1}$. The unit (read as either "inverse mole" or "per mole") reminds us that there are 6.02×10^{23} objects per one mole. A mole of atoms, a mole of molecules, or a mole of anything else all contain Avogadro's number of objects:

$$1\ \text{mol}\ ^{12}\text{C atoms} = 6.02 \times 10^{23}\ ^{12}\text{C atoms}$$

$$1\ \text{mol}\ \text{H}_2\text{O molecules} = 6.02 \times 10^{23}\ \text{H}_2\text{O molecules}$$

$$1\ \text{mol}\ \text{NO}_3^{\ -}\ \text{ions} = 6.02 \times 10^{23}\ \text{NO}_3^{\ -}\ \text{ions}$$

Avogadro's number is so large that it is difficult to imagine. Spreading 6.02×10^{23} marbles over Earth's surface would produce a layer about 3 miles thick. Avogadro's number of pennies placed side by side in a straight line would encircle Earth 300 trillion (3×10^{14}) times.

SAMPLE EXERCISE 3.7 Estimating Numbers of Atoms

Without using a calculator, arrange these samples in order of increasing numbers of carbon atoms: 12 g ^{12}C, 1 mol C_2H_2, 9×10^{23} molecules of CO_2.

SOLUTION

Analyze We are given amounts of three substances expressed in grams, moles, and number of molecules and asked to arrange the samples in order of increasing numbers of C atoms.

Plan To determine the number of C atoms in each sample, we must convert 12 g ^{12}C, 1 mol C_2H_2, and 9×10^{23} molecules CO_2 to numbers of C atoms. To make these conversions, we use the definition of mole and Avogadro's number.

Solve One mole is defined as the amount of matter that contains as many units of the matter as there are C atoms in exactly 12 g of ^{12}C. Thus, 12 g of ^{12}C contains 1 mol of C atoms $= 6.02 \times 10^{23}$ C atoms. One mol of C_2H_2 contains 6×10^{23} C_2H_2 molecules. Because there are two C atoms in each molecule, this sample contains 12×10^{23} C atoms. Because each CO_2 molecule contains one C atom, the CO_2 sample contains 9×10^{23} C atoms. Hence, the order is 12 g ^{12}C (6×10^{23} C atoms) $<$ 9×10^{23} CO_2 molecules (9×10^{23} C atoms) $<$ 1 mol C_2H_2 (12×10^{23} C atoms).

Check We can check our results by comparing numbers of moles of C atoms in the samples because the number of moles is proportional to the number of atoms. Thus, 12 g of ^{12}C is 1 mol C; 1 mol of C_2H_2 contains 2 mol C, and 9×10^{23} molecules of CO_2 contain 1.5 mol C, giving the same order as stated previously.

PRACTICE EXERCISE

Without using a calculator, arrange these samples in order of increasing number of O atoms: 1 mol H_2O, 1 mol CO_2, 3×10^{23} molecules O_3.

Answer: 1 mol H_2O (6×10^{23} O atoms) $<$ 3×10^{23} molecules O_3 (9×10^{23} O atoms) $<$ 1 mol CO_2 (12×10^{23} O atoms)

SAMPLE EXERCISE 3.8 Converting Moles to Number of Atoms

Calculate the number of H atoms in 0.350 mol of $C_6H_{12}O_6$.

SOLUTION

Analyze We are given the amount of a substance (0.350 mol) and its chemical formula $C_6H_{12}O_6$. The unknown is the number of H atoms in the sample.

Plan Avogadro's number provides the conversion factor between number of moles of $C_6H_{12}O_6$ and number of molecules of $C_6H_{12}O_6$: 1 mol $C_6H_{12}O_6 = 6.02 \times 10^{23}$ molecules $C_6H_{12}O_6$. Once we know the number of molecules of $C_6H_{12}O_6$, we can use the chemical formula, which tells us that each molecule of $C_6H_{12}O_6$ contains 12 H atoms. Thus, we convert moles of $C_6H_{12}O_6$ to molecules of $C_6H_{12}O_6$ and then determine the number of atoms of H from the number of molecules of $C_6H_{12}O_6$:

$$\text{Moles } C_6H_{12}O_6 \longrightarrow \text{molecules } C_6H_{12}O_6 \longrightarrow \text{atoms H}$$

Solve

$$\text{H atoms} = (0.350\ \cancel{\text{mol } C_6H_{12}O_6})\left(\frac{6.02 \times 10^{23}\ \cancel{\text{molecules } C_6H_{12}O_6}}{1\ \cancel{\text{mol } C_6H_{12}O_6}}\right)$$

$$\times \left(\frac{12\ \text{H atoms}}{1\ \cancel{\text{molecule } C_6H_{12}O_6}}\right) = 2.53 \times 10^{24}\ \text{H atoms}$$

Check We can do a ballpark calculation: First, $0.35(6 \times 10^{23})$ is about 2×10^{23} molecules of $C_6H_{12}O_6$, and each one of these molecules contains 12 H atoms. So $12(2 \times 10^{23})$ gives $24 \times 10^{23} = 2.4 \times 10^{24}$ H atoms, which agrees with our result. Because we were asked for the number of H atoms, the units of our answer are correct. The given data had three significant figures, so our answer has three significant figures.

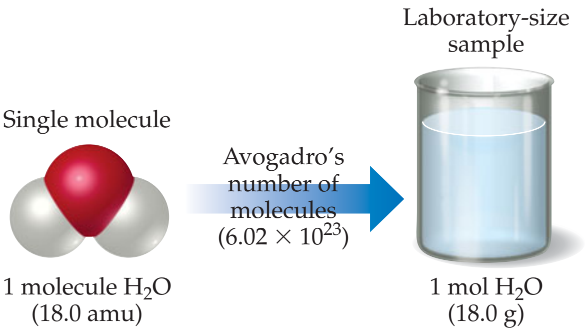
PRACTICE EXERCISE

How many oxygen atoms are in **(a)** 0.25 mol $Ca(NO_3)_2$ and **(b)** 1.50 mol of sodium carbonate?

Answers: **(a)** 9.0×10^{23}, **(b)** 2.71×10^{24}

GO FIGURE

How many H_2O molecules are in a 9.00-g sample of water?



▲ **FIGURE 3.9 Comparing the mass of 1 molecule and 1 mol of H_2O.** Both masses have the same number but different units (atomic mass units and grams). Expressing both masses in grams indicates their huge difference: 1 molecule H_2O has a mass of 2.99×10^{-23} g whereas 1 mol H_2O has a mass of 18.0 g.

Molar Mass

A dozen is the same number, 12, whether we have a dozen eggs or a dozen elephants. Clearly, however, a dozen eggs does not have the same mass as a dozen elephants. Similarly, a mole is always the *same number* (6.02×10^{23}), but 1-mol samples of different substances have *different masses.* Compare, for example, 1 mol of ^{12}C and 1 mol of ^{24}Mg. A single ^{12}C atom has a mass of 12 amu, whereas a single ^{24}Mg atom is twice as massive, 24 amu (to two significant figures). Because a mole of anything always contains the same number of particles, a mole of ^{24}Mg must be twice as massive as a mole of ^{12}C. Because a mole of ^{12}C has a mass of 12 g (by definition), a mole of ^{24}Mg must have a mass of 24 g. This example illustrates a general rule relating the mass of an atom to the mass of Avogadro's number (1 mol) of these atoms: *The atomic weight of an element in atomic mass units is numerically equal to the mass in grams of 1 mol of that element.* For example,

Cl has an atomic weight of 35.5 amu $\Rightarrow$ 1 mol Cl has a mass of 35.5 g

Au has an atomic weight of 197 amu $\Rightarrow$ 1 mol Au has a mass of 197 g

For other kinds of substances, the same numerical relationship exists between formula weight and mass of one mole of a substance:

H_2O has a formula weight of 18.0 amu $\Rightarrow$ 1 mol H_2O has a mass of 18.0 g

(◀ **FIGURE 3.9**)

NO_3^- has a formula weight of 62.0 amu $\Rightarrow$ 1 mol NO_3^- has a mass of 62.0 g

NaCl has a formula weight of 58.5 amu $\Rightarrow$ 1 mol NaCl has a mass of 58.5 g

GIVE IT SOME THOUGHT

a. Which has more mass, a mole of water (H_2O) or a mole of glucose ($C_6H_{12}O_6$)?
b. Which contains more molecules, a mole of water or a mole of glucose?

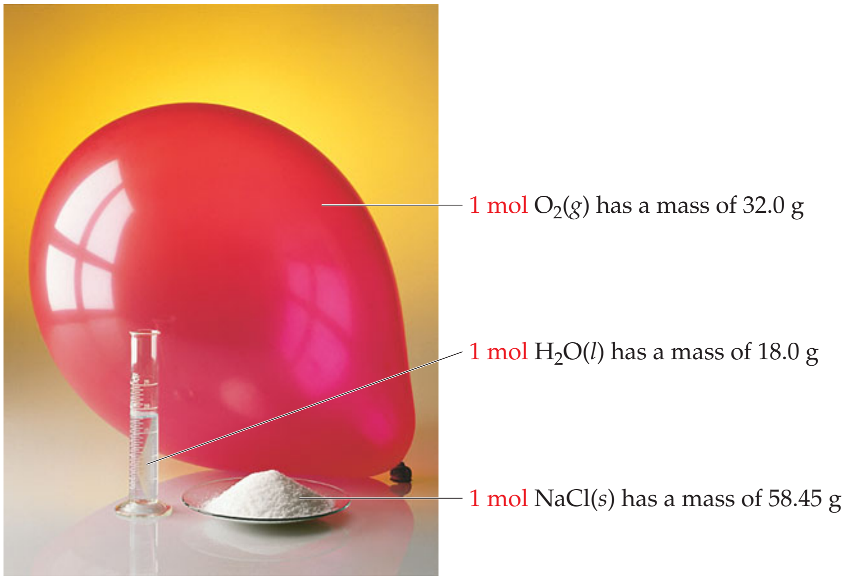
The mass in grams of one mole of a substance (that is, the mass in grams per mole) is called the **molar mass** of the substance. *The molar mass in grams per mole of any substance is numerically equal to its formula weight in atomic mass units.* For NaCl, for example, the formula weight is 58.5 amu and the molar mass is 58.5 g/mol. Mole relationships for several other substances are shown in ▼ **TABLE 3.2**, and ▶ **FIGURE 3.10** shows 1-mol quantities of three common substances.

The entries in Table 3.2 for N and N_2 point out the importance of stating the chemical form of a substance when using the mole concept. Suppose you read that 1 mol of nitrogen is produced in a particular reaction. You might interpret this statement to mean 1 mol of nitrogen atoms (14.0 g). Unless otherwise stated, however, what is

TABLE 3.2 • Mole Relationships

Name of Substance	Formula	Formula Weight (amu)	Molar Mass (g/mol)	Number and Kind of Particles in One Mole
Atomic nitrogen	N	14.0	14.0	6.02×10^{23} N atoms
Molecular nitrogen	N_2	28.0	28.0	6.02×10^{23} N_2 molecules $2(6.02 \times 10^{23})$ N atoms
Silver	Ag	107.9	107.9	6.02×10^{23} Ag atoms
Silver ions	Ag^+	107.9*	107.9	6.02×10^{23} Ag^+ ions
Barium chloride	$BaCl_2$	208.2	208.2	6.02×10^{23} $BaCl_2$ formula units 6.02×10^{23} Ba^{2+} ions $2(6.02 \times 10^{23})$ Cl^- ions

*Recall that the electron has negligible mass; thus, ions and atoms have essentially the same mass.



▲ **FIGURE 3.10 One mole each of a solid (NaCl), a liquid (H_2O), and a gas (O_2).** In each case, the mass in grams of 1 mol—that is, the molar mass—is numerically equal to the formula weight in atomic mass units. Each of these samples contains 6.02×10^{23} formula units.

probably meant is 1 mol of nitrogen molecules, N_2 (28.0 g), because N_2 is the most common chemical form of the element. To avoid ambiguity, it is important to state explicitly the chemical form being discussed. Using the chemical formula—N or N_2, for instance—avoids ambiguity.

SAMPLE EXERCISE 3.9 Calculating Molar Mass

What is the molar mass of glucose, $C_6H_{12}O_6$?

SOLUTION

Analyze We are given a chemical formula and asked to determine its molar mass.

Plan Because the molar mass of any substance is numerically equal to its formula weight, we first determine the formula weight of glucose by adding the atomic weights of its component atoms. The formula weight will have units of amu, whereas the molar mass has units of g/mol.

Solve Our first step is to determine the formula weight of glucose:

$$\begin{aligned} 6\text{ C atoms} &= 6(12.0\text{ amu}) = 72.0\text{ amu} \\ 12\text{ H atoms} &= 12(1.0\text{ amu}) = 12.0\text{ amu} \\ 6\text{ O atoms} &= 6(16.0\text{ amu}) = \underline{96.0\text{ amu}} \\ & \qquad\qquad\qquad\quad 180.0\text{ amu} \end{aligned}$$

Because glucose has a formula weight of 180.0 amu, 1 mol of this substance (6.02×10^{23} molecules) has a mass of 180.0 g. In other words, $C_6H_{12}O_6$ has a molar mass of 180.0 g/mol.

Check A magnitude below 250 seems reasonable based on the earlier examples we have encountered, and grams per mole is the appropriate unit for the molar mass.

Comment Glucose, also known as blood sugar, is found in nature in honey and fruits. Other sugars used as food are converted into glucose in the stomach or liver before the body uses them as energy sources. Because glucose requires no conversion, it is often given intravenously to patients who need immediate nourishment.

PRACTICE EXERCISE

Calculate the molar mass of $Ca(NO_3)_2$.

Answer: 164.1 g/mol

CHEMISTRY AND LIFE

GLUCOSE MONITORING

Over 20 million Americans have diabetes, and globally the number approaches 172 million. Diabetes is a metabolic disorder in which the body either cannot produce or cannot properly use the hormone insulin. One signal that a person is diabetic is that the concentration of glucose in the blood is higher than normal. Therefore, people who are diabetic need to measure their blood glucose concentrations regularly. Untreated diabetes can cause severe complications such as blindness and loss of limbs.

The body converts most of the food we eat into glucose. After digestion, glucose is delivered to cells via the blood. Cells need glucose to live, and insulin must be present in order for glucose to enter the cells. Normally, the body adjusts the concentration of insulin automatically, in concert with the glucose concentration after eating. However, in a diabetic person, either little or no insulin is produced (Type 1 diabetes) or insulin is produced but the cells cannot take it up properly (Type 2 diabetes). The result is that the blood glucose concentration is too high. People normally have a range of 70–120 mg glucose per deciliter of blood. A person who has not eaten for 8 hours or more is diagnosed as diabetic if his or her glucose level is 126 mg/dL or higher.

Glucose meters work by the introduction of blood from a person, usually by a prick of the finger, onto a small strip of paper that contains chemicals that react with glucose. Insertion of the strip into a small battery-operated reader gives the glucose concentration (▼ **FIGURE 3.11**). The mechanism of the readout varies from one monitor to another—it may be a measurement of a small electrical current or measurement of light produced in a chemical reaction. Depending on the reading on any given day, a diabetic person may need to receive an injection of insulin or simply stop eating sweets for a while.

▲ **FIGURE 3.11** **Glucose meter.**

Interconverting Masses and Moles

Conversions of mass to moles and of moles to mass are frequently encountered in calculations using the mole concept. These calculations are simplified using dimensional analysis, as shown in Sample Exercises 3.10 and 3.11.

SAMPLE EXERCISE 3.10 Converting Grams to Moles

Calculate the number of moles of glucose ($C_6H_{12}O_6$) in 5.380 g of $C_6H_{12}O_6$.

SOLUTION

Analyze We are given the number of grams of a substance and its chemical formula and asked to calculate the number of moles.

Plan The molar mass of a substance provides the factor for converting grams to moles. The molar mass of $C_6H_{12}O_6$ is 180.0 g/mol (Sample Exercise 3.9).

Solve Using 1 mol $C_6H_{12}O_6$ = 180.0 g $C_6H_{12}O_6$ to write the appropriate conversion factor, we have

$$\text{Moles } C_6H_{12}O_6 = (5.380\ \cancel{\text{g } C_6H_{12}O_6})\left(\frac{1\text{ mol } C_6H_{12}O_6}{180.0\ \cancel{\text{g } C_6H_{12}O_6}}\right) = 0.02989\text{ mol } C_6H_{12}O_6$$

Check Because 5.380 g is less than the molar mass, an answer less than one mole is reasonable. The unit mol is appropriate. The original data had four significant figures, so our answer has four significant figures.

PRACTICE EXERCISE

How many moles of sodium bicarbonate ($NaHCO_3$) are in 508 g of $NaHCO_3$?

Answer: 6.05 mol $NaHCO_3$

SAMPLE EXERCISE 3.11 Converting Moles to Grams

Calculate the mass, in grams, of 0.433 mol of calcium nitrate.

SOLUTION

Analyze We are given the number of moles and the name of a substance and asked to calculate the number of grams in the sample.

Plan To convert moles to grams, we need the molar mass, which we can calculate using the chemical formula and atomic weights.

Solve Because the calcium ion is Ca^{2+} and the nitrate ion is NO_3^-, calcium nitrate is $Ca(NO_3)_2$. Adding the atomic weights of the elements in the compound gives a formula weight of 164.1 amu. Using 1 mol $Ca(NO_3)_2$ = 164.1 g $Ca(NO_3)_2$ to write the appropriate conversion factor, we have

$$\text{Grams } Ca(NO_3)_2 = (0.433\ \cancel{\text{mol } Ca(NO_3)_2})\left(\frac{164.1\text{ g } Ca(NO_3)_2}{1\ \cancel{\text{mol } Ca(NO_3)_2}}\right) = 71.1\text{ g } Ca(NO_3)_2$$

Check The number of moles is less than 1, so the number of grams must be less than the molar mass, 164.1 g. Using rounded numbers to estimate, we have $0.5 \times 150 = 75$ g, which means the magnitude of our answer is reasonable. Both the units (g) and the number of significant figures (3) are correct.

PRACTICE EXERCISE

What is the mass, in grams, of **(a)** 6.33 mol of $NaHCO_3$ and **(b)** 3.0×10^{-5} mol of sulfuric acid?

Answers: **(a)** 532 g, **(b)** 2.9×10^{-3} g

Interconverting Masses and Numbers of Particles

The mole concept provides the bridge between mass and number of particles. To illustrate how this bridge works, let's calculate the number of copper atoms in an old copper penny. Such a penny has a mass of about 3 g, and we assume it is 100% copper:

$$\text{Cu atoms} = (3\ \cancel{\text{g Cu}})\left(\frac{1\ \cancel{\text{mol Cu}}}{63.5\ \cancel{\text{g Cu}}}\right)\left(\frac{6.02 \times 10^{23}\text{ Cu atoms}}{1\ \cancel{\text{mol Cu}}}\right)$$

$$= 3 \times 10^{22}\text{ Cu atoms}$$

We have rounded our answer to one significant figure because we used only one significant figure for the mass of the penny. Notice how dimensional analysis (Section 1.6) provides a straightforward route from grams to numbers of atoms. The molar mass and Avogadro's number are used as conversion factors to convert grams to moles and then moles to atoms. Notice also that our answer is a very large number. Any time you calculate the number of atoms, molecules, or ions in an ordinary sample of matter, you can expect the answer to be very large. In contrast, the number of moles in a sample will usually be small, often less than 1.

The general procedure for interconverting mass and number of formula units (atoms, molecules, ions, or whatever else is represented by the chemical formula) is summarized in ▼ **FIGURE 3.12**.

GO FIGURE

What number would you use to convert (a) moles of CH_4 to grams of CH_4 and (b) number of molecules of CH_4 to moles of CH_4?

▲ **FIGURE 3.12 Procedure for interconverting mass and number of formula units.** The number of moles of the substance is central to the calculation. Thus, the mole concept can be thought of as the bridge between the mass of a sample in grams and the number of formula units contained in the sample.

SAMPLE EXERCISE 3.12 Calculating Numbers of Molecules and Atoms from Mass

(**a**) How many glucose molecules are in 5.23 g of $C_6H_{12}O_6$? (**b**) How many oxygen atoms are in this sample?

SOLUTION

Analyze We are given the number of grams and the chemical formula and asked to calculate (**a**) the number of molecules and (**b**) the number of O atoms in the sample.

(a) Plan The strategy for determining the number of molecules in a given quantity of a substance is summarized in Figure 3.12. We must convert 5.23 g to moles of $C_6H_{12}O_6$ and then convert moles to molecules of $C_6H_{12}O_6$. The first conversion uses the molar mass of $C_6H_{12}O_6$, 180.0 g, and the second conversion uses Avogadro's number.

Solve Molecules $C_6H_{12}O_6$

$$= (5.23\ \cancel{\text{g } C_6H_{12}O_6})\left(\frac{1\ \cancel{\text{mol } C_6H_{12}O_6}}{180.0\ \cancel{\text{g } C_6H_{12}O_6}}\right)\left(\frac{6.02 \times 10^{23} \text{ molecules } C_6H_{12}O_6}{1\ \cancel{\text{mol } C_6H_{12}O_6}}\right)$$

$$= 1.75 \times 10^{22} \text{ molecules } C_6H_{12}O_6$$

Check Because the mass we began with is less than a mole, there should be fewer than 6.02×10^{23} molecules in the sample, which means the magnitude of our answer is reasonable. We can make a ballpark estimate of the answer: $5/200 = 2.5 \times 10^{-2}$ mol; $2.5 \times 10^{-2} \times 6 \times 10^{23} = 15 \times 10^{21} = 1.5 \times 10^{22}$ molecules. The units (molecules) and significant figures (three) are appropriate.

(b) Plan To determine the number of O atoms, we use the fact that there are six O atoms in each $C_6H_{12}O_6$ molecule. Thus, multiplying the number of molecules we calculated in (a) by the factor (6 atoms O/1 molecule $C_6H_{12}O_6$) gives the number of O atoms.

Solve

$$\text{Atoms O} = (1.75 \times 10^{22}\ \cancel{\text{molecules } C_6H_{12}O_6})\left(\frac{6 \text{ atoms O}}{1\ \cancel{\text{molecule } C_6H_{12}O_6}}\right)$$

$$= 1.05 \times 10^{23} \text{ atoms O}$$

Check The answer is 6 times as large as the answer to part (a), exactly what it should be. The number of significant figures (three) and the units (atoms O) are correct.

PRACTICE EXERCISE

(**a**) How many nitric acid molecules are in 4.20 g of HNO_3? (**b**) How many O atoms are in this sample?

Answers: (**a**) 4.01×10^{22} molecules HNO_3, (**b**) 1.20×10^{23} atoms O

3.5 EMPIRICAL FORMULAS FROM ANALYSES

As we learned in Section 2.6, the empirical formula for a substance tells us the relative number of atoms of each element in the substance. The empirical formula H_2O shows that water contains two H atoms for each O atom. This ratio also applies on the molar level: 1 mol of H_2O contains 2 mol of H atoms and 1 mol of O atoms. Conversely, *the ratio of the numbers of moles of all elements in a compound gives the subscripts in the compound's empirical formula*. Thus, the mole concept provides a way of calculating empirical formulas.

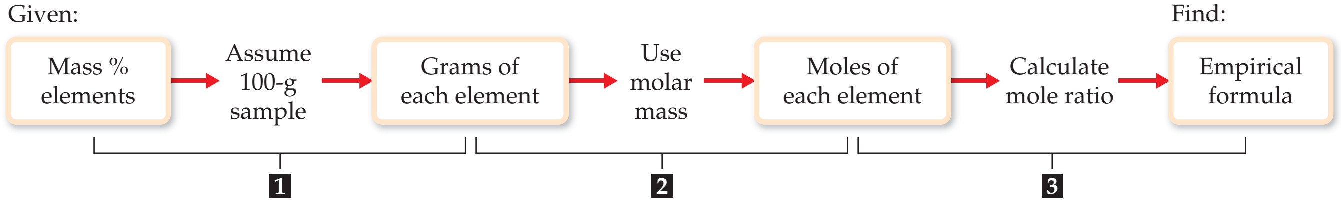
Mercury and chlorine, for example, combine to form a compound that is 73.9% mercury and 26.1% chlorine by mass. Thus, if we had a 100.0-g sample of the compound, it would contain 73.9 g of mercury and 26.1 g of chlorine. (Samples of any size can be used in problems of this type, but we will generally use 100.0 g to simplify the calculation of mass from percentage.) Using atomic weights to get molar masses, we can calculate the number of moles of each element in the sample:

$$(73.9\ \cancel{\text{g Hg}})\left(\frac{1 \text{ mol Hg}}{200.6\ \cancel{\text{g Hg}}}\right) = 0.368 \text{ mol Hg}$$

$$(26.1\ \cancel{\text{g Cl}})\left(\frac{1 \text{ mol Cl}}{35.5\ \cancel{\text{g Cl}}}\right) = 0.735 \text{ mol Cl}$$

GO FIGURE

How do you calculate the mole ratio of each element in any compound?



▲ **FIGURE 3.13 Procedure for calculating an empirical formula from percentage composition.** The key step in the calculation is step 2, determining the number of moles of each element in the compound.

We then divide the larger number of moles by the smaller number to obtain the Cl:Hg mole ratio:

$$\frac{\text{moles of Cl}}{\text{moles of Hg}} = \frac{0.735 \text{ mol Cl}}{0.368 \text{ mol Hg}} = \frac{1.99 \text{ mol Cl}}{1 \text{ mol Hg}}$$

Because of experimental errors, calculated values for a mole ratio may not be whole numbers, as in the calculation here. The number 1.99 is very close to 2, however, and so we can confidently conclude that the empirical formula for the compound is $HgCl_2$. The empirical formula is correct because its subscripts are the smallest integers that express the *ratio* of atoms present in the compound. ∞ (Section 2.6).

The general procedure for determining empirical formulas is outlined in ▲ **FIGURE 3.13**.

GIVE IT SOME THOUGHT

What is the mole ratio of nitrogen to hydrogen in N_2H_4?

SAMPLE EXERCISE 3.13 Calculating an Empirical Formula

Ascorbic acid (vitamin C) contains 40.92% C, 4.58% H, and 54.50% O by mass. What is the empirical formula of ascorbic acid?

SOLUTION

Analyze We are to determine the empirical formula of a compound from the mass percentages of its elements.

Plan The strategy for determining the empirical formula involves the three steps given in Figure 3.13.

Solve

1. For simplicity, we assume we have exactly 100 g of material (although any other mass could also be used). In 100 g of ascorbic acid, we have

40.92 g C, 4.58 g H, and 54.50 g O.

2. We calculate the number of moles of each element:

$$\text{Moles C} = (40.92\ \cancel{\text{g C}})\left(\frac{1 \text{ mol C}}{12.01\ \cancel{\text{g C}}}\right) = 3.407 \text{ mol C}$$

$$\text{Moles H} = (4.58\ \cancel{\text{g H}})\left(\frac{1 \text{ mol H}}{1.008\ \cancel{\text{g H}}}\right) = 4.54 \text{ mol H}$$

$$\text{Moles O} = (54.50\ \cancel{\text{g O}})\left(\frac{1 \text{ mol O}}{16.00\ \cancel{\text{g O}}}\right) = 3.406 \text{ mol O}$$

3. We determine the simplest whole-number ratio of moles by dividing each number of moles by the smallest number of moles:

$$\text{C: } \frac{3.407}{3.406} = 1.000 \quad \text{H: } \frac{4.54}{3.406} = 1.33 \quad \text{O: } \frac{3.406}{3.406} = 1.000$$

The ratio for H is too far from 1 to attribute the difference to experimental error; in fact, it is quite close to $1\frac{1}{3}$. This suggests we should multiply the ratios by 3 to obtain whole numbers:

$$\text{C:H:O} = 3(1:1.33:1) = 3:4:3$$

Thus, the empirical formula is

$C_3H_4O_3$

Check It is reassuring that the subscripts are moderate-size whole numbers. Also, calculating the percentage composition of C_3H_8O gives values very close to the original percentages.

PRACTICE EXERCISE

A 5.325-g sample of methyl benzoate, a compound used in the manufacture of perfumes, contains 3.758 g of carbon, 0.316 g of hydrogen, and 1.251 g of oxygen. What is the empirical formula of this substance?

Answer: C_4H_4O

Molecular Formulas from Empirical Formulas

We can obtain a molecular formula for any compound from its empirical formula if we know either the molecular weight or the molar mass of the compound. *The subscripts in the molecular formula of a substance are always whole-number multiples of the subscripts in its empirical formula.* ∞ (Section 2.6) This multiple can be found by dividing the molecular weight by the empirical formula weight:

$$\text{Whole-number multiple} = \frac{\text{molecular weight}}{\text{empirical formula weight}} \qquad [3.11]$$

In Sample Exercise 3.13, for example, the empirical formula of ascorbic acid was determined to be $C_3H_4O_3$. This means the empirical formula weight is $3(12.0\text{ amu}) + 4(1.0\text{ amu}) + 3(16.0\text{ amu}) = 88.0\text{ amu}$. The experimentally determined molecular weight is 176 amu. Thus, we find the whole-number multiple that converts the empirical formula to the molecular formula by dividing:

$$\text{Whole-number multiple} = \frac{\text{molecular weight}}{\text{empirical formula weight}} = \frac{176\text{ amu}}{88.0\text{ amu}} = 2$$

Consequently, we multiply the subscripts in the empirical formula by this multiple, giving the molecular formula: $C_6H_8O_6$.

SAMPLE EXERCISE 3.14 Determining a Molecular Formula

Mesitylene, a hydrocarbon found in crude oil, has an empirical formula of C_3H_4 and an experimentally determined molecular weight of 121 amu. What is its molecular formula?

SOLUTION

Analyze We are given an empirical formula and a molecular weight and asked to determine a molecular formula.

Plan The subscripts in a compound's molecular formula are whole-number multiples of the subscripts in its empirical formula. We find the appropriate multiple by using Equation 3.11.

Solve The formula weight of the empirical formula C_3H_4 is

$$3(12.0\text{ amu}) + 4(1.0\text{ amu}) = 40.0\text{ amu}$$

Next, we use this value in Equation 3.11:

$$\text{Whole-number multiple} = \frac{\text{molecular weight}}{\text{empirical formula weight}} = \frac{121}{40.0} = 3.02$$

Only whole-number ratios make physical sense because molecules contain whole atoms. The 3.02 in this case could result from a small experimental error in the molecular weight. We therefore multiply each subscript in the empirical formula by 3 to give the molecular formula: C_9H_{12}.

Check We can have confidence in the result because dividing molecular weight by empirical formula weight yields nearly a whole number.

PRACTICE EXERCISE

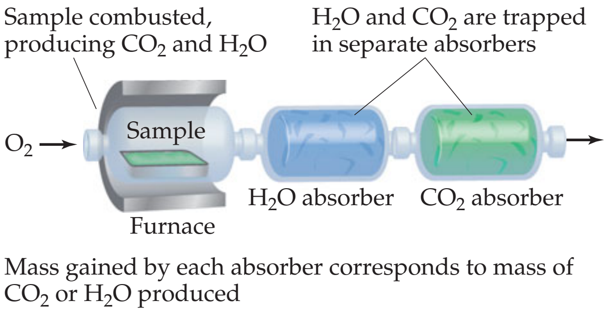
Ethylene glycol, used in automobile antifreeze, is 38.7% C, 9.7% H, and 51.6% O by mass. Its molar mass is 62.1 g/mol. (**a**) What is the empirical formula of ethylene glycol? (**b**) What is its molecular formula?

Answers: (**a**) CH_3O, (**b**) $C_2H_6O_2$

Combustion Analysis

One technique for determining empirical formulas in the laboratory is *combustion analysis*, commonly used for compounds containing principally carbon and hydrogen.

When a compound containing carbon and hydrogen is completely combusted in an apparatus such as that shown in ▶ **FIGURE 3.14**, the carbon is converted to CO_2 and the hydrogen is converted to H_2O. (Section 3.2) The amounts of CO_2 and H_2O produced are determined by measuring the mass increase in the CO_2 and H_2O absorbers. From the masses of CO_2 and H_2O we can calculate the number of moles of C and H in the original sample and thereby the empirical formula. If a third element is present in the compound, its mass can be determined by subtracting the measured masses of C and H from the original sample mass.



▲ **FIGURE 3.14 Apparatus for combustion analysis.**

SAMPLE EXERCISE 3.15 Determining an Empirical Formula by Combustion Analysis

Isopropyl alcohol, sold as rubbing alcohol, is composed of C, H, and O. Combustion of 0.255 g of isopropyl alcohol produces 0.561 g of CO_2 and 0.306 g of H_2O. Determine the empirical formula of isopropyl alcohol.

SOLUTION

Analyze We are told that isopropyl alcohol contains C, H, and O atoms and given the quantities of CO_2 and H_2O produced when a given quantity of the alcohol is combusted. We must determine the empirical formula for isopropyl alcohol, a task that requires us to calculate the number of moles of C, H, and O in the sample.

Plan We can use the mole concept to calculate grams of C in the CO_2 and grams of H in the H_2O. These masses are the masses of C and H in the alcohol before combustion. The mass of O in the compound equals the mass of the original sample minus the sum of the C and H masses. Once we have the C, H, and O masses, we can proceed as in Sample Exercise 3.13.

Solve

To calculate the mass of C from the measured mass of CO_2, we first use the molar mass of CO_2, 44.0 g/mol, to convert grams of CO_2 to moles of CO_2. Because each CO_2 molecule has only one C atom, there is 1 mol of C atoms per mole of CO_2 molecules. This fact allows us to convert moles of CO_2 to moles of C. Finally, we use the molar mass of C, 12.0 g, to convert moles of C to grams of C:

$$\text{Grams C} = (0.561\ \cancel{\text{g CO}_2})\left(\frac{1\ \cancel{\text{mol CO}_2}}{44.0\ \cancel{\text{g CO}_2}}\right)\left(\frac{1\ \cancel{\text{mol C}}}{1\ \cancel{\text{mol CO}_2}}\right)\left(\frac{12.0\ \text{g C}}{1\ \cancel{\text{mol C}}}\right) = 0.153\ \text{g C}$$

The calculation for determining H mass from H_2O mass is similar, although we must remember that there are 2 mol of H atoms per 1 mol of H_2O molecules:

$$\text{Grams H} = (0.306\ \cancel{\text{g H}_2\text{O}})\left(\frac{1\ \cancel{\text{mol H}_2\text{O}}}{18.0\ \cancel{\text{g H}_2\text{O}}}\right)\left(\frac{2\ \cancel{\text{mol H}}}{1\ \cancel{\text{mol H}_2\text{O}}}\right)\left(\frac{1.01\ \text{g H}}{1\ \cancel{\text{mol H}}}\right) = 0.0343\ \text{g H}$$

The mass of the sample, 0.255 g, is the sum of the masses of C, H, and O. Thus, the O mass is

$$\begin{aligned}\text{Mass of O} &= \text{mass of sample} - (\text{mass of C} + \text{mass of H})\\ &= 0.255\ \text{g} - (0.153\ \text{g} + 0.0343\ \text{g}) = 0.068\ \text{g O}\end{aligned}$$

The number of moles of C, H, and O in the sample is therefore

$$\text{Moles C} = (0.153\ \cancel{\text{g C}})\left(\frac{1\ \text{mol C}}{12.0\ \cancel{\text{g C}}}\right) = 0.0128\ \text{mol C}$$

$$\text{Moles H} = (0.0343\ \cancel{\text{g H}})\left(\frac{1\ \text{mol H}}{1.01\ \cancel{\text{g H}}}\right) = 0.0340\ \text{mol H}$$

$$\text{Moles O} = (0.068\ \cancel{\text{g O}})\left(\frac{1\ \text{mol O}}{16.0\ \cancel{\text{g O}}}\right) = 0.0043\ \text{mol O}$$

To find the empirical formula, we must compare the relative number of moles of each element in the sample. We determine relative number of moles by dividing each of our calculated number of moles by the smallest number:

$$\text{C:}\ \frac{0.0128}{0.0043} = 3.0 \qquad \text{H:}\ \frac{0.0340}{0.0043} = 7.9 \qquad \text{O:}\ \frac{0.0043}{0.0043} = 1.0$$

The first two numbers are very close to the whole numbers 3 and 8, giving the empirical formula

C_3H_8O.

Check The subscripts work out to be moderate-size whole numbers, as expected.

PRACTICE EXERCISE

(**a**) Caproic acid, responsible for the odor of dirty socks, is composed of C, H, and O atoms. Combustion of a 0.225-g sample of this compound produces 0.512 g CO_2 and 0.209 g H_2O. What is the empirical formula of caproic acid? (**b**) Caproic acid has a molar mass of 116 g/mol. What is its molecular formula?

Answers: (**a**) C_3H_6O, (**b**) $C_6H_{12}O_2$

GIVE IT SOME THOUGHT

In Sample Exercise 3.15, how do you explain the fact that the values in our calculated C:H:O ratio are 3.0:7.9:1.0 rather than exact integers 3:8:1?

3.6 QUANTITATIVE INFORMATION FROM BALANCED EQUATIONS

The coefficients in a chemical equation represent the relative numbers of molecules in a reaction. The mole concept allows us to convert this information to the masses of the substances in the reaction. For instance, the coefficients in the balanced equation

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l) \qquad [3.12]$$

indicate that two molecules of H_2 react with one molecule of O_2 to form two molecules of H_2O. It follows that the relative numbers of moles are identical to the relative numbers of molecules:

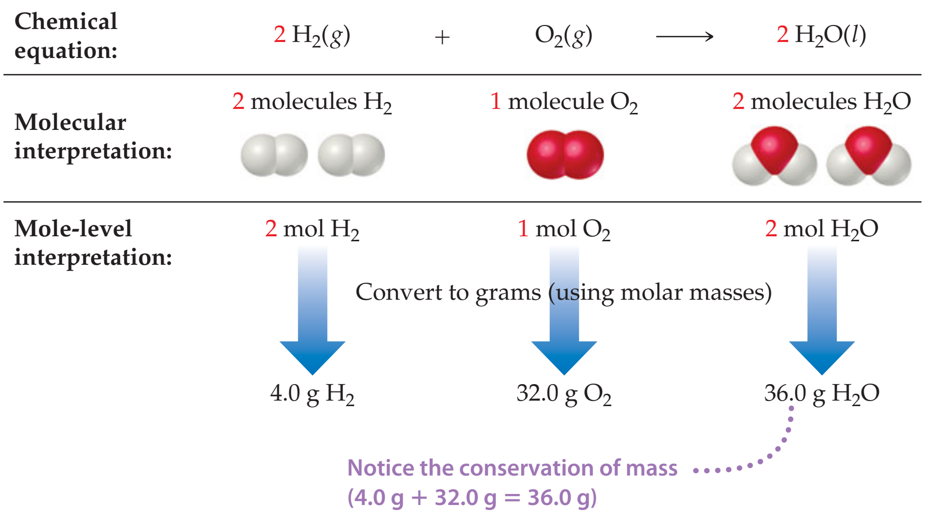
$$\begin{array}{ccccc} 2\,H_2(g) & + & O_2(g) & \longrightarrow & 2\,H_2O(l) \\ \text{2 molecules} & & \text{1 molecule} & & \text{2 molecules} \\ 2(6.02 \times 10^{23}\text{ molecules}) & & 1(6.02 \times 10^{23}\text{ molecules}) & & 2(6.02 \times 10^{23}\text{ molecules}) \\ \text{2 mol} & & \text{1 mol} & & \text{2 mol} \end{array}$$

We can generalize this observation to all balanced chemical equations: *The coefficients in a balanced chemical equation indicate both the relative numbers of molecules (or formula units) in the reaction and the relative numbers of moles.* ▼ **FIGURE 3.15** shows how this result corresponds to the law of conservation of mass.

The quantities 2 mol H_2, 1 mol O_2, and 2 mol H_2O given by the coefficients in Equation 3.12 are called *stoichiometrically equivalent quantities*. The relationship between these quantities can be represented as

$$2\text{ mol }H_2 \mathrel{\hat{=}} 1\text{ mol }O_2 \mathrel{\hat{=}} 2\text{ mol }H_2O$$

where the $\hat{=}$ symbol means "is stoichiometrically equivalent to." Stoichiometric relations such as these can be used to convert between quantities of reactants and products



Notice the conservation of mass (4.0 g + 32.0 g = 36.0 g)

▶ **FIGURE 3.15** **Interpreting a balanced chemical equation quantitatively.**

in a chemical reaction. For example, the number of moles of H_2O produced from 1.57 mol of O_2 is

$$\text{Moles } H_2O = (1.57\ \cancel{\text{mol } O_2})\left(\frac{2\text{ mol } H_2O}{1\ \cancel{\text{mol } O_2}}\right) = 3.14\text{ mol } H_2O$$

GIVE IT SOME THOUGHT

When 1.57 mol O_2 reacts with H_2 to form H_2O, how many moles of H_2 are consumed in the process?

As an additional example, consider the combustion of butane (C_4H_{10}), the fuel in disposable general-purpose lighters:

$$2\,C_4H_{10}(l) + 13\,O_2(g) \longrightarrow 8\,CO_2(g) + 10\,H_2O(g) \qquad [3.13]$$

Let's calculate the mass of CO_2 produced when 1.00 g of C_4H_{10} is burned. The coefficients in Equation 3.13 tell us how the amount of C_4H_{10} consumed is related to the amount of CO_2 produced: 2 mol $C_4H_{10} \simeq$ 8 mol CO_2. To use this stoichiometric relationship, we must convert grams of C_4H_{10} to moles using the molar mass of C_4H_{10}, 58.0 g/mol:

$$\begin{aligned}\text{Moles } C_4H_{10} &= (1.00\ \cancel{\text{g } C_4H_{10}})\left(\frac{1\text{ mol } C_4H_{10}}{58.0\ \cancel{\text{g } C_4H_{10}}}\right)\\ &= 1.72 \times 10^{-2}\text{ mol } C_4H_{10}\end{aligned}$$

We then use the stoichiometric factor from the balanced equation to calculate moles of CO_2:

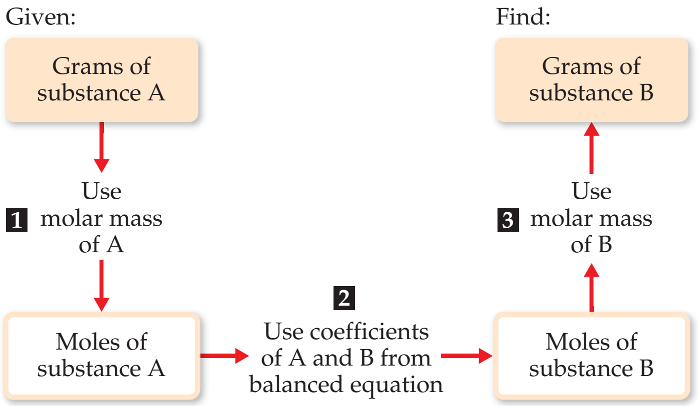
$$\begin{aligned}\text{Moles } CO_2 &= (1.72 \times 10^{-2}\ \cancel{\text{mol } C_4H_{10}})\left(\frac{8\text{ mol } CO_2}{2\ \cancel{\text{mol } C_4H_{10}}}\right)\\ &= 6.88 \times 10^{-2}\text{ mol } CO_2\end{aligned}$$

Finally, we use the molar mass of CO_2, 44.0 g/mol, to calculate the CO_2 mass in grams:

$$\begin{aligned}\text{Grams } CO_2 &= (6.88 \times 10^{-2}\ \cancel{\text{mol } CO_2})\left(\frac{44.0\text{ g } CO_2}{1\ \cancel{\text{mol } CO_2}}\right)\\ &= 3.03\text{ g } CO_2\end{aligned}$$

This conversion sequence involves three steps, as illustrated in ▼ **FIGURE 3.16**. These three conversions can be combined in a single equation:

$$\begin{aligned}\text{Grams } CO_2 &= (1.00\ \cancel{\text{g } C_4H_{10}})\left(\frac{1\ \cancel{\text{mol } C_4H_{10}}}{58.0\ \cancel{\text{g } C_4H_{10}}}\right)\left(\frac{8\ \cancel{\text{mol } CO_2}}{2\ \cancel{\text{mol } C_4H_{10}}}\right)\left(\frac{44.0\text{ g } CO_2}{1\ \cancel{\text{mol } CO_2}}\right)\\ &= 3.03\text{ g } CO_2\end{aligned}$$



◀ **FIGURE 3.16 Procedure for calculating amounts of reactants consumed or products formed in a reaction.** The number of grams of a reactant consumed or product formed can be calculated in three steps, starting with the number of grams of any reactant or product. Notice how molar masses and the coefficients in the balanced equation are used.

To calculate the amount of O_2 consumed in the reaction of Equation 3.13, we again rely on the coefficients in the balanced equation for our stoichiometric factor: 2 mol $C_4H_{10} \simeq$ 13 mol O_2:

$$\text{Grams } O_2 = (1.00\ \cancel{\text{g } C_4H_{10}})\left(\frac{1\ \cancel{\text{mol } C_4H_{10}}}{58.0\ \cancel{\text{g } C_4H_{10}}}\right)\left(\frac{13\ \cancel{\text{mol } O_2}}{2\ \cancel{\text{mol } C_4H_{10}}}\right)\left(\frac{32.0\text{ g } O_2}{1\ \cancel{\text{mol } O_2}}\right)$$

$$= 3.59\text{ g } O_2$$

GIVE IT SOME THOUGHT

If 20.00 g of a compound reacts completely with 30.00 g of another compound in a combination reaction, how many grams of product are formed?

SAMPLE EXERCISE 3.16 Calculating Amounts of Reactants and Products

Determine how many grams of water are produced in the oxidation of 1.00 g of glucose, $C_6H_{12}O_6$:

$$C_6H_{12}O_6(s) + 6\,O_2(g) \longrightarrow 6\,CO_2(g) + 6\,H_2O(l)$$

SOLUTION

Analyze We are given the mass of a reactant and must determine the mass of a product in the given reaction.

Plan The general strategy, as outlined in Figure 3.16, requires three steps:

1. Convert grams of $C_6H_{12}O_6$ to moles using the molar mass of $C_6H_{12}O_6$.
2. Convert moles of $C_6H_{12}O_6$ to moles of H_2O using the stoichiometric relationship 1 mol $C_6H_{12}O_6 \simeq$ 6 mol H_2O.
3. Convert moles of H_2O to grams using the molar mass of H_2O.

Solve

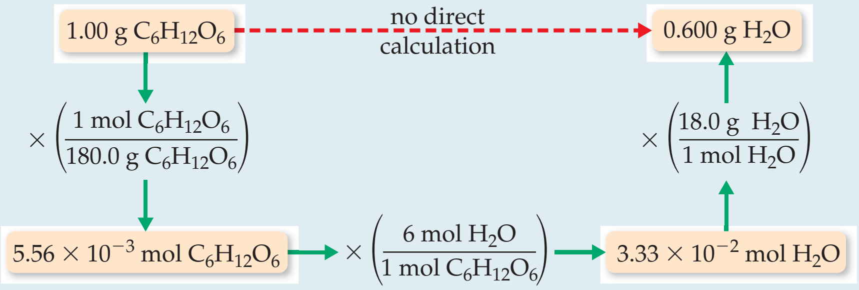
1. $$\text{Moles } C_6H_{12}O_6 = (1.00\ \cancel{\text{g } C_6H_{12}O_6})\left(\frac{1\text{ mol } C_6H_{12}O_6}{180.0\ \cancel{\text{g } C_6H_{12}O_6}}\right)$$

2. $$\text{Moles } H_2O = (1.00\ \cancel{\text{g } C_6H_{12}O_6})\left(\frac{1\ \cancel{\text{mol } C_6H_{12}O_6}}{180.0\ \cancel{\text{g } C_6H_{12}O_6}}\right)\left(\frac{6\text{ mol } H_2O}{1\ \cancel{\text{mol } C_6H_{12}O_6}}\right)$$

3. $$\text{Grams } H_2O = (1.00\text{ g } \cancel{C_6H_{12}O_6})\left(\frac{1\ \cancel{\text{mol } C_6H_{12}O_6}}{180.0\text{ g } \cancel{C_6H_{12}O_6}}\right)\left(\frac{6\ \cancel{\text{mol } H_2O}}{1\ \cancel{\text{mol } C_6H_{12}O_6}}\right)\left(\frac{18.0\text{ g } H_2O}{1\ \cancel{\text{mol } H_2O}}\right)$$

$$= 0.600\text{ g } H_2O$$

The steps can be summarized in a diagram like that in Figure 3.16:



Check We can check how reasonable our result is by doing a ballpark estimate of the mass of H_2O. Because the molar mass of glucose is 180 g/mol, 1 gram of glucose equals 1/180 mol. Because one mole of glucose yields 6 mol H_2O, we would have $6/180 = 1/30$ mol H_2O. The molar mass of water is 18 g/mol, so we have $1/30 \times 18 = 6/10 = 0.6$ g of H_2O, which agrees with the full calculation. The units, grams H_2O, are correct. The initial data had three significant figures, so three significant figures for the answer is correct.

Comment An average adult ingests 2 L of water daily and eliminates 2.4 L. The "extra" 0.4 L is produced in the metabolism of foodstuffs, such as oxidation of glucose. The desert rat (kangaroo rat), on the other hand, apparently never drinks water. It survives on its metabolic water.

PRACTICE EXERCISE

Decomposition of $KClO_3$ is sometimes used to prepare small amounts of O_2 in the laboratory: $2\,KClO_3(s) \longrightarrow 2\,KCl(s) + 3\,O_2(g)$. How many grams of O_2 can be prepared from 4.50 g of $KClO_3$?

Answer: 1.77 g

SAMPLE EXERCISE 3.17 Calculating Amounts of Reactants and Products

Solid lithium hydroxide is used in space vehicles to remove the carbon dioxide gas exhaled by astronauts. The hydroxide reacts with the carbon dioxide to form solid lithium carbonate and liquid water. How many grams of carbon dioxide can be absorbed by 1.00 g of lithium hydroxide?

SOLUTION

Analyze We are given a verbal description of a reaction and asked to calculate the number of grams of one reactant that reacts with 1.00 g of another.

Plan The verbal description of the reaction can be used to write a balanced equation:

$$2\,LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(l)$$

We are given the mass in grams of LiOH and asked to calculate the mass in grams of CO_2. We can accomplish this task by using the three conversion steps in Figure 3.16. The conversion of step 1 requires the molar mass of LiOH ($6.94 + 16.00 + 1.01 = 23.95$ g/mol). The conversion of step 2 is based on a stoichiometric relationship from the balanced chemical equation: 2 mol LiOH $\simeq$ 1 mol CO_2. For the step 3 conversion, we use the molar mass of CO_2: $12.01 + 2(16.00) = 44.01$ g/mol.

Solve

$$(1.00\ \cancel{\text{g LiOH}})\left(\frac{1\ \cancel{\text{mol LiOH}}}{23.95\ \cancel{\text{g LiOH}}}\right)\left(\frac{1\ \cancel{\text{mol CO}_2}}{2\ \cancel{\text{mol LiOH}}}\right)\left(\frac{44.01\ \text{g CO}_2}{1\ \cancel{\text{mol CO}_2}}\right) = 0.919\ \text{g CO}_2$$

Check Notice that 23.95 g LiOH/mol $\approx$ 24 g LiOH/mol, that 24 g LiOH/mol $\times$ 2 mol LiOH = 48 g LiOH, and (44 g CO_2/mol)/(48 g LiOH) is slightly less than 1. Thus, the magnitude of our answer, 0.919 g CO_2, is reasonable based on the amount of starting LiOH. The significant figures and units are also appropriate.

PRACTICE EXERCISE

Propane, C_3H_8 (Figure 3.8), is a common fuel used for cooking and home heating. What mass of O_2 is consumed in the combustion of 1.00 g of propane?

Answer: 3.64 g

3.7 LIMITING REACTANTS

Suppose you wish to make several sandwiches using one slice of cheese and two slices of bread for each. Using Bd = bread, Ch = cheese, and Bd_2Ch = sandwich, the recipe for making a sandwich can be represented like a chemical equation:

$$2\,Bd + Ch \longrightarrow Bd_2Ch$$

If you have 10 slices of bread and 7 slices of cheese, you can make only 5 sandwiches and will have 2 slices of cheese left over. The amount of bread available limits the number of sandwiches.

An analogous situation occurs in chemical reactions when one reactant is used up before the others. The reaction stops as soon as any reactant is totally consumed, leaving the excess reactants as leftovers. Suppose, for example, we have a mixture of 10 mol H_2 and 7 mol O_2, which react to form water:

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$$

Because 2 mol $H_2 \simeq$ 1 mol O_2, the number of moles of O_2 needed to react with all the H_2 is

$$\text{Moles } O_2 = (10\ \cancel{\text{mol H}_2})\left(\frac{1\ \text{mol O}_2}{2\ \cancel{\text{mol H}_2}}\right) = 5\ \text{mol O}_2$$

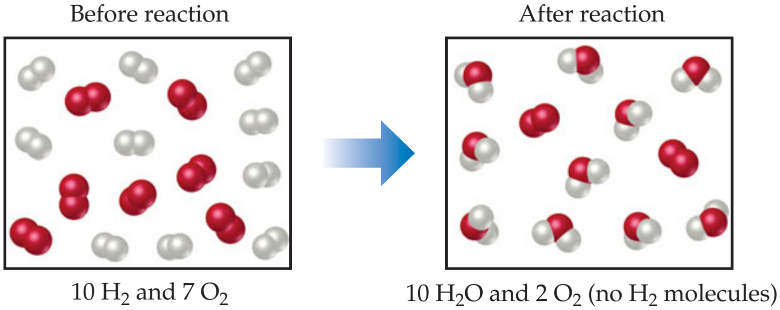
Because 7 mol O_2 is available at the start of the reaction, 7 mol O_2 − 5 mol O_2 = 2 mol O_2 is present when all the H_2 is consumed.

The reactant that is completely consumed in a reaction is called the **limiting reactant** because it determines, or limits, the amount of product formed. The other reactants are sometimes called *excess reactants*. In our example, shown in ◀ **FIGURE 3.17**, H_2 is the limiting reactant, which means that once all the H_2 has been consumed, the reaction stops. The excess reactant is O_2; some is left over when the reaction stops.

There are no restrictions on the starting amounts of reactants in any reaction. Indeed, many reactions are carried out using an excess of one reactant. The quantities of reactants consumed and products formed, however, are restricted by the quantity of the limiting reactant. For example, when a combustion reaction takes place in the open air, oxygen is plentiful and is therefore the excess reactant. If you run out of gasoline while driving, the car stops because the gasoline is the limiting reactant in the combustion reaction that moves the car.

GO FIGURE

If O_2 had been the limiting reactant, how many moles of H_2O would have formed?


Before reaction
After reaction
10 H_2 and 7 O_2
10 H_2O and 2 O_2 (no H_2 molecules)

▲ **FIGURE 3.17** **Limiting reactant.** Because H_2 is completely consumed, it is the limiting reactant. Because some O_2 is left over after the reaction is complete, O_2 is the excess reactant. The amount of H_2O formed depends on the amount of limiting reactant, H_2.

Before we leave the example illustrated in Figure 3.17, let's summarize the data:

	$2\,H_2(g)$	$+$	$O_2(g)$	$\longrightarrow$	$2\,H_2O(g)$
Initial quantities:	10 mol		7 mol		0 mol
Change (reaction):	−10 mol		−5 mol		+10 mol
Final quantities:	0 mol		2 mol		10 mol

The second line in the table (Change) summarizes the amounts of reactants consumed (where this consumption is indicated by the minus signs) and the amount of the product formed (indicated by the plus sign). These quantities are restricted by the quantity of the limiting reactant and depend on the coefficients in the balanced equation. The mole ratio H_2:O_2:H_2O = 10:5:10 conforms to the ratio of the coefficients in the balanced equation, 2:1:2. The final quantities, which depend on the initial quantities and their changes, are found by adding the initial quantity and change quantity for each column. None of the limiting reactant (H_2) remains at the end of the reaction. What remains is 2 mol O_2 (excess reactant) and 10 mol H_2O (product).

SAMPLE EXERCISE 3.18 Calculating the Amount of Product Formed from a Limiting Reactant

The most important commercial process for converting N_2 from the air into nitrogen-containing compounds is based on the reaction of N_2 and H_2 to form ammonia (NH_3):

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

How many moles of NH_3 can be formed from 3.0 mol of N_2 and 6.0 mol of H_2?

SOLUTION

Analyze We are asked to calculate the number of moles of product, NH_3, given the quantities of each reactant, N_2 and H_2, available in a reaction. This is a limiting reactant problem.

Plan If we assume one reactant is completely consumed, we can calculate how much of the second reactant is needed. By comparing the calculated quantity of the second reactant with the amount available, we can determine which reactant is limiting. We then proceed with the calculation, using the quantity of the limiting reactant.

Solve

The number of moles of H_2 needed for complete consumption of 3.0 mol of N_2 is:

$$\text{Moles } H_2 = (3.0\ \cancel{\text{mol } N_2})\left(\frac{3\text{ mol } H_2}{1\ \cancel{\text{mol } N_2}}\right) = 9.0\text{ mol } H_2$$

Because only 6.0 mol H_2 is available, we will run out of H_2 before the N_2 is gone, which tells us that H_2 is the limiting reactant. Therefore, we use the quantity of H_2 to calculate the quantity of NH_3 produced:

$$\text{Moles } NH_3 = (6.0\ \cancel{\text{mol } H_2})\left(\frac{2\text{ mol } NH_3}{3\ \cancel{\text{mol } H_2}}\right) = 4.0\text{ mol } NH_3$$

Comment The table on the right summarizes this example:

	$N_2(g)$	+	$3\ H_2(g)$	$\longrightarrow$	$2\ NH_3(g)$
Initial quantities:	3.0 mol		6.0 mol		0 mol
Change (reaction):	−2.0 mol		−6.0 mol		+4.0 mol
Final quantities:	1.0 mol		0 mol		4.0 mol

Notice that we can calculate not only the number of moles of NH_3 formed but also the number of moles of each reactant remaining after the reaction. Notice also that although the initial number of moles of H_2 is greater than the final number of moles of N_2, the H_2 is nevertheless the limiting reactant because of its larger coefficient in the balanced equation.

Check The Change row of the summary table shows that the mole ratio of reactants consumed and product formed, 2:6:4, conforms to the coefficients in the balanced equation, 1:3:2. Because H_2 is the limiting reactant, it is completely consumed in the reaction, leaving 0 mol at the end. Because 6.0 mol H_2 has two significant figures, our answer has two significant figures.

PRACTICE EXERCISE

(**a**) When 1.50 mol of Al and 3.00 mol of Cl_2 combine in the reaction $2\ Al(s) + 3\ Cl_2(g) \longrightarrow 2\ AlCl_3(s)$, which is the limiting reactant? (**b**) How many moles of $AlCl_3$ are formed? (**c**) How many moles of the excess reactant remain at the end of the reaction?

Answers: (**a**) Al, (**b**) 1.50 mol, (**c**) 0.75 mol Cl_2

SAMPLE EXERCISE 3.19 Calculating the Amount of Product Formed from a Limiting Reactant

The reaction

$$2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(g)$$

is used to produce electricity in a hydrogen fuel cell. Suppose a fuel cell contains 150 g of $H_2(g)$ and 1500 g of $O_2(g)$ (each measured to two significant figures). How many grams of water can form?

SOLUTION

Analyze We are asked to calculate the amount of a product, given the amounts of two reactants, so this is a limiting reactant problem.

Plan To identify the limiting reactant, we can calculate the number of moles of each reactant and compare their ratio with the ratio of coefficients in the balanced equation. We then use the quantity of the limiting reactant to calculate the mass of water that forms.

Solve From the balanced equation, we have the stoichiometric relations

$$2 \text{ mol } H_2 \simeq 1 \text{ mol } O_2 \simeq 2 \text{ mol } H_2O$$

Using the molar mass of each substance, we calculate the number of moles of each reactant:

$$\text{Moles } H_2 = (150\ \cancel{\text{g } H_2})\left(\frac{1 \text{ mol } H_2}{2.00\ \cancel{\text{g } H_2}}\right) = 75 \text{ mol } H_2$$

$$\text{Moles } O_2 = (1500\ \cancel{\text{g } O_2})\left(\frac{1 \text{ mol } O_2}{32.0\ \cancel{\text{g } O_2}}\right) = 47 \text{ mol } O_2$$

The coefficients in the balanced equation indicate that the reaction requires 2 mol of H_2 for every 1 mol of O_2. Therefore, for all the O_2 to completely react, we would need $2 \times 47 = 94$ mol of H_2. Since there are only 75 mol of H_2, all of the O_2 cannot react, so it is the excess reactant, and H_2 must be the limiting reactant. (Notice that the limiting reactant is not merely the one present in the lowest amount.)

We use the given quantity of H_2 (the limiting reactant) to calculate the quantity of water formed. We could begin this calculation with the given H_2 mass, 150 g, but we can save a step by starting with the moles of H_2, 75 mol, we just calculated:

$$\text{Grams } H_2O = (75\ \cancel{\text{mol } H_2})\left(\frac{2\ \cancel{\text{mol } H_2O}}{2\ \cancel{\text{mol } H_2}}\right)\left(\frac{18.0 \text{ g } H_2O}{1\ \cancel{\text{mol } H_2O}}\right)$$

$$= 1400 \text{ g } H_2O = 1.4 \times 10^2 \text{ g } H_2O \text{ (two significant figures)}$$

Check The magnitude of the answer seems reasonable based on the amounts of the reactants. The units are correct, and the number of significant figures (two) corresponds to those in the values given in the problem statement.

Comment The quantity of the limiting reactant, H_2, can also be used to determine the quantity of O_2 used:

$$\text{Grams } O_2 = (75 \cancel{\text{mol } H_2})\left(\frac{1 \cancel{\text{mol } O_2}}{2 \cancel{\text{mol } H_2}}\right)\left(\frac{32.0 \text{ g } O_2}{1 \cancel{\text{mol } O_2}}\right)$$
$$= 1.2 \times 10^3 \text{ g } H_2O$$

The mass of O_2 remaining at the end of the reaction equals the starting amount minus the amount consumed:

$$1500 \text{ g} - 1200 \text{ g} = 300 \text{ g}.$$

PRACTICE EXERCISE

When a 2.00-g strip of zinc metal is placed in an aqueous solution containing 2.50 g of silver nitrate, the reaction is

$$Zn(s) + 2\,AgNO_3(aq) \longrightarrow 2\,Ag(s) + Zn(NO_3)_2(aq)$$

(a) Which reactant is limiting? **(b)** How many grams of Ag form? **(c)** How many grams of $Zn(NO_3)_2$ form? **(d)** How many grams of the excess reactant are left at the end of the reaction?

Answers: **(a)** $AgNO_3$, **(b)** 1.59 g, **(c)** 1.39 g, **(d)** 1.52 g Zn

Theoretical Yields

The quantity of product calculated to form when all of a limiting reactant is consumed is called the **theoretical yield**. The amount of product actually obtained, called the *actual yield,* is almost always less than (and can never be greater than) the theoretical yield. There are many reasons for this difference. Part of the reactants may not react, for example, or they may react in a way different from that desired (side reactions). In addition, it is not always possible to recover all of the product from the reaction mixture. The **percent yield** of a reaction relates actual and theoretical yields:

$$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \qquad [3.14]$$

SAMPLE EXERCISE 3.20 Calculating Theoretical Yield and Percent Yield

Adipic acid, $H_2C_6H_8O_4$, used to produce nylon, is made commercially by a reaction between cyclohexane (C_6H_{12}) and O_2:

$$2\,C_6H_{12}(l) + 5\,O_2(g) \longrightarrow 2\,H_2C_6H_8O_4(l) + 2\,H_2O(g)$$

(a) Assume that you carry out this reaction with 25.0 g of cyclohexane and that cyclohexane is the limiting reactant. What is the theoretical yield of adipic acid? **(b)** If you obtain 33.5 g of adipic acid, what is the percent yield for the reaction?

SOLUTION

Analyze We are given a chemical equation and the quantity of the limiting reactant (25.0 g of C_6H_{12}). We are asked to calculate the theoretical yield of a product $H_2C_6H_8O_4$ and the percent yield if only 33.5 g of product is obtained.

Plan

(a) The theoretical yield, which is the calculated quantity of adipic acid formed, can be calculated using the sequence of conversions shown in Figure 3.16.

(b) The percent yield is calculated by using Equation 3.14 to compare the given actual yield (33.5 g) with the theoretical yield.

Solve

(a) The theoretical yield is

$$\text{Grams } H_2C_6H_8O_4 = (25.0 \cancel{\text{g } C_6H_{12}})\left(\frac{1 \cancel{\text{mol } C_6H_{12}}}{84.0 \cancel{\text{g } C_6H_{12}}}\right)\left(\frac{2 \cancel{\text{mol } H_2C_6H_8O_4}}{2 \cancel{\text{mol } C_6H_{12}}}\right)\left(\frac{146.0 \text{ g } H_2C_6H_8O_4}{1 \cancel{\text{mol } H_2C_6H_8O_4}}\right)$$
$$= 43.5 \text{ g } H_2C_6H_8O_4$$

(b) $$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{33.5\ \text{g}}{43.5\ \text{g}} \times 100\% = 77.0\%$$

Check We can check our answer in (a) by doing a ballpark calculation. From the balanced equation we know that each mole of cyclohexane gives 1 mol adipic acid. We have $25/84 \approx 25/75 = 0.3$ mol hexane, so we expect 0.3 mol adipic acid, which equals about $0.3 \times 150 = 45$ g, about the same magnitude as the 43.5 g obtained in the more detailed calculation given previously. In addition, our answer has the appropriate units and significant figures. In (b) the answer is less than 100%, as it must be from the definition of percent yield.

PRACTICE EXERCISE

Imagine you are working on ways to improve the process by which iron ore containing Fe_2O_3 is converted into iron:

$$Fe_2O_3(s) + 3\ CO(g) \longrightarrow 2\ Fe(s) + 3\ CO_2(g)$$

(a) If you start with 150 g of Fe_2O_3 as the limiting reactant, what is the theoretical yield of Fe? **(b)** If your actual yield is 87.9 g, what is the percent yield?

Answers: **(a)** 105 g Fe, **(b)** 83.7%

STRATEGIES IN CHEMISTRY

HOW TO TAKE A TEST

At about this time in your study of chemistry, you are likely to face your first hour-long examination. The best way to prepare is to study, do homework diligently, and get help from the instructor on any material that is unclear or confusing. (See the advice for learning and studying chemistry presented in the preface of the book.) We present here some general guidelines for taking tests.

Depending on the nature of your course, the exam could consist of a variety of different types of questions.

1. **Multiple-choice questions** In large-enrollment courses, the most common kind of test question is the multiple-choice question. You are given the problem and presented with four or five answers from which you must select the correct one. The first thing to realize is that the instructor has written the question so that at first glance all the answers appear to be correct. (There would be little point in offering choices you could tell were wrong even without knowing much about the concept being tested.) Thus, you should not jump to the conclusion that because one of the choices looks correct, it must be correct.

   If a multiple-choice question involves a calculation, do the calculation, check your work, and *only then* compare your answer with the choices. If you find a match, you have probably found the correct answer. Keep in mind, though, that your instructor has anticipated the most common errors you might make in solving a given problem and has probably listed the incorrect answers resulting from those errors. Always double-check your reasoning and use dimensional analysis to arrive at the correct numeric answer and the correct units.

   In multiple-choice questions that do not involve calculations, if you are not sure of the correct choice, eliminate all the choices you know for sure to be incorrect. The reasoning you use in eliminating incorrect choices will help you in reasoning about which of the remaining choices is correct.

2. **Calculations in which you must show your work** In questions of this kind, you may receive partial credit even if you do not arrive at the correct answer, depending on whether the instructor can follow your line of reasoning. It is important, therefore, to be neat and organized in your calculations. Pay particular attention to what information is given and to what your unknown is. Think about how you can get from the given information to your unknown.

   You may want to write a few words or a diagram on the test paper to indicate your approach. Then write out your calculations as neatly as you can. Show the units for every number you write down, and use dimensional analysis as much as you can, showing how units cancel.

3. **Questions requiring drawings** Questions of this kind will come later in the course, but it is useful to talk about them here. (You should review this box before each exam to remind yourself of good exam-taking practices.) Be sure to label your drawing as completely as possible.

4. **Other types of questions** Other exam questions you might encounter include true-false questions and ones in which you are given a list and asked to indicate which members of the list match some criterion given in the question. Often students answer such questions incorrectly because, in their haste, they misunderstand the nature of the question. Whatever the form of the question, ask yourself this: What is the instructor testing here? What material am I supposed to know that this question covers?

Finally, if you find that you simply do not understand how to arrive at a reasoned response to a question, do not linger over the question. Put a check next to it and go on to the next one. If time permits, you can come back to the unanswered questions, but lingering over a question when nothing is coming to mind is wasting time you may need to finish the exam.

CHAPTER SUMMARY AND KEY TERMS

INTRODUCTION AND SECTION 3.1 The study of the quantitative relationships between chemical formulas and chemical equations is known as **stoichiometry**. One of the important concepts of stoichiometry is the law of conservation of mass, which states that the total mass of the products of a chemical reaction is the same as the total mass of the reactants. The same numbers of atoms of each type are present before and after a chemical reaction. A balanced **chemical equation** shows equal numbers of atoms of each element on each side of the equation. Equations are balanced by placing coefficients in front of the chemical formulas for the **reactants** and **products** of a reaction, *not* by changing the subscripts in chemical formulas.

SECTION 3.2 Among the reaction types described in this chapter are (1) **combination reactions**, in which two reactants combine to form one product; (2) **decomposition reactions**, in which a single reactant forms two or more products; and (3) **combustion reactions** in oxygen, in which a hydrocarbon or related compound reacts with O_2 to form CO_2 and H_2O.

SECTION 3.3 Much quantitative information can be determined from chemical formulas and balanced chemical equations by using atomic weights. The **formula weight** of a compound equals the sum of the atomic weights of the atoms in its formula. If the formula is a molecular formula, the formula weight is also called the **molecular weight**. Atomic weights and formula weights can be used to determine the elemental composition of a compound.

SECTION 3.4 A mole of any substance is **Avogadro's number** (6.02×10^{23}) of formula units of that substance. The mass of a **mole** of atoms, molecules, or ions (the **molar mass**) equals the formula weight of that material expressed in grams. The mass of one molecule of H_2O, for example, is 18 amu, so the mass of 1 mol of H_2O is 18 g. That is, the molar mass of H_2O is 18 g/mol.

SECTION 3.5 The empirical formula of any substance can be determined from its percent composition by calculating the relative number of moles of each atom in 100 g of the substance. If the substance is molecular in nature, its molecular formula can be determined from the empirical formula if the molecular weight is also known.

SECTIONS 3.6 AND 3.7 The mole concept can be used to calculate the relative quantities of reactants and products in chemical reactions. The coefficients in a balanced equation give the relative numbers of moles of the reactants and products. To calculate the number of grams of a product from the number of grams of a reactant, first convert grams of reactant to moles of reactant. Then use the coefficients in the balanced equation to convert the number of moles of reactant to moles of product. Finally, convert moles of product to grams of product.

A **limiting reactant** is completely consumed in a reaction. When it is used up, the reaction stops, thus limiting the quantities of products formed. The **theoretical yield** of a reaction is the quantity of product calculated to form when all of the limiting reactant reacts. The actual yield of a reaction is always less than the theoretical yield. The **percent yield** compares the actual and theoretical yields.

KEY SKILLS

- Balance chemical equations. (Section 3.1)
- Predict the products of simple combination, decomposition, and combustion reactions. (Section 3.2)
- Calculate formula weights. (Section 3.3)
- Convert grams to moles and moles to grams using molar masses. (Section 3.4)
- Convert number of molecules to moles and moles to number of molecules using Avogadro's number. (Section 3.4)
- Calculate the empirical and molecular formulas of a compound from percentage composition and molecular weight. (Section 3.5)
- Calculate amounts, in grams or moles, of reactants and products for a reaction. (Section 3.6)
- Calculate the percent yield of a reaction. (Section 3.7)

KEY EQUATIONS

- $$\%\ \text{element} = \frac{\begin{pmatrix}\text{number of atoms}\\ \text{of that element}\end{pmatrix}\begin{pmatrix}\text{atomic weight}\\ \text{of element}\end{pmatrix}}{(\text{formula weight of compound})} \times 100\% \qquad [3.10]$$

  This is the formula to calculate the mass percentage of each element in a compound. The sum of all the percentages of all the elements in a compound should add up to 100%.

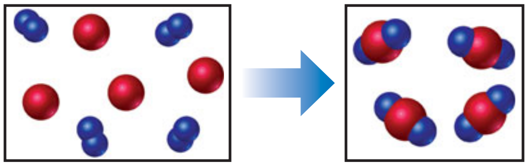
- $$\%\ \text{yield} = \frac{(\text{actual yield})}{(\text{theoretical yield})} \times 100\% \qquad [3.14]$$

  This is the formula to calculate the percent yield of a reaction. The percent yield can never be more than 100%.

EXERCISES

VISUALIZING CONCEPTS

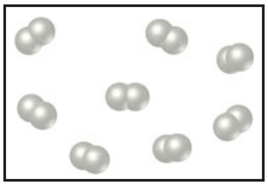
3.1 The reaction between reactant A (blue spheres) and reactant B (red spheres) is shown in the following diagram:



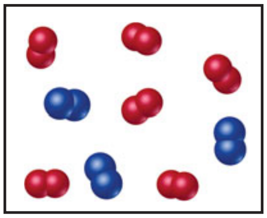
Based on this diagram, which equation best describes the reaction? [Section 3.1]

(a) $A_2 + B \longrightarrow A_2B$
(b) $A_2 + 4\,B \longrightarrow 2\,AB_2$
(c) $2\,A + B_4 \longrightarrow 2\,AB_2$
(d) $A + B_2 \longrightarrow AB_2$

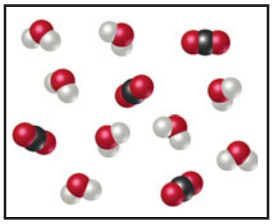
3.2 Under appropriate experimental conditions, H_2 and CO undergo a combination reaction to form CH_3OH. The following drawing represents a sample of H_2. Make a corresponding drawing of the CO needed to react completely with the H_2. How did you arrive at the number of CO molecules in your drawing? [Section 3.2]



3.3 The following diagram represents the collection of elements formed by a decomposition reaction. **(a)** If the blue spheres represent N atoms and the red ones represent O atoms, what was the empirical formula of the original compound? **(b)** Could you draw a diagram representing the molecules of the compound that had been decomposed? Why or why not? [Section 3.2]

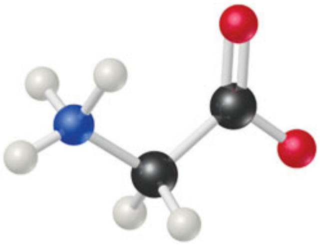


3.4 The following diagram represents the collection of CO_2 and H_2O molecules formed by complete combustion of a hydrocarbon. What is the empirical formula of the hydrocarbon? [Section 3.2]

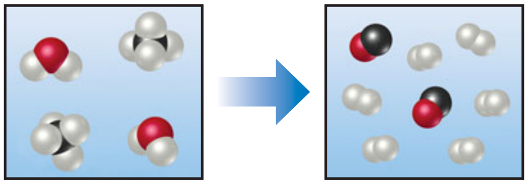


3.5 Glycine, an amino acid used by organisms to make proteins, is represented by the following molecular model.

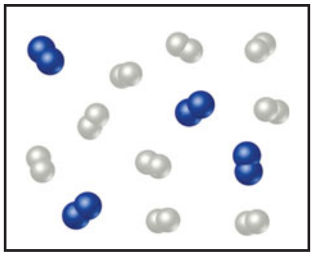
(a) Write its molecular formula.
(b) Determine its molar mass.
(c) Calculate the mass of 3 moles of glycine.
(d) Calculate the percent nitrogen by mass in glycine. [Sections 3.3 and 3.5]



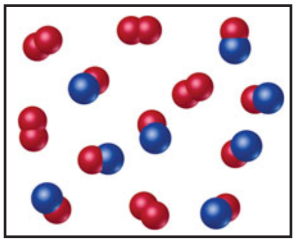
3.6 The following diagram represents a high-temperature reaction between CH_4 and H_2O. Based on this reaction, how many moles of each product can be obtained starting with 4.0 mol CH_4? [Section 3.6]



3.7 Nitrogen (N_2) and hydrogen (H_2) react to form ammonia (NH_3). Consider the mixture of N_2 and H_2 shown in the accompanying diagram. The blue spheres represent N, and the white ones represent H. Draw a representation of the product mixture, assuming that the reaction goes to completion. How did you arrive at your representation? What is the limiting reactant in this case? [Section 3.7]



3.8 Nitrogen monoxide and oxygen react to form nitrogen dioxide. Consider the mixture of NO and O_2 shown in the accompanying diagram. The blue spheres represent N, and the red ones represent O. **(a)** Draw a representation of the product mixture, assuming that the reaction goes to completion. What is the limiting reactant in this case? **(b)** How many NO_2 molecules would you draw as products if the reaction had a percent yield of 75%? [Section 3.7]



BALANCING CHEMICAL EQUATIONS (section 3.1)

3.9 **(a)** What scientific principle or law is used in the process of balancing chemical equations? **(b)** In balancing equations, why should you not change subscripts in chemical formulas? **(c)** How would you write out liquid water, water vapor, aqueous sodium chloride, and solid sodium chloride in chemical equations?

3.10 **(a)** What is the difference between adding a subscript 2 to the end of the formula for CO to give CO_2 and adding a coefficient in front of the formula to give 2 CO? **(b)** Is the following chemical equation, as written, consistent with the law of conservation of mass?

$$3\,Mg(OH)_2(s) + 2\,H_3PO_4(aq) \longrightarrow Mg_3(PO_4)_2(s) + 6\,H_2O(l)$$

Why or why not?

3.11 Balance the following equations:

(a) $CO(g) + O_2(g) \longrightarrow CO_2(g)$
(b) $N_2O_5(g) + H_2O(l) \longrightarrow HNO_3(aq)$
(c) $CH_4(g) + Cl_2(g) \longrightarrow CCl_4(l) + HCl(g)$
(d) $Al_4C_3(s) + H_2O(l) \longrightarrow Al(OH)_3(s) + CH_4(g)$
(e) $C_5H_{10}O_2(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$
(f) $Fe(OH)_3(s) + H_2SO_4(aq) \longrightarrow Fe_2(SO_4)_3(aq) + H_2O(l)$
(g) $Mg_3N_2(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + (NH_4)_2SO_4(aq)$

3.12 Balance the following equations:

(a) $Li(s) + N_2(g) \longrightarrow Li_3N(s)$
(b) $TiCl_4(l) + H_2O(l) \longrightarrow TiO_2(s) + HCl(aq)$
(c) $NH_4NO_3(s) \longrightarrow N_2(g) + O_2(g) + H_2O(g)$
(d) $Ca_3P_2(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq) + PH_3(g)$
(e) $Al(OH)_3(s) + H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + H_2O(l)$
(f) $AgNO_3(aq) + Na_2CO_3(aq) \longrightarrow Ag_2NO_3(s) + Na_2CO_3(aq)$
(g) $C_2H_5NH_2(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g) + N_2(g)$

3.13 Write balanced chemical equations to correspond to each of the following descriptions: **(a)** Solid calcium carbide, CaC_2, reacts with water to form an aqueous solution of calcium hydroxide and acetylene gas, C_2H_2. **(b)** When solid potassium chlorate is heated, it decomposes to form solid potassium chloride and oxygen gas. **(c)** Solid zinc metal reacts with sulfuric acid to form hydrogen gas and an aqueous solution of zinc sulfate. **(d)** When liquid phosphorus trichloride is added to water, it reacts to form aqueous phosphorous acid, $H_3PO_3(aq)$, and aqueous hydrochloric acid. **(e)** When hydrogen sulfide gas is passed over solid hot iron(III) hydroxide, the resultant reaction produces solid iron(III) sulfide and gaseous water.

3.14 Write balanced chemical equations to correspond to each of the following descriptions: **(a)** When sulfur trioxide gas reacts with water, a solution of sulfuric acid forms. **(b)** Boron sulfide, $B_2S_3(s)$, reacts violently with water to form dissolved boric acid, H_3BO_3, and hydrogen sulfide gas. **(c)** Phosphine, $PH_3(g)$, combusts in oxygen gas to form water vapor and solid tetraphosphorus decaoxide. **(d)** When solid mercury(II) nitrate is heated, it decomposes to form solid mercury(II) oxide, gaseous nitrogen dioxide, and oxygen. **(e)** Copper metal reacts with hot concentrated sulfuric acid solution to form aqueous copper(II) sulfate, sulfur dioxide gas, and water.

PATTERNS OF CHEMICAL REACTIVITY (section 3.2)

3.15 **(a)** When the metallic element sodium combines with the nonmetallic element bromine, $Br_2(l)$, how can you determine the chemical formula of the product? How do you know whether the product is a solid, liquid, or gas at room temperature? Write the balanced chemical equation for the reaction. **(b)** When a hydrocarbon burns in air, what reactant besides the hydrocarbon is involved in the reaction? What products are formed? Write a balanced chemical equation for the combustion of benzene, $C_6H_6(l)$, in air.

3.16 **(a)** Determine the chemical formula of the product formed when the metallic element aluminum combines with the nonmetallic element bromine, Br_2. Write the balanced chemical equation for the reaction. **(b)** What products form when a compound containing C, H, and O is completely combusted in air? Write a balanced chemical equation for the combustion of acetone, $C_3H_6O(l)$, in air.

3.17 Write a balanced chemical equation for the reaction that occurs when **(a)** $Mg(s)$ reacts with $Cl_2(g)$; **(b)** barium carbonate decomposes into barium oxide and carbon dioxide gas when heated; **(c)** the hydrocarbon styrene, $C_8H_8(l)$, is combusted in air; **(d)** dimethylether, $CH_3OCH_3(g)$, is combusted in air.

3.18 Write a balanced chemical equation for the reaction that occurs when **(a)** calcium metal undergoes a combination reaction with $O_2(g)$; **(b)** copper(II) hydroxide decomposes into copper(II) oxide and water when heated; **(c)** heptane, $C_7H_{16}(l)$, burns in air; **(d)** methyl tert-butyl ether, $C_5H_{12}O(l)$, burns in air.

3.19 Balance the following equations and indicate whether they are combination, decomposition, or combustion reactions:

(a) $C_3H_6(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$
(b) $NH_4NO_3(s) \longrightarrow N_2O(g) + H_2O(g)$
(c) $C_5H_6O(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$
(d) $N_2(g) + H_2(g) \longrightarrow NH_3(g)$
(e) $K_2O(s) + H_2O(l) \longrightarrow KOH(aq)$

3.20 Balance the following equations and indicate whether they are combination, decomposition, or combustion reactions:

(a) $PbCO_3(s) \longrightarrow PbO(s) + CO_2(g)$
(b) $C_2H_4(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$
(c) $Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$
(d) $C_7H_8O_2(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$
(e) $Al(s) + Cl_2(g) \longrightarrow AlCl_3(s)$

FORMULA WEIGHTS (section 3.3)

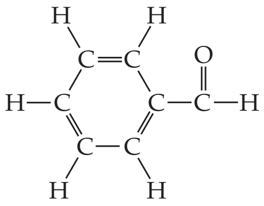
3.21 Determine the formula weights of each of the following compounds: **(a)** nitric acid, HNO_3; **(b)** $KMnO_4$; **(c)** $Ca_3(PO_4)_2$; **(d)** quartz, SiO_2; **(e)** gallium sulfide, **(f)** chromium(III) sulfate, **(g)** phosphorus trichloride.

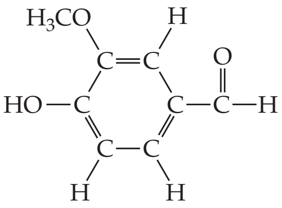
3.22 Determine the formula weights of each of the following compounds: **(a)** nitrous oxide, N_2O, known as laughing gas and used as an anesthetic in dentistry; **(b)** benzoic acid, $HC_7H_5O_2$, a substance used as a food preservative; **(c)** $Mg(OH)_2$, the active ingredient in milk of magnesia; **(d)** urea, $(NH_2)_2CO$, a compound used as a nitrogen fertilizer; **(e)** isopentyl acetate, $CH_3CO_2C_5H_{11}$, responsible for the odor of bananas.

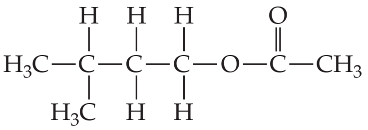
3.23 Calculate the percentage by mass of oxygen in the following compounds: **(a)** morphine, $C_{17}H_{19}NO_3$; **(b)** codeine, $C_{18}H_{21}NO_3$ **(c)** cocaine, $C_{17}H_{21}NO_4$; **(d)** tetracycline, $C_{22}H_{24}N_2O_8$; **(e)** digitoxin, $C_{41}H_{64}O_{13}$; **(f)** vancomycin, $C_{66}H_{75}Cl_2N_9O_{24}$.

3.24 Calculate the percentage by mass of the indicated element in the following compounds: **(a)** carbon in acetylene, C_2H_2, a gas used in welding; **(b)** hydrogen in ascorbic acid, $HC_6H_7O_6$, also known as vitamin C; **(c)** hydrogen in ammonium sulfate, $(NH_4)_2SO_4$, a substance used as a nitrogen fertilizer; **(d)** platinum in $PtCl_2(NH_3)_2$, a chemotherapy agent called cisplatin; **(e)** oxygen in the female sex hormone estradiol, $C_{18}H_{24}O_2$; **(f)** carbon in capsaicin, $C_{18}H_{27}NO_3$, the compound that gives the hot taste to chili peppers.

3.25 Based on the following structural formulas, calculate the percentage of carbon by mass present in each compound:

(a) 
Benzaldehyde
(almond fragrance)

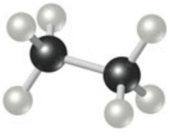
(b) 
Vanillin
(vanilla flavor)

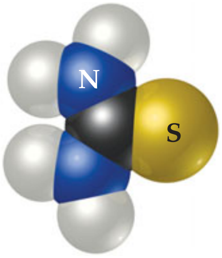
(c) 
Isopentyl acetate
(banana flavor)

3.26 Calculate the percentage of carbon by mass in each of the compounds represented by the following models:


(a)


(b)


(c)



(d)

AVOGADRO'S NUMBER AND THE MOLE (section 3.4)

3.27 **(a)** What is Avogadro's number, and how is it related to the mole? **(b)** What is the relationship between the formula weight of a substance and its molar mass?

3.28 **(a)** What is the mass, in grams, of a mole of ^{12}C? **(b)** How many carbon atoms are present in a mole of ^{12}C?

3.29 Without doing any detailed calculations (but using a periodic table to give atomic weights), rank the following samples in order of increasing number of atoms: 0.50 mol H_2O, 23 g Na, 6.0×10^{23} N_2 molecules.

3.30 Without doing any detailed calculations (but using a periodic table to give atomic weights), rank the following samples in order of increasing number of atoms: 9.0×10^{23} molecules of H_2O_2, 2.0 mol CH_4, 16 g O_2.

3.31 What is the mass, in kilograms, of an Avogadro's number of people, if the average mass of a person is 160 lb? How does this compare with the mass of Earth, 5.98×10^{24} kg?

3.32 If Avogadro's number of pennies is divided equally among the 300 million men, women, and children in the United States, how many dollars would each receive? How does this compare with the gross domestic product (GDP) of the United States, which was $14.4 trillion in 2008? (The GDP is the total market value of the nation's goods and services.)

3.33 Calculate the following quantities:
- **(a)** mass, in grams, of 0.105 mole of sucrose ($C_{12}H_{22}O_{11}$)
- **(b)** moles of $Zn(NO_3)_2$ in 143.50 g of this substance
- **(c)** number of molecules in 1.0×10^{-6} mol CH_3CH_2OH
- **(d)** number of N atoms in 0.410 mol NH_3

3.34 Calculate the following quantities:
- **(a)** mass, in grams, of 1.50×10^{-2} mol of CdS
- **(b)** number of moles of NH_4Cl in 86.6 g of this substance
- **(c)** number of molecules in 8.447×10^{-2} mol C_6H_6
- **(d)** number of O atoms in 6.25×10^{-3} mol $Al(NO_3)_3$

3.35 **(a)** What is the mass, in grams, of 2.50×10^{-3} mol of ammonium phosphate?
(b) How many moles of chloride ions are in 0.2550 g of aluminum chloride?

(c) What is the mass, in grams, of 7.70×10^{20} molecules of caffeine, $C_8H_{10}N_4O_2$?

(d) What is the molar mass of cholesterol if 0.00105 mol has a mass of 0.406 g?

3.36 **(a)** What is the mass, in grams, of 1.223 mol of iron(III) sulfate?

(b) How many moles of ammonium ions are in 6.955 g of ammonium carbonate?

(c) What is the mass, in grams, of 1.50×10^{21} molecules of aspirin, $C_9H_8O_4$?

(d) What is the molar mass of diazepam (Valium®) if 0.05570 mol has a mass of 15.86 g?

3.37 The molecular formula of allicin, the compound responsible for the characteristic smell of garlic, is $C_6H_{10}OS_2$. **(a)** What is the molar mass of allicin? **(b)** How many moles of allicin are present in 5.00 mg of this substance? **(c)** How many molecules of allicin are in 5.00 mg of this substance? **(d)** How many S atoms are present in 5.00 mg of allicin?

3.38 The molecular formula of aspartame, the artificial sweetener marketed as NutraSweet®, is $C_{14}H_{18}N_2O_5$. **(a)** What is the molar mass of aspartame? **(b)** How many moles of aspartame are present in 1.00 mg of aspartame? **(c)** How many molecules of aspartame are present in 1.00 mg of aspartame? **(d)** How many hydrogen atoms are present in 1.00 mg of aspartame?

3.39 A sample of glucose, $C_6H_{12}O_6$, contains 1.250×10^{21} carbon atoms. **(a)** How many atoms of hydrogen does it contain? **(b)** How many molecules of glucose does it contain? **(c)** How many moles of glucose does it contain? **(d)** What is the mass of this sample in grams?

3.40 A sample of the male sex hormone testosterone, $C_{19}H_{28}O_2$, contains 3.88×10^{21} hydrogen atoms. **(a)** How many atoms of carbon does it contain? **(b)** How many molecules of testosterone does it contain? **(c)** How many moles of testosterone does it contain? **(d)** What is the mass of this sample in grams?

3.41 The allowable concentration level of vinyl chloride, C_2H_3Cl, in the atmosphere in a chemical plant is 2.0×10^{-6} g/L. How many moles of vinyl chloride in each liter does this represent? How many molecules per liter?

3.42 At least 25 μg of tetrahydrocannabinol (THC), the active ingredient in marijuana, is required to produce intoxication. The molecular formula of THC is $C_{21}H_{30}O_2$. How many moles of THC does this 25 μg represent? How many molecules?

EMPIRICAL FORMULAS (section 3.5)

3.43 Give the empirical formula of each of the following compounds if a sample contains **(a)** 0.0130 mol C, 0.0390 mol H, and 0.0065 mol O; **(b)** 11.66 g iron and 5.01 g oxygen; **(c)** 40.0% C, 6.7% H, and 53.3% O by mass.

3.44 Determine the empirical formula of each of the following compounds if a sample contains **(a)** 0.104 mol K, 0.052 mol C, and 0.156 mol O; **(b)** 5.28 g Sn and 3.37 g F; **(c)** 87.5% N and 12.5% H by mass.

3.45 Determine the empirical formulas of the compounds with the following compositions by mass:

(a) 10.4% C, 27.8% S, and 61.7% Cl

(b) 21.7% C, 9.6% O, and 68.7% F

(c) 32.79% Na, 13.02% Al, and the remainder F

3.46 Determine the empirical formulas of the compounds with the following compositions by mass:

(a) 55.3% K, 14.6% P, and 30.1% O

(b) 24.5% Na, 14.9% Si, and 60.6% F

(c) 62.1% C, 5.21% H, 12.1% N, and the remainder O

3.47 A compound whose empirical formula is XF_3 consists of 65% F by mass. What is the atomic mass of X?

3.48 The compound XCl_4 contains 75.0% Cl by mass. What is the element X?

3.49 What is the molecular formula of each of the following compounds?

(a) empirical formula CH_2, molar mass = 84 g/mol

(b) empirical formula NH_2Cl, molar mass = 51.5 g/mol

3.50 What is the molecular formula of each of the following compounds?

(a) empirical formula HCO_2, molar mass = 90.0 g/mol

(b) empirical formula C_2H_4O, molar mass = 88 g/mol

3.51 Determine the empirical and molecular formulas of each of the following substances:

(a) Styrene, a compound substance used to make Styrofoam® cups and insulation, contains 92.3% C and 7.7% H by mass and has a molar mass of 104 g/mol.

(b) Caffeine, a stimulant found in coffee, contains 49.5% C, 5.15% H, 28.9% N, and 16.5% O by mass and has a molar mass of 195 g/mol.

(c) Monosodium glutamate (MSG), a flavor enhancer in certain foods, contains 35.51% C, 4.77% H, 37.85% O, 8.29% N, and 13.60% Na, and has a molar mass of 169 g/mol.

3.52 Determine the empirical and molecular formulas of each of the following substances:

(a) Ibuprofen, a headache remedy, contains 75.69% C, 8.80% H, and 15.51% O by mass, and has a molar mass of 206 g/mol.

(b) Cadaverine, a foul-smelling substance produced by the action of bacteria on meat, contains 58.55% C, 13.81% H, and 27.40% N by mass; its molar mass is 102.2 g/mol.

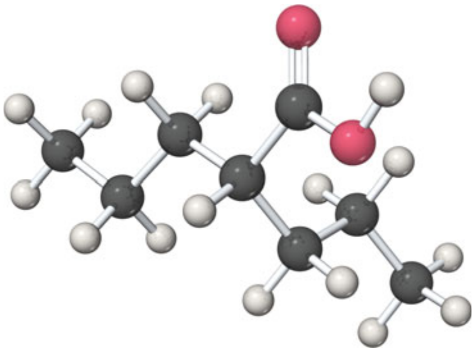
(c) Epinephrine (adrenaline), a hormone secreted into the bloodstream in times of danger or stress, contains 59.0% C, 7.1% H, 26.2% O, and 7.7% N by mass; its MW is about 180 amu.

3.53 **(a)** Combustion analysis of toluene, a common organic solvent, gives 5.86 mg of CO_2 and 1.37 mg of H_2O. If the compound contains only carbon and hydrogen, what is its empirical formula? **(b)** Menthol, the substance we can smell in mentholated cough drops, is composed of C, H, and O. A 0.1005-g sample of menthol is combusted, producing 0.2829 g of CO_2 and 0.1159 g of H_2O. What is the empirical formula for menthol? If menthol has a molar mass of 156 g/mol, what is its molecular formula?

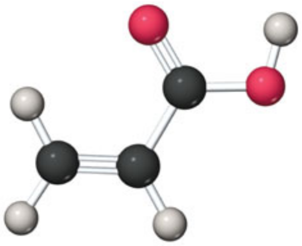
3.54 **(a)** The characteristic odor of pineapple is due to ethyl butyrate, a compound containing carbon, hydrogen, and oxygen. Combustion of 2.78 mg of ethyl butyrate produces 6.32 mg of CO_2 and 2.58 mg of H_2O. What is the empirical formula of the compound? **(b)** Nicotine, a component of tobacco, is composed of C, H, and N. A 5.250-mg sample of nicotine was combusted, producing 14.242 mg of CO_2 and 4.083 mg of

H_2O. What is the empirical formula for nicotine? If nicotine has a molar mass of 160 ± 5 g/mol, what is its molecular formula?

3.55 Valproic acid, used to treat seizures and bipolar disorder, is composed of C, H, and O. A 0.165-g sample is combusted in an apparatus such as that shown in Figure 3.14. The gain in mass of the H_2O absorber is 0.166 g, whereas that of the CO_2 absorber is 0.403 g. What empirical formula for valproic acid do these results indicate? Is this empirical formula consistent with the molecular model shown here?



3.56 Propenoic acid, as shown here,



is a reactive organic liquid used in the manufacture of plastics, coatings, and adhesives. An unlabeled container is thought to contain this acid. A 0.2033-g sample is combusted in an apparatus such as that shown in Figure 3.14. The gain in mass of the H_2O absorber is 0.102 g, whereas that of the CO_2 absorber is 0.374 g. Is this analysis consistent with the contents of the container being propenoic acid?

3.57 Washing soda, a compound used to prepare hard water for washing laundry, is a hydrate, which means that a certain number of water molecules are included in the solid structure. Its formula can be written as $Na_2CO_3 \cdot xH_2O$, where x is the number of moles of H_2O per mole of Na_2CO_3. When a 2.558-g sample of washing soda is heated at 25 °C, all the water of hydration is lost, leaving 0.948 g of Na_2CO_3. What is the value of x?

3.58 Epsom salts, a strong laxative used in veterinary medicine, is a hydrate, which means that a certain number of water molecules are included in the solid structure. The formula for Epsom salts can be written as $MgSO_4 \cdot xH_2O$, where x indicates the number of moles of H_2O per mole of $MgSO_4$. When 5.061 g of this hydrate is heated to 250 °C, all the water of hydration is lost, leaving 2.472 g of $MgSO_4$. What is the value of x?

CALCULATIONS BASED ON CHEMICAL EQUATIONS (section 3.6)

3.59 Why is it essential to use balanced chemical equations when determining the quantity of a product formed from a given quantity of a reactant?

3.60 What parts of balanced chemical equations give information about the relative numbers of moles of reactants and products involved in a reaction?

3.61 Hydrofluoric acid, HF(aq), cannot be stored in glass bottles because compounds called silicates in the glass are attacked by the HF(aq). Sodium silicate (Na_2SiO_3), for example, reacts as follows:

$$Na_2SiO_3(s) + 8\,HF(aq) \longrightarrow H_2SiF_6(aq) + 2\,NaF(aq) + 3\,H_2O(l)$$

(a) How many moles of HF are needed to react with 0.300 mol of Na_2SiO_3?
(b) How many grams of NaF form when 0.500 mol of HF reacts with excess Na_2SiO_3?
(c) How many grams of Na_2SiO_3 can react with 0.800 g of HF?

3.62 The reaction between potassium superoxide, KO_2, and CO_2,

$$4\,KO_2 + 2\,CO_2 \longrightarrow 2K_2CO_3 + 3\,O_2$$

is used as a source of O_2 and absorber of CO_2 in self-contained breathing equipment used by rescue workers.

(a) How many moles of O_2 are produced when 0.400 mol of KO_2 reacts in this fashion?
(b) How many grams of KO_2 are needed to form 7.50 g of O_2?
(c) How many grams of CO_2 are used when 7.50 g of O_2 are produced?

3.63 Several brands of antacids use $Al(OH)_3$ to react with stomach acid, which contains primarily HCl:

$$Al(OH)_3(s) + HCl(aq) \longrightarrow AlCl_3(aq) + H_2O(l)$$

(a) Balance this equation.
(b) Calculate the number of grams of HCl that can react with 0.500 g of $Al(OH)_3$.
(c) Calculate the number of grams of $AlCl_3$ and the number of grams of H_2O formed when 0.500 g of $Al(OH)_3$ reacts.
(d) Show that your calculations in parts (b) and (c) are consistent with the law of conservation of mass.

3.64 An iron ore sample contains Fe_2O_3 together with other substances. Reaction of the ore with CO produces iron metal:

$$Fe_2O_3(s) + CO(g) \longrightarrow Fe(s) + CO_2(g)$$

(a) Balance this equation.
(b) Calculate the number of grams of CO that can react with 0.350 kg of Fe_2O_3.
(c) Calculate the number of grams of Fe and the number of grams of CO_2 formed when 0.350 kg of Fe_2O_3 reacts.
(d) Show that your calculations in parts (b) and (c) are consistent with the law of conservation of mass.

3.65 Aluminum sulfide reacts with water to form aluminum hydroxide and hydrogen sulfide. **(a)** Write the balanced chemical equation for this reaction. **(b)** How many grams of aluminum hydroxide are obtained from 14.2 g of aluminum sulfide?

3.66 Calcium hydride reacts with water to form calcium hydroxide and hydrogen gas. **(a)** Write a balanced chemical equation for the reaction. **(b)** How many grams of calcium hydride are needed to form 4.500 g of hydrogen?

3.67 Automotive air bags inflate when sodium azide, NaN_3, rapidly decomposes to its component elements:

$$2\ NaN_3(s) \longrightarrow 2\ Na(s) + 3\ N_2(g)$$

(a) How many moles of N_2 are produced by the decomposition of 1.50 mol of NaN_3?
(b) How many grams of NaN_3 are required to form 10.0 g of nitrogen gas?
(c) How many grams of NaN_3 are required to produce 10.0 ft^3 of nitrogen gas, about the size of an automotive air bag, if the gas has a density of 1.25 g/L?

3.68 The complete combustion of octane, C_8H_{18}, the main component of gasoline, proceeds as follows:

$$2\ C_8H_{18}(l) + 25\ O_2(g) \longrightarrow 16\ CO_2(g) + 18\ H_2O(g)$$

(a) How many moles of O_2 are needed to burn 1.50 mol of C_8H_{18}?
(b) How many grams of O_2 are needed to burn 10.0 g of C_8H_{18}?
(c) Octane has a density of 0.692 g/mL at 20 °C. How many grams of O_2 are required to burn 15.0 gal of C_8H_{18} (the capacity of an average fuel tank)?
(d) How many grams of CO_2 are produced when 15.0 gal of C_8H_{18} are combusted?

3.69 A piece of aluminum foil 1.00 cm square and 0.550 mm thick is allowed to react with bromine to form aluminum bromide.

(a) How many moles of aluminum were used? (The density of aluminum is 2.699 g/cm^3.) **(b)** How many grams of aluminum bromide form, assuming the aluminum reacts completely?

3.70 Detonation of nitroglycerin proceeds as follows:

$$4\ C_3H_5N_3O_9(l) \longrightarrow 12\ CO_2(g) + 6\ N_2(g) + O_2(g) + 10\ H_2O(g)$$

(a) If a sample containing 2.00 mL of nitroglycerin (density = 1.592 g/mL) is detonated, how many total moles of gas are produced? **(b)** If each mole of gas occupies 55 L under the conditions of the explosion, how many liters of gas are produced? **(c)** How many grams of N_2 are produced in the detonation?

LIMITING REACTANTS (section 3.7)

3.71 **(a)** Define the terms *limiting reactant* and *excess reactant*. **(b)** Why are the amounts of products formed in a reaction determined only by the amount of the limiting reactant? **(c)** Why should you base your choice of which compound is the limiting reactant on its number of initial moles, not on its initial mass in grams?

3.72 **(a)** Define the terms *theoretical yield, actual yield,* and *percent yield*. **(b)** Why is the actual yield in a reaction almost always less than the theoretical yield? **(c)** Can a reaction ever have 110% actual yield?

3.73 A manufacturer of bicycles has 4815 wheels, 2305 frames, and 2255 handlebars. **(a)** How many bicycles can be manufactured using these parts? **(b)** How many parts of each kind are left over? **(c)** Which part limits the production of bicycles?

3.74 A bottling plant has 126,515 bottles with a capacity of 355 mL, 108,500 caps, and 48,775 L of beverage. **(a)** How many bottles can be filled and capped? **(b)** How much of each item is left over? **(c)** Which component limits the production?

3.75 Sodium hydroxide reacts with carbon dioxide as follows:

$$2\ NaOH(s) + CO_2(g) \longrightarrow Na_2CO_3(s) + H_2O(l)$$

Which is the limiting reactant when 1.85 mol NaOH and 1.00 mol CO_2 are allowed to react? How many moles of Na_2CO_3 can be produced? How many moles of the excess reactant remain after the completion of the reaction?

3.76 Aluminum hydroxide reacts with sulfuric acid as follows:

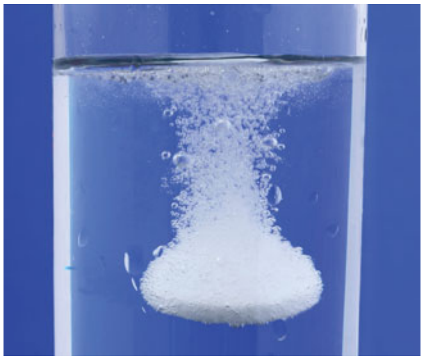
$$2\ Al(OH)_3(s) + 3\ H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 6\ H_2O(l)$$

Which is the limiting reactant when 0.500 mol $Al(OH)_3$ and 0.500 mol H_2SO_4 are allowed to react? How many moles of $Al_2(SO_4)_3$ can form under these conditions? How many moles of the excess reactant remain after the completion of the reaction?

3.77 The fizz produced when an Alka-Seltzer® tablet is dissolved in water is due to the reaction between sodium bicarbonate ($NaHCO_3$) and citric acid ($H_3C_6H_5O_7$):

$$3\,NaHCO_3(aq) + H_3C_6H_5O_7(aq) \longrightarrow 3\,CO_2(g) + 3\,H_2O(l) + Na_3C_6H_5O_7(aq)$$

In a certain experiment 1.00 g of sodium bicarbonate and 1.00 g of citric acid are allowed to react. **(a)** Which is the limiting reactant? **(b)** How many grams of carbon dioxide form? **(c)** How many grams of the excess reactant remain after the limiting reactant is completely consumed?



3.78 One of the steps in the commercial process for converting ammonia to nitric acid is the conversion of NH_3 to NO:

$$4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$$

In a certain experiment, 2.00 g of NH_3 reacts with 2.50 g of O_2 **(a)** Which is the limiting reactant? **(b)** How many grams of NO and of H_2O form? **(c)** How many grams of the excess reactant remain after the limiting reactant is completely consumed? **(d)** Show that your calculations in parts (b) and (c) are consistent with the law of conservation of mass.

3.79 Solutions of sodium carbonate and silver nitrate react to form solid silver carbonate and a solution of sodium nitrate. A solution containing 3.50 g of sodium carbonate is mixed with one containing 5.00 g of silver nitrate. How many grams of sodium carbonate, silver nitrate, silver carbonate, and sodium nitrate are present after the reaction is complete?

3.80 Solutions of sulfuric acid and lead(II) acetate react to form solid lead(II) sulfate and a solution of acetic acid. If 5.00 g of sulfuric acid and 5.00 g of lead(II) acetate are mixed, calculate the number of grams of sulfuric acid, lead(II) acetate, lead(II) sulfate, and acetic acid present in the mixture after the reaction is complete.

3.81 When benzene (C_6H_6) reacts with bromine (Br_2), bromobenzene (C_6H_5Br) is obtained:

$$C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr$$

(a) When 30.0 g of benzene reacts with 65.0 g of bromine, what is the theoretical yield of bromobenzene? **(b)** If the actual yield of bromobenzene is 42.3 g, what is the percentage yield?

3.82 When ethane (C_2H_6) reacts with chlorine (Cl_2), the main product is C_2H_5Cl, but other products containing Cl, such as $C_2H_4Cl_2$, are also obtained in small quantities. The formation of these other products reduces the yield of C_2H_5Cl. **(a)** Calculate the theoretical yield of C_2H_5Cl when 125 g of C_2H_6 reacts with 255 g of Cl_2, assuming that C_2H_6 and Cl_2 react only to form C_2H_2Cl and HCl. **(b)** Calculate the percent yield of C_2H_5Cl if the reaction produces 206 g of C_2H_5Cl.

3.83 Hydrogen sulfide is an impurity in natural gas that must be removed. One common removal method is called the Claus process, which relies on the reaction:

$$8\,H_2S(g) + 4\,O_2(g) \longrightarrow S_8(l) + 8\,H_2O(g)$$

Under optimal conditions the Claus process gives 98% yield of S_8 from H_2S. If you started with 30.0 grams of H_2S and 50.0 grams of O_2, how many grams of S_8 would be produced, assuming 98% yield?

3.84 When hydrogen sulfide gas is bubbled into a solution of sodium hydroxide, the reaction forms sodium sulfide and water. How many grams of sodium sulfide are formed if 1.25 g of hydrogen sulfide is bubbled into a solution containing 2.00 g of sodium hydroxide, assuming that the sodium sulfide is made in 92.0% yield?

ADDITIONAL EXERCISES

3.85 Write the balanced chemical equations for **(a)** the complete combustion of acetic acid (CH_3COOH), the main active ingredient in vinegar; **(b)** the decomposition of solid calcium hydroxide into solid calcium(II) oxide (lime) and water vapor; **(c)** the combination reaction between nickel metal and chlorine gas.

3.86 If 1.5 mol C_2H_5OH, 1.5 mol C_3H_8, and 1.5 mol $CH_3CH_2COCH_3$ are completely combusted in oxygen, which produces the largest number of moles of H_2O? Which produces the least? Explain.

3.87 The effectiveness of nitrogen fertilizers depends on both their ability to deliver nitrogen to plants and the amount of nitrogen they can deliver. Four common nitrogen-containing fertilizers are ammonia, ammonium nitrate, ammonium sulfate, and urea [$(NH_2)_2CO$]. Rank these fertilizers in terms of the mass percentage nitrogen they contain.

3.88 **(a)** The molecular formula of acetylsalicylic acid (aspirin), one of the most common pain relievers, is $C_9H_8O_4$. How many moles of $C_9H_8O_4$ are in a 0.500-g tablet of aspirin? **(b)** How many molecules of $C_9H_8O_4$ are in this tablet? **(c)** How many carbon atoms are in the tablet?

3.89 Very small crystals composed of 1000 to 100,000 atoms, called quantum dots, are being investigated for use in electronic devices.

(a) A quantum dot was made of solid silicon in the shape of a sphere, with a diameter of 4 nm. Calculate the mass of the quantum dot, using the density of silicon ($2.3\ g/cm^3$).

(b) How many silicon atoms are in the quantum dot?

(c) The density of germanium is $5.325\ g/cm^3$. If you made a 4-nm quantum dot of germanium, how many Ge atoms would it contain? Assume the dot is spherical.

3.90 **(a)** One molecule of the antibiotic penicillin G has a mass of 5.342×10^{-21} g. What is the molar mass of penicillin G? **(b)** Hemoglobin, the oxygen-carrying protein in red blood cells, has four iron atoms per molecule and contains 0.340% iron by mass. Calculate the molar mass of hemoglobin.

3.91 Serotonin is a compound that conducts nerve impulses in the brain. It contains 68.2 mass percent C, 6.86 mass percent H, 15.9 mass percent N, and 9.08 mass percent O. Its molar mass is 176 g/mol. Determine its molecular formula.

3.92 The koala dines exclusively on eucalyptus leaves. Its digestive system detoxifies the eucalyptus oil, a poison to other animals. The chief constituent in eucalyptus oil is a substance called eucalyptol, which contains 77.87% C, 11.76% H, and the remainder O. (**a**) What is the empirical formula for this substance? (**b**) A mass spectrum of eucalyptol shows a peak at about 154 amu. What is the molecular formula of the substance?

3.93 Vanillin, the dominant flavoring in vanilla, contains C, H, and O. When 1.05 g of this substance is completely combusted, 2.43 g of CO_2 and 0.50 g of H_2O are produced. What is the empirical formula of vanillin?

[**3.94**] An organic compound was found to contain only C, H, and Cl. When a 1.50-g sample of the compound was completely combusted in air, 3.52 g of CO_2 was formed. In a separate experiment the chlorine in a 1.00-g sample of the compound was converted to 1.27 g of AgCl. Determine the empirical formula of the compound.

[**3.95**] A compound, $KBrO_x$, where x is unknown, is analyzed and found to contain 52.92% Br. What is the value of x?

[**3.96**] An element X forms an iodide (XI_3) and a chloride (XCl_3). The iodide is quantitatively converted to the chloride when it is heated in a stream of chlorine:

$$2\,XI_3 + 3\,Cl_2 \longrightarrow 2\,XCl_3 + 3\,I_2$$

If 0.5000 g of XI_3 is treated, 0.2360 g of XCl_3 is obtained. (**a**) Calculate the atomic weight of the element X. (**b**) Identify the element X.

3.97 A method used by the U.S. Environmental Protection Agency (EPA) for determining the concentration of ozone in air is to pass the air sample through a "bubbler" containing sodium iodide, which removes the ozone according to the following equation:

$$O_3(g) + 2\,NaI(aq) + H_2O(l) \longrightarrow O_2(g) + I_2(s) + 2\,NaOH(aq)$$

(**a**) How many moles of sodium iodide are needed to remove 5.95×10^{-6} mol of O_3? (**b**) How many grams of sodium iodide are needed to remove 1.3 mg of O_3?

3.98 A chemical plant uses electrical energy to decompose aqueous solutions of NaCl to give Cl_2, H_2, and NaOH:

$$2\,NaCl(aq) + 2\,H_2O(l) \longrightarrow 2\,NaOH(aq) + H_2(g) + Cl_2(g)$$

If the plant produces 1.5×10^6 kg (1500 metric tons) of Cl_2 daily, estimate the quantities of H_2 and NaOH produced.

3.99 The fat stored in a camel's hump is a source of both energy and water. Calculate the mass of H_2O produced by metabolism of 1.0 kg of fat, assuming the fat consists entirely of tristearin ($C_{57}H_{110}O_6$), a typical animal fat, and assuming that during metabolism, tristearin reacts with O_2 to form only CO_2 and H_2O.

[**3.100**] When hydrocarbons are burned in a limited amount of air, both CO and CO_2 form. When 0.450 g of a particular hydrocarbon was burned in air, 0.467 g of CO, 0.733 g of CO_2, and 0.450 g of H_2O were formed. (**a**) What is the empirical formula of the compound? (**b**) How many grams of O_2 were used in the reaction? (**c**) How many grams would have been required for complete combustion?

3.101 A mixture of $N_2(g)$ and $H_2(g)$ reacts in a closed container to form ammonia, $NH_3(g)$. The reaction ceases before either reactant has been totally consumed. At this stage 3.0 mol N_2, 3.0 mol H_2, and 3.0 mol NH_3 are present. How many moles of N_2 and H_2 were present originally?

[**3.102**] A mixture containing $KClO_3$, K_2CO_3, $KHCO_3$, and KCl was heated, producing CO_2, O_2, and H_2O gases according to the following equations:

$$2\,KClO_3(s) \longrightarrow 2\,KCl(s) + 3\,O_2(g)$$
$$2\,KHCO_3(s) \longrightarrow K_2O(s) + H_2O(g) + 2\,CO_2(g)$$
$$K_2CO_3(s) \longrightarrow K_2O(s) + CO_2(g)$$

The KCl does not react under the conditions of the reaction. If 100.0 g of the mixture produces 1.80 g of H_2O, 13.20 g of CO_2, and 4.00 g of O_2, what was the composition of the original mixture? (Assume complete decomposition of the mixture.)

3.103 When a mixture of 10.0 g of acetylene (C_2H_2); and 10.0 g of oxygen (O_2) is ignited, the resultant combustion reaction produces CO_2 and H_2O. (**a**) Write the balanced chemical equation for this reaction. (**b**) Which is the limiting reactant? (**c**) How many grams of C_2H_2, O_2, CO_2, and H_2O are present after the reaction is complete?

3.104 Aspirin ($C_9H_8O_4$) is produced from salicylic acid ($C_7H_6O_3$) and acetic anhydride ($C_4H_6O_3$):

$$C_7H_6O_3 + C_4H_6O_3 \longrightarrow C_9H_8O_4 + HC_2H_3O_2$$

(**a**) How much salicylic acid is required to produce 1.5×10^2 kg of aspirin, assuming that all of the salicylic acid is converted to aspirin? (**b**) How much salicylic acid would be required if only 80% of the salicylic acid is converted to aspirin? (**c**) What is the theoretical yield of aspirin if 185 kg of salicylic acid is allowed to react with 125 kg of acetic anhydride? (**d**) If the situation described in part (c) produces 182 kg of aspirin, what is the percentage yield?

INTEGRATIVE EXERCISES

These exercises require skills from earlier chapters as well as skills from the present chapter.

3.105 Consider a sample of calcium carbonate in the form of a cube measuring 2.005 in. on each edge. If the sample has a density of 2.71 $\mathrm{g/cm^3}$, how many oxygen atoms does it contain?

3.106 **(a)** You are given a cube of silver metal that measures 1.000 cm on each edge. The density of silver is 10.5 $\mathrm{g/cm^3}$. How many atoms are in this cube? **(b)** Because atoms are spherical, they cannot occupy all of the space of the cube. The silver atoms pack in the solid in such a way that 74% of the volume of the solid is actually filled with the silver atoms. Calculate the volume of a single silver atom. **(c)** Using the volume of a silver atom and the formula for the volume of a sphere, calculate the radius in angstroms of a silver atom.

3.107 **(a)** If an automobile travels 225 mi with a gas mileage of 20.5 mi/gal, how many kilograms of CO_2 are produced? Assume that the gasoline is composed of octane, $C_8H_{18}(l)$, whose density is 0.69 g/mL. **(b)** Repeat the calculation for a truck that has a gas mileage of 5 mi/gal.

3.108 Section 2.9 introduced the idea of structural isomerism, with 1-propanol and 2-propanol as examples. Determine which of these properties would distinguish these two substances: **(a)** boiling point; **(b)** combustion analysis results; **(c)** molecular weight; **(d)** density at a given temperature and pressure. You can check on the properties of these two compounds in *Wolfram Alpha* (*http://www.wolframalpha.com/*) or the *CRC Handbook of Chemistry and Physics*.

3.109 A particular coal contains 2.5% sulfur by mass. When this coal is burned at a power plant, the sulfur is converted into sulfur dioxide gas, which is a pollutant. To reduce sulfur dioxide emissions, calcium oxide (lime) is used. The sulfur dioxide reacts with calcium oxide to form solid calcium sulfite. **(a)** Write the balanced chemical equation for the reaction. **(b)** If the coal is burned in a power plant that uses 2000 tons of coal per day, what mass of calcium oxide is required daily to eliminate the sulfur dioxide? **(c)** How many grams of calcium sulfite are produced daily by this power plant?

3.110 Copper is an excellent electrical conductor widely used in making electric circuits. In producing a printed circuit board for the electronics industry, a layer of copper is laminated on a plastic board. A circuit pattern is then printed on the board using a chemically resistant polymer. The board is then exposed to a chemical bath that reacts with the exposed copper, leaving the desired copper circuit, which has been protected by the overlaying polymer. Finally, a solvent removes the polymer. One reaction used to remove the exposed copper from the circuit board is

$$\mathrm{Cu}(s) + \mathrm{Cu(NH_3)_4Cl_2}(aq) + 4\,\mathrm{NH_3}(aq) \longrightarrow 2\,\mathrm{Cu(NH_3)_4Cl}(aq)$$

A plant needs to produce 5000 circuit boards, each with a surface area measuring 2.0 in. × 3.0 in. The boards are covered with a 0.65-mm layer of copper. In subsequent processing, 85% of the copper is removed. Copper has a density of 8.96 $\mathrm{g/cm^3}$. Calculate the masses of $\mathrm{Cu(NH_3)_4Cl_2}$ and NH_3 needed to produce the circuit boards, assuming that the reaction used gives a 97% yield.

3.111 Hydrogen cyanide, HCN, is a poisonous gas. The lethal dose is approximately 300 mg HCN per kilogram of air when inhaled. **(a)** Calculate the amount of HCN that gives the lethal dose in a small laboratory room measuring 12 × 15 × 8.0 ft. The density of air at 26 °C is 0.00118 $\mathrm{g/cm^3}$. **(b)** If the HCN is formed by reaction of NaCN with an acid such as H_2SO_4, what mass of NaCN gives the lethal dose in the room?

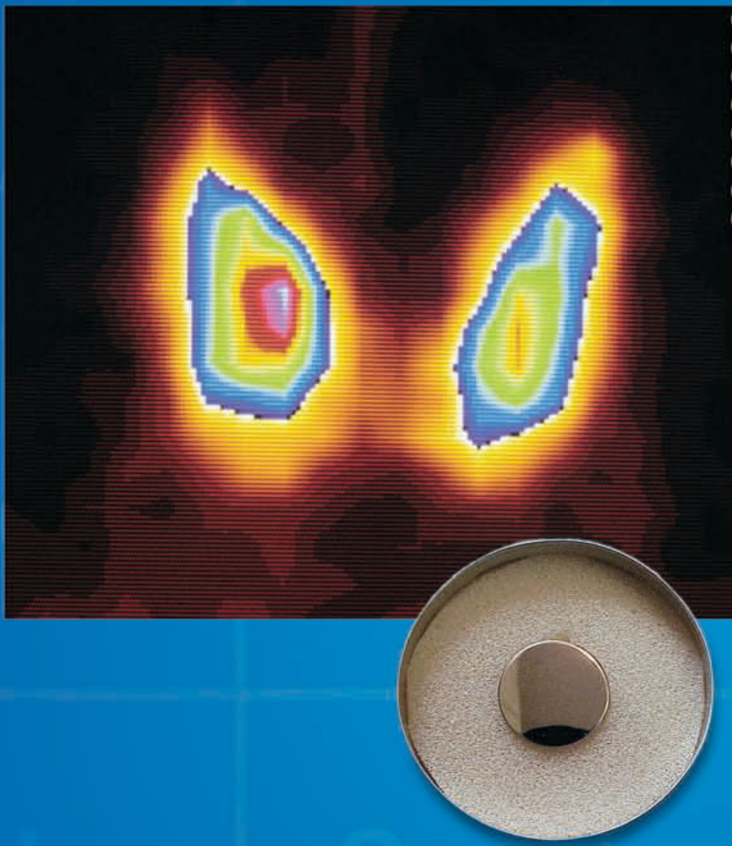
$$2\,\mathrm{NaCN}(s) + \mathrm{H_2SO_4}(aq) \longrightarrow \mathrm{Na_2SO_4}(aq) + 2\,\mathrm{HCN}(g)$$

(c) HCN forms when synthetic fibers containing Orlon® or Acrilan® burn. Acrilan® has an empirical formula of CH_2CHCN, so HCN is 50.9% of the formula by mass. A rug measures 12 × 15 ft and contains 30 oz of Acrilan® fibers per square yard of carpet. If the rug burns, will a lethal dose of HCN be generated in the room? Assume that the yield of HCN from the fibers is 20% and that the carpet is 50% consumed.

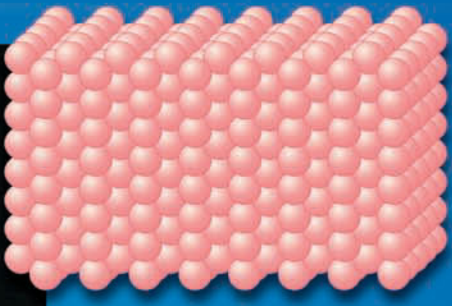
3.112 The source of oxygen that drives the internal combustion engine in an automobile is air. Air is a mixture of gases, principally N_2 (~79%) and O_2 (~20%). In the cylinder of an automobile engine, nitrogen can react with oxygen to produce nitric oxide gas, NO. As NO is emitted from the tailpipe of the car, it can react with more oxygen to produce nitrogen dioxide gas. **(a)** Write balanced chemical equations for both reactions. **(b)** Both nitric oxide and nitrogen dioxide are pollutants that can lead to acid rain and global warming; collectively, they are called "NO_x" gases. In 2007, the United States emitted an estimated 22 million tons of nitrogen dioxide into the atmosphere. How many grams of nitrogen dioxide is this? **(c)** The production of NO_x gases is an unwanted side reaction of the main engine combustion process that turns octane, C_8H_{18}, into CO_2 and water. If 85% of the oxygen in an engine is used to combust octane and the remainder used to produce nitrogen dioxide, calculate how many grams of nitrogen dioxide would be produced during the combustion of 500 grams of octane.

20

Nuclear Chemistry



Technetium-99m is the most widely used radioisotope for medical diagnostics. Small amounts of a radioactive tracer (Tc-99) were injected into the patient's bloodstream and detected as gamma rays by a gamma camera to create this scintigram of a human thyroid gland. The thin plating of Tc-99 on this disk gives about 200 counts per minute.



Contents and Concepts

Radioactivity and Nuclear Bombardment Reactions

We begin by learning what radiation is and what makes something radioactive.

20.1 Radioactivity
20.2 Nuclear Bombardment Reactions
20.3 Radiations and Matter: Detection and Biological Effects
20.4 Rate of Radioactive Decay
20.5 Applications of Radioactive Isotopes

Energy of Nuclear Reactions

We investigate the source of the tremendous amount of energy released during nuclear reactions.

20.6 Mass–Energy Calculations
20.7 Nuclear Fission and Nuclear Fusion

Technetium is an unusual element. Although a *d*-transition element (under manganese in Group VIIB) with a small atomic number (Z = 43), it has no stable isotopes. The nucleus of every technetium isotope is radioactive and decays, or disintegrates, to give an isotope of another element. Many of the technetium isotopes decay by emitting an electron from the nucleus.

Because of its nuclear instability, technetium is not found naturally on earth. Nevertheless, it is produced commercially in kilogram quantities from other elements by nuclear reactions, processes in which nuclei are transformed into different nuclei. Technetium (from the Greek *tekhnetos,* meaning "artificial") was the first new element produced in the laboratory from another element. It was discovered in 1937 by Carlo Perrier and Emilio Segrè when the element molybdenum was bombarded with deuterons (nuclei of hydrogen, each having one proton and one neutron). Later, technetium was found to be a product of the fission, or splitting, of uranium nuclei. Technetium is produced in nuclear fission reactors used to generate electricity.

Technetium is one of the principal isotopes used in medical diagnostics based on radioactivity. A compound of technetium is injected into a vein, where it concentrates in certain body organs. The energy emitted by technetium nuclei is detected by special equipment and gives an image of these body organs. Figure 20.1 shows the image of a person's skeleton obtained from technetium administered in this manner. The technetium is eliminated by the body after several hours.

In this chapter, we will look at nuclear processes such as those we have described for technetium. We will answer such questions as the following: How do you describe the radioactive decay of technetium? How do you describe the transformation of a molybdenum nucleus into technetium? How is technetium produced from uranium by nuclear fission, or splitting? What are some practical applications of nuclear processes?

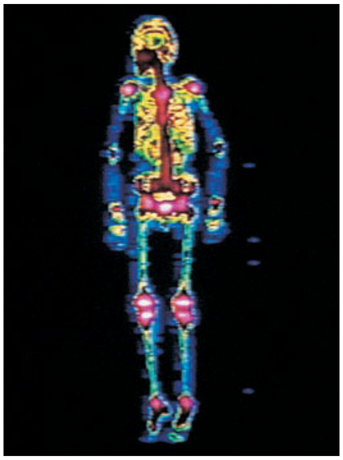


FIGURE 20.1 ▲

Image of a person's skeleton obtained using an excited form of technetium-99

A technetium compound was injected into the body, where it concentrated in bone tissue. Gamma rays (similar to x rays) emitted by technetium were detected by special equipment to produce this image.

■ **See page 859 for the Media Summary.**

Radioactivity and Nuclear Bombardment Reactions

In chemical reactions, only the outer electrons of the atoms are disturbed. The nuclei of the atoms are not affected. In nuclear reactions, however, the nuclear changes that occur are independent of the chemical environment of the atom. For example, the nuclear changes in a radioactive $^3_1$H atom are the same if the atom is part of an H_2 molecule or incorporated into H_2O.

We will look at two types of nuclear reactions. One type is **radioactive decay,** *the process in which a nucleus spontaneously disintegrates, giving off radiation.* The radiation consists of one or more of the following, depending on the nucleus: electrons, nuclear particles (such as neutrons), smaller nuclei (usually helium-4 nuclei), and electromagnetic radiation.

The second type of nuclear reaction is a **nuclear bombardment reaction,** *a nuclear reaction in which a nucleus is bombarded, or struck, by another nucleus or by a nuclear particle.* If there is sufficient energy in this collision, the nuclear particles of the reactants rearrange to give a product nucleus or nuclei. First, we will look at radioactive decay.

20.1 Radioactivity

The phenomenon of radioactivity was discovered by Antoine Henri Becquerel in 1896. He discovered that photographic plates develop bright spots when exposed to uranium minerals, and he concluded that the minerals give off some sort of radiation.

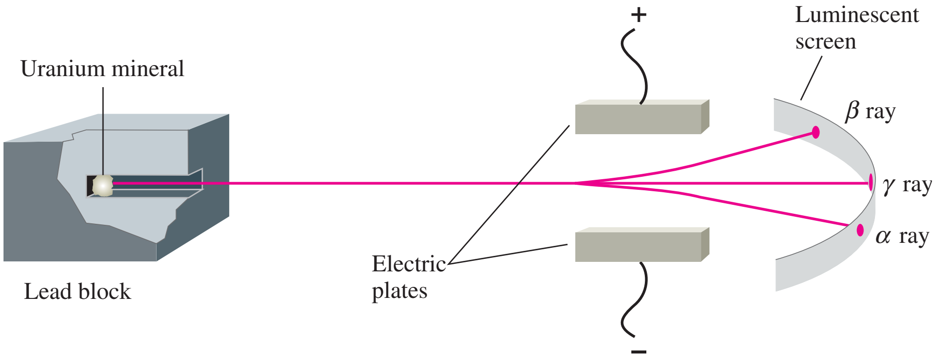


FIGURE 20.2 **Separation of the radiation from a radioactive material (uranium mineral)** The radiation separates into alpha (α), beta (β), and gamma (γ) rays when it passes through an electric field.

The radiation from uranium minerals was later shown to be separable by electric (and magnetic) fields into three types, alpha (α), beta (β), and gamma (γ) rays (Figure 20.2). *Alpha rays* bend away from a positive plate and toward a negative plate, indicating that they have a positive charge; they are now known to consist of helium-4 nuclei (nuclei with two protons and two neutrons). *Beta rays* bend in the opposite direction, indicating that they have a negative charge; they are now known to consist of high-speed electrons. *Gamma rays* are unaffected by electric and magnetic fields: they have been shown to be a form of electromagnetic radiation that is similar to x rays, except they are higher in energy with shorter wavelengths (about 1 pm, or 1×10^{-12} m). Uranium minerals contain a number of radioactive elements, each emitting one or more of these radiations. Uranium-238, the main uranium isotope in uranium minerals, emits alpha rays and thereby decays, or disintegrates, to thorium-234 nuclei.

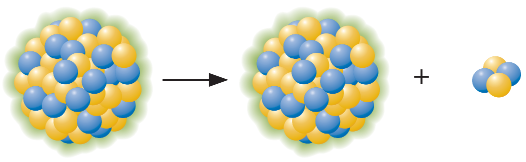
A sample of uranium-238 decays, or disintegrates, spontaneously over a period of billions of years. After about 30 billion years, the sample would be nearly gone. Strontium-90, formed by nuclear reactions that occur in nuclear weapons testing and nuclear power reactors, decays more rapidly. A sample of strontium-90 would be nearly gone after several hundred years. In either case, it is impossible to know when a particular nucleus will decay, although, as you will see in Section 20.4, precise information can be given about the rate of decay of any radioactive sample.

Nuclear Equations

You can write an equation for the nuclear reaction corresponding to the decay of uranium-238 much as you would write an equation for a chemical reaction. You represent the uranium-238 nucleus by the *nuclide symbol* $^{238}_{92}$U. < The radioactive decay of $^{238}_{92}$U by alpha-particle emission (loss of a $^{4}_{2}$He nucleus) is written

Nuclide symbols were introduced in Section 2.3. For uranium-238, you write

$$\begin{array}{l} \text{mass number} \longrightarrow {}^{238} \\ \text{atomic number} \longrightarrow {}_{92}\text{U} \end{array}$$



$$^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$$

The product, in addition to helium-4, is thorium-234. This is an example of a **nuclear equation,** which is *a symbolic representation of a nuclear reaction.* Normally, only the nuclei are represented. It is not necessary to indicate the chemical compound or the electron charges for any ions involved, because the chemical environment has no effect on nuclear processes.

Reactant and product nuclei are represented in nuclear equations by their nuclide symbols. Other particles are given the following symbols, in which the subscript equals the charge and the superscript equals the total number of protons and neutrons in the particle (mass number):

Proton	$^{1}_{1}\text{H}$	or	$^{1}_{1}\text{P}$
Neutron	$^{1}_{0}\text{n}$		
Electron	$^{0}_{-1}\text{e}$	or	$^{0}_{-1}\beta$
Positron	$^{0}_{1}\text{e}$	or	$^{0}_{1}\beta$
Gamma photon	$^{0}_{0}\gamma$		

The decay of a nucleus with the emission of an electron, $^{0}_{-1}\text{e}$, is usually called beta emission, and the emitted electron is sometimes labeled $^{0}_{-1}\beta$. A **positron** is *a particle similar to an electron, having the same mass but a positive charge.* A **gamma photon** is *a particle of electromagnetic radiation of short wavelength (about 1 pm, or 10^{-12} m) and high energy.*

Example 20.1 Writing a Nuclear Equation

Write the nuclear equation for the radioactive decay of radium-226 by alpha decay to give radon-222. A radium-226 nucleus emits one alpha particle, leaving behind a radon-222 nucleus.

Problem Strategy Use the list of elements on the inside back cover to obtain the atomic numbers of radium and radon, so you can write their nuclide symbols for the nuclear equation. The nuclide symbol of the alpha particle is $^{4}_{2}\text{He}$.

Solution The nuclear equation is

$$^{226}_{88}\text{Ra} \longrightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$$

Answer Check Make sure that you have written the nuclide symbols with the correct superscripts and subscripts.

Exercise 20.1 Potassium-40 is a naturally occurring radioactive isotope. It decays to calcium-40 by beta emission. When a potassium-40 nucleus decays by beta emission, it emits one beta particle and gives a calcium-40 nucleus. Write the nuclear equation for this decay.

■ See Problems 20.33, 20.34, 20.35, and 20.36.

The total charge is conserved, or remains constant, during a nuclear reaction. This means that the sum of the subscripts (number of protons, or positive charges, in the nuclei) for the products must equal the sum of the subscripts for the reactants. For the equation in Example 20.1, the subscript for the reactant $^{226}_{88}\text{Ra}$ is 88. For the products, the sum of the subscripts is 86 + 2 = 88.

Similarly, the total number of *nucleons* (protons and neutrons) is conserved, or remains constant, during a nuclear reaction. This means that the sum of the superscripts (the mass numbers) for the reactants equals the sum of the superscripts for the products. For the equation in Example 20.1, the superscript for the reactant nucleus is 226. For the products, the sum of the superscripts is 222 + 4 = 226.

Note that if all reactants and products but one are known in a nuclear equation, the identity of that one nucleus or particle can be easily obtained. This is illustrated in the next example.

Example 20.2 Deducing a Product or Reactant in a Nuclear Equation

Technetium-99 is a long-lived radioactive isotope of technetium. Each nucleus decays by emitting one beta particle. What is the product nucleus?

Problem Strategy First, write the nuclear equation using the symbol $^{A}_{Z}\text{X}$ for the unknown nuclide or particle.

(continued)

(continued)

Then, solve for A and Z using the following relations: (1) the sum of the subscripts for the reactants equals the sum of the subscripts for the products, and (2) the sum of the superscripts for the reactants equals the sum of the superscripts for the products.

Solution Technetium-99 has the nuclide symbol ${}^{99}_{43}\text{Tc}$. A beta particle is an electron; the symbol is ${}^{0}_{-1}\text{e}$. The nuclear equation is

$$ {}^{99}_{43}\text{Tc} \longrightarrow {}^{A}_{Z}\text{X} + {}^{0}_{-1}\text{e} $$

From the superscripts, you can write

$$ 99 = A + 0, \text{ or } A = 99 $$

Similarly, from the subscripts, you get

$$ 43 = Z - 1, \text{ or } Z = 43 + 1 = 44 $$

Hence $A = 99$ and $Z = 44$, so the product is ${}^{99}_{44}\text{X}$. Because element 44 is ruthenium, symbol Ru, you write the product nucleus as $\mathbf{{}^{99}_{44}Ru}$.

Answer Check Although problems of this type are relatively simple, a very common error is not to account properly for the -1 subscript of the beta particle.

Exercise 20.2 Plutonium-239 decays by alpha emission, with each nucleus emitting one alpha particle. What is the other product of this decay?

■ See Problems 20.37, 20.38, 20.39, and 20.40.

Nuclear Stability

At first glance, the existence of several protons in the small space of a nucleus is puzzling. Why wouldn't the protons be strongly repelled by their like electric charges? The existence of stable nuclei with more than one proton is due to the nuclear force. The **nuclear force** is *a strong force of attraction between nucleons that acts only at very short distances (about* 10^{-15} *m).* Beyond nuclear distances, these nuclear forces become negligible. Therefore, two protons that are much farther apart than 10^{-15} m repel one another by their like electric charges. Inside the nucleus, however, two protons are close enough together for the nuclear force between them to be effective. This force in a nucleus can more than compensate for the repulsion of electric charges and thereby give a stable nucleus.

The protons and neutrons in a nucleus appear to have energy levels much as the electrons in an atom have energy levels. The **shell model of the nucleus** is *a nuclear model in which protons and neutrons exist in levels, or shells, analogous to the shell structure that exists for electrons in an atom.* Recall that in an atom, filled shells of electrons are associated with the special stability of the noble gases. The total numbers of electrons for these stable atoms are 2 (for He), 10 (for Ne), 18 (for Ar), and so forth. Experimentally, note that nuclei with certain numbers of protons or neutrons appear to be very stable. These numbers, called *magic numbers* and associated with specially stable nuclei, were later explained by the shell model. According to this theory, a **magic number** is *the number of nuclear particles in a completed shell of protons or neutrons.* Because nuclear forces differ from electrical forces, these numbers are not the same as those for electrons in atoms. For protons, the magic numbers are 2, 8, 20, 28, 50, and 82. Neutrons have these same magic numbers, as well as the magic number 126. For protons, calculations show that 114 should also be a magic number.

Some of the evidence for these magic numbers, and therefore for the shell model of the nucleus, is as follows. Many radioactive nuclei decay by emitting alpha particles, or ${}^{4}_{2}\text{He}$ nuclei. There appears to be special stability in the ${}^{4}_{2}\text{He}$ nucleus. It contains two protons and two neutrons; that is, it contains a magic number of protons (2) and a magic number of neutrons (also 2).

Another piece of evidence is seen in the final products obtained in natural radioactive decay. For example, uranium-238 decays to thorium-234, which in turn decays to protactinium-234, and so forth. Each product is radioactive and decays to another nucleus until the final product, ${}^{206}_{82}\text{Pb}$, is reached. This nucleus is stable. Note that it contains 82 protons, a magic number. Other radioactive decay series end at ${}^{207}_{82}\text{Pb}$ and ${}^{208}_{82}\text{Pb}$, each of which has a magic number of protons. Note that ${}^{208}_{82}\text{Pb}$ also has a magic number of neutrons ($208 - 82 = 126$).

TABLE 20.1 Number of Stable Isotopes with Even and Odd Numbers of Protons and Neutrons

	Number of Stable Isotopes			
	157	52	50	5
Number of protons	Even	Even	Odd	Odd
Number of neutrons	Even	Odd	Even	Odd

Evidence also points to the special stability of pairs of protons and pairs of neutrons, analogous to the stability of pairs of electrons in molecules. Table 20.1 lists the number of stable isotopes that have an even number of protons and an even number of neutrons (157). By comparison, only 5 stable isotopes have an odd number of protons and an odd number of neutrons.

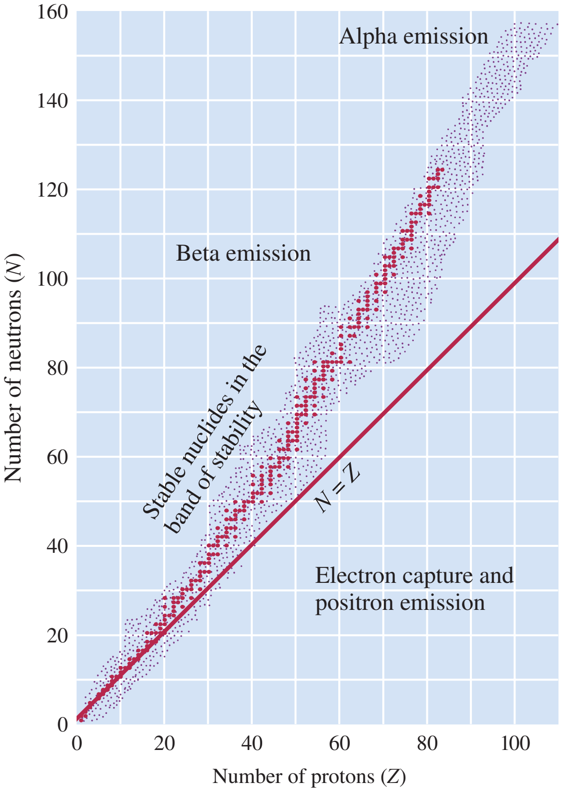
When you plot each stable nuclide on a graph with the number of protons (Z) on the horizontal axis and the number of neutrons (N) on the vertical axis, these stable nuclides fall in a certain region, or band, of the graph. The **band of stability** is *the region in which stable nuclides lie in a plot of number of protons against number of neutrons.* Figure 20.3 shows the band of stability; the rest of the figure is explained later in this section. For nuclides up to $Z = 20$, the ratio of neutrons to protons is about 1.0 to 1.1. As Z increases, however, the neutron-to-proton ratio increases to about 1.5. This increase in neutron-to-proton ratio with increasing Z is believed to result from the increasing repulsions of protons from their electric charges. More neutrons are required to give attractive nuclear forces to offset these repulsions.

It appears that when the number of protons becomes very large, the proton–proton repulsions become so great that stable nuclides are impossible. No stable nuclides are

FIGURE 20.3

Band of stability

The stable nuclides, indicated by black dots, cluster in a band. Nuclides to the left of the band of stability usually decay by beta emission, whereas those to the right usually decay by positron emission or electron capture. Nuclides of $Z > 83$ often decay by alpha emission.



known with atomic numbers greater than 83. On the other hand, all elements with Z equal to 83 or less have one or more stable nuclides, with the exception of technetium ($Z = 43$), as noted in the chapter opening, and promethium ($Z = 61$).

Example 20.3 Predicting the Relative Stabilities of Nuclides

One of the nuclides in each of the following pairs is radioactive; the other is stable. Which is radioactive and which is stable? Explain.

a. $^{208}_{84}\text{Po}$, $^{209}_{83}\text{Bi}$ b. $^{39}_{19}\text{K}$, $^{40}_{19}\text{K}$ c. $^{71}_{31}\text{Ga}$, $^{76}_{31}\text{Ga}$

Problem Strategy You must decide which nuclide of each pair is more likely to be stable, based on the general principles stated in the preceding text.

Solution a. Polonium has an atomic number greater than 83, so **$^{208}_{84}\text{Po}$ is radioactive.** Bismuth-209 has 126 neutrons (a magic number), so **$^{209}_{83}\text{Bi}$ is expected to be stable.**

b. Of these two isotopes, $^{39}_{19}\text{K}$ has a magic number of neutrons (20), so **$^{39}_{19}\text{K}$ is expected to be stable.** The isotope $^{40}_{19}\text{K}$ has an odd number of protons (19) and an odd number of neutrons (21). Because stable odd–odd nuclei are rare, **you might expect $^{40}_{19}\text{K}$ to be radioactive.**

c. Of the two isotopes, $^{76}_{31}\text{Ga}$ lies farther from the center of the band of stability, so it is more likely to be radioactive. For this reason, **you expect $^{76}_{31}\text{Ga}$ to be radioactive and $^{71}_{31}\text{Ga}$, which has an even number of neutrons and is close to the atomic mass of gallium, to be stable.**

Answer Check When trying to determine whether a nuclide is radioactive, always first perform the simple check to see if the atomic number is greater than 83.

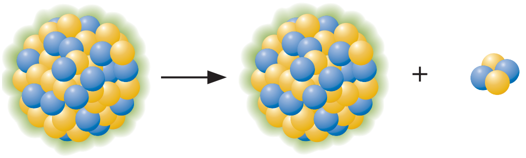
Exercise 20.3 Of the following nuclides, two are radioactive. Which are radioactive and which is stable? Explain. a. $^{118}_{50}\text{Sn}$; b. $^{76}_{33}\text{As}$; c. $^{227}_{89}\text{Ac}$.

■ See Problems 20.41 and 20.42.

Types of Radioactive Decay

There are six common types of radioactive decay; the first five are listed in Table 20.2.

1. **Alpha emission** (abbreviated α): *emission of a $^{4}_{2}$He nucleus, or alpha particle, from an unstable nucleus.* An example is the radioactive decay of radium-226.

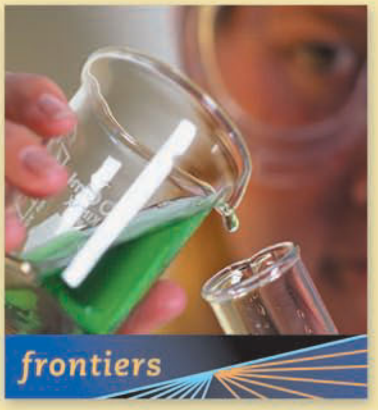


$$^{226}_{88}\text{Ra} \longrightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$$

TABLE 20.2 Types of Radioactive Decay

Type of Decay	Radiation	Equivalent Process	Resulting Nuclear Change: Atomic Number	Resulting Nuclear Change: Mass Number	Usual Nuclear Condition
Alpha emission (α)	$^{4}_{2}\text{He}$	—	-2	-4	$Z > 83$
Beta emission (β)	$^{0}_{-1}\text{e}$	$^{1}_{0}\text{n} \longrightarrow {}^{1}_{1}\text{p} + {}^{0}_{-1}\text{e}$	$+1$	0	N/Z too large
Positron emission (β^+)	$^{0}_{1}\text{e}$	$^{1}_{1}\text{p} \longrightarrow {}^{1}_{0}\text{n} + {}^{0}_{1}\text{e}$	-1	0	N/Z too small
Electron capture (EC)	x rays	$^{1}_{1}\text{p} + {}^{0}_{-1}\text{e} \longrightarrow {}^{1}_{0}\text{n}$	-1	0	N/Z too small
Gamma emission (γ)	$^{0}_{0}\gamma$	—	0	0	Excited

A Chemist Looks at . . .



Magic Numbers

Maria Goeppert-Mayer (Figure 20.4) (1906–1972) received the 1963 Nobel Prize in Physics for her discovery of the shell structure of the nucleus (independently discovered by the German physicist J. Hans D. Jensen). Notably, she was the second woman to receive the Nobel Prize (Marie Curie was the first). In 1948, Goeppert-Mayer had noticed that the most abundant nuclei were those with special numbers of protons and neutrons. (These special numbers came to be called *magic numbers*.) Although these numbers had been noted earlier, her work was especially detailed and convincing, and it strongly pointed to a shell structure of the nucleus.

FIGURE 20.4 ▲

Maria Goeppert-Mayer

According to the shell model of the nucleus, protons and neutrons occupy independent sets of orbitals, similar to those of electrons in atoms. Nucleon orbitals have similar quantum numbers too: n (principal quantum number) and l (orbital angular momentum quantum number). Each nucleon also has a spin of 1/2. Unlike electrons, though, the l quantum number of a nucleon is not restricted by n. It can have any positive integer value, whatever the value of n, beginning with $l = 0$. For example, the orbitals corresponding to $n = 1$ are 1s, 1p, 1d, 1f, . . . (where s stands for $l = 0$, p for $l = 1$, and so forth).

A simple scheme based on nucleons oscillating within the nucleus gives energy levels proportional to $2(n - 1) + l$, which leads to the following increasing order of energy levels:

1s, 1p, 1d and 2s (with about the same energies), 1f, . . .

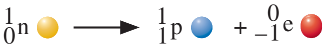
Similar to electrons, an s orbital holds 2 nucleons, a p orbital holds 6 nucleons, a d orbital holds 10 electrons, and an f orbital holds 14 nucleons. Thus it takes 2 nucleons to fill a 1s level, 8 nucleons to fill the 1s and 1p levels, 20 nucleons to fill the 1s, 1p, 1d, and 2s levels, and 34 nucleons to fill the 1s, 1p, 1d, 2s and 1f levels. The numbers 2, 8, and 20 are the first three magic numbers. After that, however, this simple scheme fails.

Goeppert-Mayer was able to solve this problem by noting that in nuclei, the orbital angular momentum of each nucleon couples to its spin (equal to 1/2) to give a total angular momentum of either $l + 1/2$ or $l - 1/2$. Each level of given l thus splits by this *spin-orbit coupling* into two sublevels, with the sublevel of angular momentum $l + 1/2$ being lower in energy. For example, a 1f level is split to give a lower level that Goeppert-Mayer showed can hold 8 nucleons and an upper level that can hold 6 nucleons for a total of 14 for an f shell. Therefore, the magic number after 20 is 20 + 8 = 28 (not 20 + 14 = 34). She was able to show that the shell model reproduced the other magic numbers, as well.

■ See Problems 20.103 and 20.104.

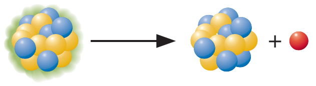
The product nucleus has an atomic number that is two less, and a mass number that is four less, than that of the original nucleus.

2. **Beta emission** (abbreviated β or β^-): *emission of a high-speed electron from an unstable nucleus.* Beta emission is equivalent to the conversion of a neutron to a proton.



$$^1_0\text{n} \longrightarrow {}^1_1\text{p} + {}^0_{-1}\text{e}$$

An example of beta emission is the radioactive decay of carbon-14.



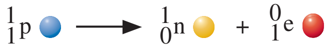
$$ {}^{14}_{6}\text{C} \longrightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e} $$

The product nucleus has an atomic number that is one more than that of the original nucleus. The mass number remains the same.

3. **Positron emission** (abbreviated β^+): *emission of a positron from an unstable nucleus.* A positron, denoted in nuclear equations as ${}^{0}_{1}\text{e}$, is a particle identical to an electron in mass but having a positive instead of a negative charge. Positron emission is equivalent to the conversion of a proton to a neutron. <

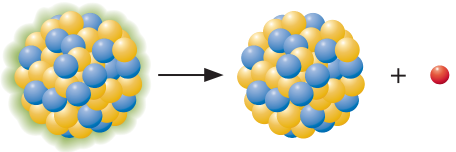
Positrons are annihilated as soon as they encounter electrons. When a positron and an electron collide, both particles vanish with the emission of two gamma photons that carry away the energy.

$$ {}^{0}_{1}e + {}^{0}_{-1}e \longrightarrow 2\,{}^{0}_{0}\gamma $$



$$ {}^{1}_{1}\text{p} \longrightarrow {}^{1}_{0}\text{n} + {}^{0}_{1}\text{e} $$

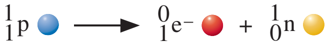
The radioactive decay of technetium-95 is an example of positron emission.



$$ {}^{95}_{43}\text{Tc} \longrightarrow {}^{95}_{42}\text{Mo} + {}^{0}_{1}\text{e} $$

The product nucleus has an atomic number that is one less than that of the original nucleus. The mass number remains the same.

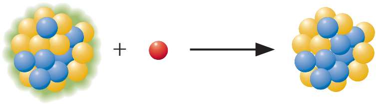
4. **Electron capture** (abbreviated EC): *the decay of an unstable nucleus by capturing, or picking up, an electron from an inner orbital of an atom.* In effect, a proton is changed to a neutron, as in positron emission.



$$ {}^{1}_{1}\text{p} + {}^{0}_{-1}\text{e} \longrightarrow {}^{1}_{0}\text{n} $$

An example is given by potassium-40, which has a natural abundance of 0.012%. < Potassium-40 can decay by electron capture, as well as by beta and positron emissions. The equation for electron capture is

Most of the argon in the atmosphere is believed to have resulted from the radioactive decay of ${}^{40}_{19}K$.

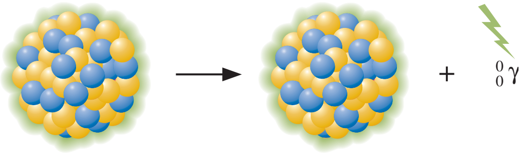


$$ {}^{40}_{19}\text{K} + {}^{0}_{-1}\text{e} \longrightarrow {}^{40}_{18}\text{Ar} $$

The product nucleus has an atomic number that is one less than that of the original nucleus. The mass number remains the same. When another orbital electron fills the vacancy in the inner-shell orbital created by electron capture, an x-ray photon is emitted.

5. **Gamma emission** (abbreviated γ): *emission from an excited nucleus of a gamma photon, corresponding to radiation with a wavelength of about 10^{-12} m.* In many cases, radioactive decay results in a product nucleus that is in an excited state. As in the case of atoms, the excited state is unstable and goes to a lower-energy state with the emission of electromagnetic radiation. For nuclei, this radiation is in the gamma-ray region of the spectrum.

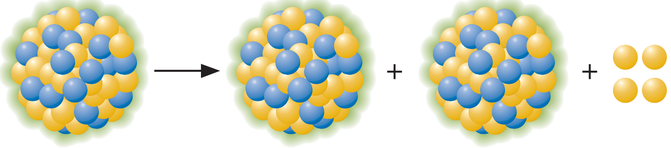
Often gamma emission occurs very quickly after radioactive decay. In some cases, however, an excited state has significant lifetime before it emits a gamma photon. A **metastable nucleus** is *a nucleus in an excited state with a lifetime of at least one nanosecond* (10^{-9} *s*). In time, the metastable nucleus decays by gamma emission. An example is metastable technetium-99, denoted ${}^{99m}_{43}\text{Tc}$, which is used in medical diagnosis, as discussed in Section 20.5.



$$ {}^{99m}_{43}\text{Tc} \longrightarrow {}^{99}_{43}\text{Tc} + {}^{0}_{0}\gamma $$

The product nucleus is simply a lower-energy state of the original nucleus, so there is no change of atomic number or mass number.

6. **Spontaneous fission:** *the spontaneous decay of an unstable nucleus in which a heavy nucleus of mass number greater than 89 splits into lighter nuclei and energy is released.* For example, a uranium-236 atom can spontaneously undergo the following nuclear reaction:



$$ {}^{236}_{92}\text{U} \longrightarrow {}^{96}_{39}\text{Y} + {}^{136}_{53}\text{I} + 4{}^{1}_{0}\text{n} $$

This process will be discussed further in Section 20.6.

Nuclides outside the band of stability (Figure 20.3) are generally radioactive. Nuclides to the left of the band of stability have a neutron-to-proton ratio (N/Z) larger than that needed for stability. These nuclides tend to decay by beta emission. Beta emission reduces the neutron-to-proton ratio, because in this process a neutron is changed to a proton. The product is a stabler nuclide. In contrast, nuclides to the right of the band of stability have a neutron-to-proton ratio smaller than that needed for stability. These nuclides tend to decay by either positron emission or electron capture. Both processes convert a proton to a neutron, increasing the neutron-to-proton ratio and giving a stabler product nuclide. The types of radioactive decay expected of unstable nuclides are noted in Figure 20.3.

Consider a series of isotopes of a given element, such as carbon. Carbon-12 and carbon-13 are stable isotopes, whereas the other isotopes of carbon are radioactive. The isotopes of mass number smaller than 12 decay by positron emission. For example, carbon-11 decays by positron emission to boron-11.

$$ {}^{11}_{6}\text{C} \longrightarrow {}^{11}_{5}\text{B} + {}^{0}_{1}\text{e} $$

Carbon-11 has a neutron-to-proton ratio of 5/6 (= 0.8), which increases in the product boron-11 to 6/5 (1.2). The isotopes of carbon with mass number greater than 13 decay by beta emission. Carbon-14 decays by beta emission to produce nitrogen-14.

$$ {}^{14}_{6}\text{C} \longrightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e} $$

Carbon-14 has a neutron-to-proton ratio of 8/6 (1.3), which decreases in the product nitrogen-14 to 7/7 (1.0).

Now consider the radioactive isotope phosphorus-30. You can predict the expected type of radioactive decay of this isotope by noting whether the mass number is less than or greater than the mass number of stable isotopes. Generally, the mass numbers of stable isotopes will be close to the numerical value of the atomic mass of the element. The atomic mass of phosphorus is 31.0 amu, so you might expect phosphorus-31 to be a stable isotope (which it is). Phosphorus-30 has a mass number less than that of the stable isotope phosphorus-31. Therefore, you expect that phosphorus-30 will decay by either positron emission or electron capture. Positron emission is actually observed.

Positron emission and electron capture are competing radioactive decay processes, and what is observed depends on the relative rates of the two processes. The rate of electron capture increases with atomic number of the decaying nuclide and therefore becomes important in heavier elements. Positron emission is generally seen in lighter elements (recall that phosphorus-30 decays by positron emission). However, in the very heavy elements, especially those with Z greater than 83, radioactive decay is often by alpha emission (noted in Figure 20.3 at the top of the figure). $^{238}_{92}\mathrm{U}$, $^{226}_{88}\mathrm{Ra}$, and $^{232}_{90}\mathrm{Th}$ are examples of alpha emitters.

Example 20.4 Predicting the Type of Radioactive Decay

Predict the expected type of radioactive decay for each of the following radioactive nuclides: a. $^{47}_{20}\mathrm{Ca}$; b. $^{25}_{13}\mathrm{Al}$.

Problem Strategy Compare each nuclide with the stable nuclides of the same element. A nuclide with an N/Z ratio greater than that of the stable nuclides is expected to exhibit beta emission. A nuclide with an N/Z ratio less than that of the stable nuclides is expected to exhibit positron emission or electron capture; electron capture is important with heavier elements. Since you are comparing nuclides of the same Z, you can compare mass numbers ($= N + Z$), rather than N/Z.

Solution a. The atomic mass calcium is 40.1 amu, so you expect calcium-40 to be a stable isotope. Calcium-47 has a mass number greater than that of the stable isotope, so you expect it to decay by **beta emission.** (This is the observed behavior of calcium-47.)

b. The atomic mass of aluminum is 27.0 amu, so you expect aluminum-27 to be a stable isotope. The mass number of aluminum-25 is less than 27, so you expect aluminum-25 to decay by either **positron emission or electron capture.** Positron emission is actually observed.

Answer Check To answer these types of questions correctly, you must understand how the N/Z ratio of nuclides determines the type of emission from radioactive nuclides.

Exercise 20.4 Predict the type of decay expected for each of the following radioactive nuclides: a. $^{13}_{7}\mathrm{N}$; b. $^{26}_{11}\mathrm{Na}$.

■ See Problems 20.43 and 20.44.

Radioactive Decay Series

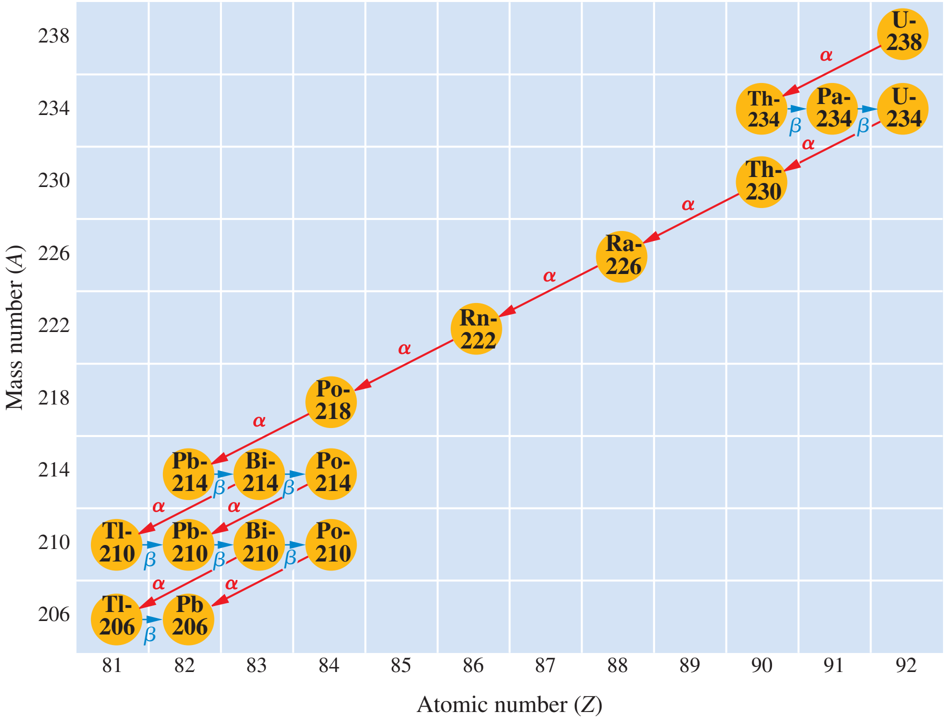
All nuclides with atomic number greater than $Z = 83$ are radioactive, as we have noted. Many of these nuclides decay by alpha emission. Alpha particles, or $^{4}_{2}\mathrm{He}$ nuclei, are especially stable and are formed in the radioactive nucleus at the moment of decay. By emitting an alpha particle, the nucleus reduces its atomic number, becoming more stable. However, if the nucleus has a very large atomic number, the product nucleus is also radioactive. Natural radioactive elements, such as uranium-238, give a **radioactive decay series,** *a sequence in which one radioactive nucleus decays to a second, which then decays to a third, and so forth.* Eventually, a stable nucleus, which is an isotope of lead, is reached.

Three radioactive decay series are found naturally. One of these series begins with uranium-238. Figure 20.5 shows the sequence of nuclear decay processes. In the first step, uranium-238 decays by alpha emission to thorium-234.

$$^{238}_{92}\mathrm{U} \longrightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}$$

FIGURE 20.5

Uranium-238 radioactive decay series
Each nuclide occupies a position on the graph determined by its atomic number and mass number. Alpha decay is shown by a red diagonal line. Beta decay is shown by a short blue horizontal line.



This step is represented in Figure 20.5 by a red arrow labeled α. Each alpha decay reduces the atomic number by 2 and the mass number by 4. The atomic number and mass number of each nuclide are given by its horizontal and vertical position on the graph. Thorium-234 in turn decays by beta emission to protactinium-234, which decays by beta emission to uranium-234.

$$^{234}_{90}\mathrm{Th} \longrightarrow {}^{234}_{91}\mathrm{Pa} + {}^{0}_{-1}\mathrm{e}$$
$$^{234}_{91}\mathrm{Pa} \longrightarrow {}^{234}_{92}\mathrm{U} + {}^{0}_{-1}\mathrm{e}$$

Beta emission is represented in Figure 20.5 by a blue arrow labeled β. Each beta decay increases the atomic number by one but has no effect on the mass number. After the decay of protactinium-234 and the formation of uranium-234, there are a number of alpha-decay steps. The final product of the series is lead-206.

Natural uranium is 99.28% $^{238}_{92}\mathrm{U}$, which decays as we have described. However, the natural element also contains 0.72% $^{235}_{92}\mathrm{U}$. This isotope starts a second radioactive decay series, which consists of a sequence of alpha and beta decays, ending with lead-207. The third naturally occurring radioactive decay series begins with thorium-232 and ends with lead-208. All three radioactive decay series found naturally end with an isotope of lead.

Concept Check 20.1

You have two samples of water, each made up of different isotopes of hydrogen: one contains $^{1}_{1}\mathrm{H_2O}$ and the other, $^{3}_{1}\mathrm{H_2O}$.

a. Would you expect these two water samples to be chemically similar?

b. Would you expect these two water samples to be physically the same?

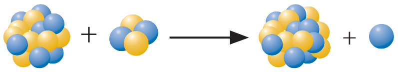
c. Which one of these water samples would you expect to be radioactive?

20.2 Nuclear Bombardment Reactions

The nuclear reactions discussed in the previous section are radioactive decay reactions, in which a nucleus spontaneously decays to another nucleus and emits a particle, such as an alpha or beta particle. In 1919, Ernest Rutherford discovered that it is possible to change the nucleus of one element into the nucleus of another element by processes that can be controlled in the laboratory. **Transmutation** is *the change of one element to another by bombarding the nucleus of the element with nuclear particles or nuclei.*

Transmutation

Rutherford used a radioactive element as a source of alpha particles and allowed these particles to collide with nitrogen nuclei. He discovered that protons are ejected in the process. The equation for the nuclear reaction is



$$^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H$$

The experiments were repeated on other light nuclei, most of which were transmuted to other elements with the ejection of a proton. These experiments yielded two significant results. First, they strengthened the view that all nuclei contain protons. Second, they showed for the first time that it is possible to change one element into another under laboratory control.

When beryllium is bombarded with alpha particles, a penetrating radiation is given off that is not deflected by electric or magnetic fields. Therefore, the radiation does not consist of charged particles. The British physicist James Chadwick (1891–1974) suggested in 1932 that the radiation from beryllium consists of neutral particles, each with a mass approximately that of a proton. The particles are called neutrons. The reaction that resulted in the discovery of the neutron is

$$^{9}_{4}Be + ^{4}_{2}He \longrightarrow ^{12}_{6}C + ^{1}_{0}n$$

In 1933, a nuclear bombardment reaction was used to produce the first artificial radioactive isotope. Irène and Frédéric Joliot-Curie found that aluminum bombarded with alpha particles produces phosphorus-30, which decays by emitting positrons. The reactions are

$$^{27}_{13}Al + ^{4}_{2}He \longrightarrow ^{30}_{15}P + ^{1}_{0}n$$
$$^{30}_{15}P \longrightarrow ^{30}_{14}Si + ^{0}_{1}e$$

Phosphorus-30 was the first radioactive nucleus produced in the laboratory. Since then over a thousand radioactive isotopes have been made. <

Some of the uses of radioactive isotopes are discussed in Section 20.5.

Nuclear bombardment reactions are often referred to by an abbreviated notation. For example, the reaction

$$^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H$$

is abbreviated $^{14}_{7}N(\alpha, p)^{17}_{8}O$. In this, notation, you first write the nuclide symbol for the original nucleus (target). Then, in parentheses, you write the symbol for the projectile particle (incoming particle), followed by a comma and the symbol for the ejected particle. After the last parenthesis, you write the nuclide symbol for the product nucleus. The following symbols are used for particles:

Neutron	n
Proton	p
Deuteron, $^{2}_{1}H$	d
Alpha, $^{4}_{2}He$	α

Example 20.5 Using the Notation for a Bombardment Reaction

a. Write the abbreviated notation for the following bombardment reaction, in which neutrons were first discovered.

$$ {}^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}\text{n} $$

b. Write the nuclear equation for the bombardment reaction denoted ${}^{27}_{13}\text{Al}(\text{p, d}){}^{26}_{13}\text{Al}$.

Problem Strategy Understand and use the abbreviated notation and particle symbols for nuclear reactions.

Solution a. The notation is $\mathbf{{}^{9}_{4}Be(\alpha, n){}^{12}_{6}C}$.

b. The nuclear equation is

$$ \mathbf{{}^{27}_{13}Al + {}^{1}_{1}H \longrightarrow {}^{26}_{13}Al + {}^{2}_{1}H} $$

Answer Check You can check your answers by working backward to see whether they lead to the representations given in the problem.

Exercise 20.5 a. Write the abbreviated notation for the reaction

$$ {}^{40}_{20}\text{Ca} + {}^{2}_{1}\text{H} \longrightarrow {}^{41}_{20}\text{Ca} + {}^{1}_{1}\text{H} $$

b. Write the nuclear equation for the bombardment reaction ${}^{12}_{6}\text{C}(\text{d, p}){}^{13}_{6}\text{C}$.

- See Problems 20.47, 20.48, 20.49, and 20.50.

Elements of large atomic number merely scatter, or deflect, alpha particles from natural sources, rather than giving a transmutation reaction. These elements have nuclei of large positive charge, and the alpha particle must be traveling very fast in order to penetrate the nucleus and react. Alpha particles from natural sources do not have sufficient kinetic energy. To shoot charged particles into heavy nuclei, it is necessary to accelerate the charged particles.

A **particle accelerator** is *a device used to accelerate electrons, protons, and alpha particles and other ions to very high speeds.* The basis of a particle accelerator is the fact that a charged particle will accelerate toward a plate having a charge opposite in sign to that of the particle. It is customary to measure the kinetic energies of these particles in units of electron volts. An **electron volt (eV)** is *the quantity of energy that would have to be imparted to an electron (whose charge is 1.602×10^{-19} C) to accelerate it by one volt potential difference.*

$$ 1 \text{ eV} = (1.602 \times 10^{-19} \text{ C}) \times (1 \text{ V}) = 1.602 \times 10^{-19} \text{ J} $$

Typically, particle accelerators give charged particles energies of millions of electron volts (MeV). To keep the accelerated particles from colliding with molecules of gas, the apparatus is enclosed and evacuated to low pressures, about 10^{-6} mmHg or less.

A charged particle can be accelerated in stages to very high kinetic energy. Figure 20.6 shows a diagram of a **cyclotron,** *a type of particle accelerator consisting of two hollow, semicircular metal electrodes called dees (because the shape resembles the letter D), in which charged particles are accelerated by stages to higher and higher kinetic energies.* Ions introduced at the center of the cyclotron are accelerated in the space between the two dees. Magnet poles (not shown in the figure) above and below the dees keep the ions moving in an enlarging spiral path. The dees are connected to a high-frequency electric current that changes their polarity so that each time an ion moves into the space between the dees, it is accelerated. Thus, the ion is continually accelerated until it finally leaves the cyclotron at high speed. Outside the cyclotron, the ions are directed toward a target element so that investigators may study nuclear reactions or prepare isotopes.

Technetium was first prepared by directing **deuterons,** or *nuclei of hydrogen-2 atoms,* from a cyclotron to a molybdenum target. < The nuclear reaction is ${}^{96}_{42}\text{Mo}(\text{d, n}){}^{97}_{43}\text{Tc}$, or

$$ {}^{96}_{42}\text{Mo} + {}^{2}_{1}\text{H} \longrightarrow {}^{97}_{43}\text{Tc} + {}^{1}_{0}\text{n} $$

The hydrogen-2 atom is often called deuterium and given the symbol D. It is a stable isotope with a natural abundance of 0.015%. Deuterium was discovered in 1931 by Harold Urey and coworkers and was prepared in pure form by G. N. Lewis.

FIGURE 20.6

A cyclotron

Positive ions are introduced at the center of the cyclotron. A fraction of the ions will be crossing the gap between the dees when the electric polarities are just right to accelerate them. (The positive ions are accelerated toward the negative dee and away from the positive dee.) The dees alternate in polarities, so that these ions continue to be accelerated each time they pass between the gap in the dees. Magnet poles above and below the dees produce a magnetic field that keeps the ions moving in a spiral path within the dees. At the end of their path, the ions encounter a negative electrode that deflects them to a target material.

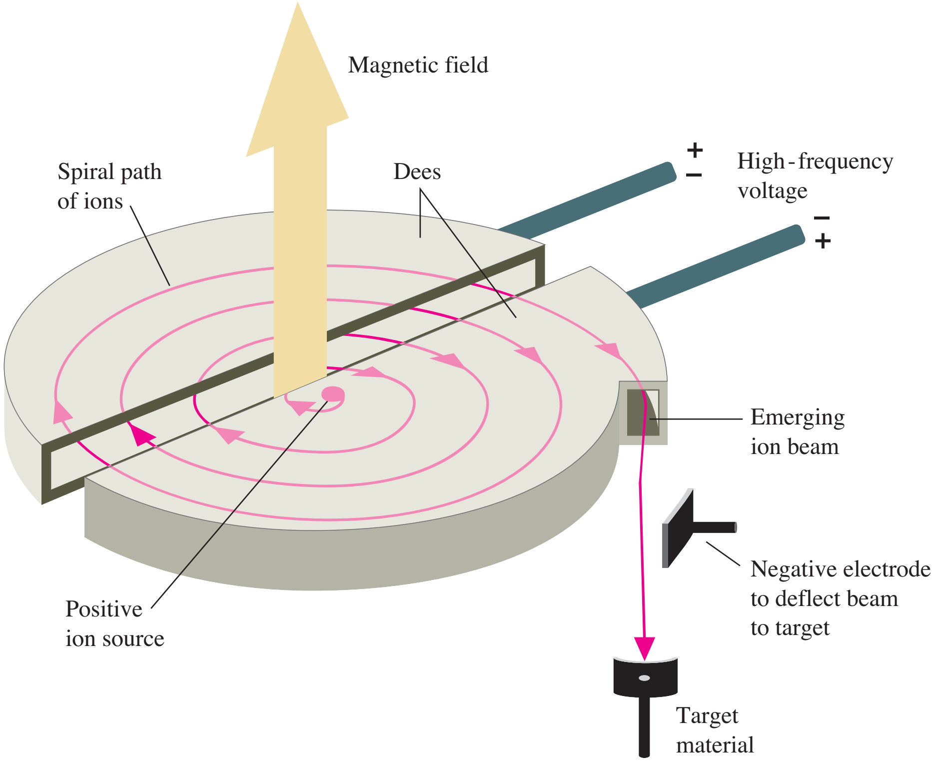


FIGURE 20.7

The Fermilab accelerator in Batavia, Illinois

The tunnel of the main accelerator is shown here. Protons are accelerated in the upper ring of conventional magnets (red and blue) to 400 billion electron volts. These protons are then injected into the lower ring of superconducting magnets (yellow), where they are accelerated to almost a trillion electron volts.

The energies of particles obtained from a cyclotron are limited (to about 20 MeV for deuterons, for example). For higher energies, more sophisticated accelerators are required. Figure 20.7 shows the accelerator at Fermilab in Batavia, Illinois. Larger and larger particle accelerators are being built to study the basic constituents of matter.

Transuranium Elements

The **transuranium elements** are *elements with atomic numbers greater than that of uranium (Z = 92), the naturally occurring element of greatest Z.* In 1940, E. M. McMillan and P. H. Abelson, at the University of California at Berkeley, discovered the first transuranium element. They produced an isotope of element 93, which they named neptunium, by bombarding uranium-238 with neutrons. This gave uranium-239, by the capture of a neutron, and this nucleus decayed in a few days by beta emission to neptunium-239.

$$^{238}_{92}\text{U} + ^{1}_{0}\text{n} \longrightarrow ^{239}_{92}\text{U}$$

$$^{239}_{92}\text{U} \longrightarrow ^{239}_{93}\text{Np} + ^{0}_{-1}\text{e}$$

The next transuranium element to be discovered was plutonium ($Z = 94$). Deuterons, the positively charged nuclei of hydrogen-2, were accelerated by a cyclotron and directed at a uranium target to give neptunium-238, which decayed to plutonium-238.

$$^{238}_{92}\text{U} + ^{2}_{1}\text{H} \longrightarrow ^{238}_{93}\text{Np} + 2^{1}_{0}\text{n}$$

$$^{238}_{93}\text{Np} \longrightarrow ^{238}_{94}\text{Pu} + ^{0}_{-1}\text{e}$$

Another isotope of plutonium, plutonium-239, is now produced in large quantity in nuclear reactors, as described in Section 20.7. Plutonium-239 is used for nuclear weapons.

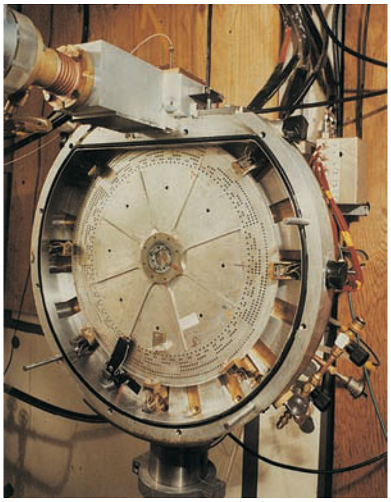


FIGURE 20.8

The vertical wheel, an apparatus used in the discovery of elements 104, 105, and 106

The apparatus was designed by Albert Ghiorso and colleagues. They synthesized element 106 by bombarding californium-249 with oxygen-18. The products were whisked by gas jets to the vertical wheel, where they were deposited (at the top). Detectors around the periphery of the wheel monitored the alpha activity to identify the products. Binary-coded holes label the positions around the wheel for computer collection of data.

The discovery of the next two transuranium elements, americium ($Z = 95$) and curium ($Z = 96$), depended on an understanding of the correct positions in the periodic table of the elements beyond actinium ($Z = 89$). It had been thought that these elements should be placed after actinium under the *d*-transition elements, so uranium was placed in Group VIB under tungsten. However, Glenn T. Seaborg, then at the University of California, Berkeley, postulated a second series of elements to be placed at the bottom of the periodic table, under the lanthanides, as shown in modern tables (see inside front cover). These elements, the actinides, would be expected to have chemical properties similar to those of the lanthanides. Once they understood this, Seaborg and others were able to use the predicted chemical behaviors of the actinides to separate americium and curium.

Figure 20.8 shows the apparatus used by Albert Ghiorso at the Lawrence Berkeley Laboratory in Berkeley, California, for the discovery of elements 104, 105, and 106. A team of scientists led by Peter Armbruster in Darmstadt, Germany, created elements 107 to 109 in the early 1980s by bombarding other elements with heavy-metal ions. During the 1994–1996 period, they reported the discovery of elements 110, 111, and 112. Recent work has yielded other elements, including the heaviest to date, 118.

The transuranium elements have a number of commercial uses. Plutonium-238 emits only alpha radiation, which is easily stopped by shielding. The isotope has been used as a power source for space satellites, navigation buoys, and heart pacemakers. Americium-241 is both an alpha-ray and a gamma-ray emitter. The gamma rays are used in devices that measure the thickness of materials such as metal sheets. Americium-241 is also used in home smoke detectors, in which the alpha radiation ionizes the air in a chamber within the detector and renders it electrically conducting. Smoke reduces the conductivity of the air, and this reduced conductivity is detected by an alarm circuit.

Figure 20.9 shows the High Flux Isotope Reactor at Oak Ridge National Laboratory, where technicians produce transuranium elements by bombarding plutonium-239 with neutrons. Neutrons are produced by nuclear fission, a process discussed in Section 20.7.

Example 20.6 Determining the Product Nucleus in a Nuclear Bombardment Reaction

Plutonium-239 was bombarded by alpha particles. Each ${}^{239}_{94}\text{Pu}$ nucleus was struck by one alpha particle and emitted one neutron. What was the product nucleus?

Problem Strategy Apply a strategy similar to that used to solve Example 20.2.

Solution You can write the nuclear equation as follows:

$$ {}^{239}_{94}\text{Pu} + {}^{4}_{2}\text{He} \longrightarrow {}^{A}_{Z}\text{X} + {}^{1}_{0}\text{n} $$

To balance this equation, write

$$ 239 + 4 = A + 1 \qquad \text{(from superscripts)} $$

$$ 94 + 2 = Z + 0 \qquad \text{(from subscripts)} $$

Hence,

$$ A = 239 + 4 - 1 = 242 $$

$$ Z = 94 + 2 = 96 $$

The product is $\mathbf{{}^{242}_{96}Cm}$.

Answer Check Be careful in problems like this where the nuclides have coefficients; in those cases, make sure that you count correctly.

Exercise 20.6 Carbon-14 is produced in the upper atmosphere when a particular nucleus is bombarded with neutrons. A proton is ejected for each nucleus that reacts. What is the identity of the nucleus that produces carbon-14 by this reaction?

■ See Problems 20.53, 20.54, 20.55, and 20.56.

20.3 Radiations and Matter: Detection and Biological Effects

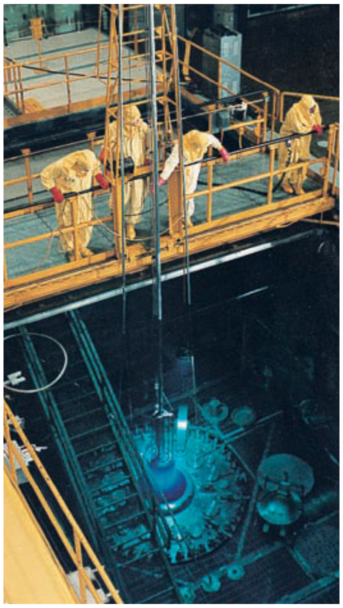


FIGURE 20.9

The High Flux Isotope Reactor at Oak Ridge National Laboratory
The reactor in which transuranium isotopes are produced lies beneath a protecting pool of water. Visible light is emitted by high-energy particles moving through the water.

Radiations from nuclear processes affect matter in part by dissipating energy in it. An alpha, beta, or gamma particle traveling through matter dissipates energy by ionizing atoms or molecules, producing positive ions and electrons. In some cases, these radiations may also excite electrons in matter. When these electrons undergo transitions back to their ground states, light is emitted. The ions, free electrons, and light produced in matter can be used to detect nuclear radiations. Because nuclear radiations can ionize molecules and break chemical bonds, they adversely affect biological organisms. We will first look at the detection of nuclear radiations and then briefly discuss biological effects and radiation dosage in humans.

Radiation Counters

Two types of devices—*ionization counters* and *scintillation counters*—are used to count particles emitted from radioactive nuclei and other nuclear processes. Ionization counters detect the production of ions in matter. Scintillation counters detect the production of scintillations, or flashes of light.

A **Geiger counter** (Figure 20.10), *a kind of ionization counter used to count particles emitted by radioactive nuclei, consists of a metal tube filled with gas, such as argon.* The tube is fitted with a thin glass or plastic window through which radiation enters. A wire runs down the tube's center, from which the wire is insulated. The tube and wire are connected to a high-voltage source so that the tube becomes the negative electrode and the wire the positive electrode. Normally the gas in the tube is an insulator and no current flows through it. However, when radiation, such as an alpha particle, ${}^{4}_{2}\mathrm{He}^{2+}$, passes through the window of the tube and into the gas, atoms are ionized. Free electrons are quickly accelerated to the wire. As they are accelerated to the wire, additional atoms may be ionized from collisions with these electrons and more electrons set free. An avalanche of electrons is created, and this gives a pulse of current that is detected by electronic equipment. The amplified pulse activates a digital counter or gives an audible "click."

Alpha and beta particles can be detected directly by a Geiger counter. < To detect neutrons, boron trifluoride is added to the gas in the tube. Neutrons react with boron-10 nuclei to produce alpha particles, which can then be detected.

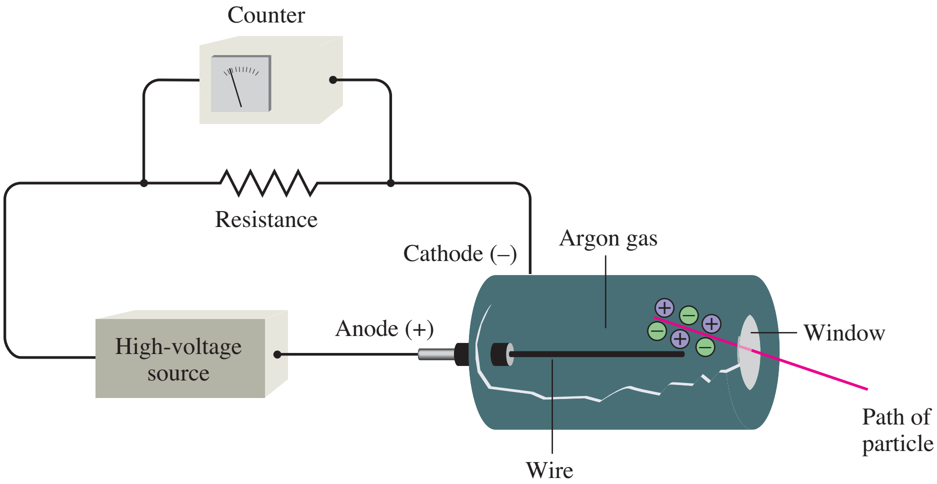
Gamma and low-energy alpha particles are better detected by scintillation counters. These counters are filled with solids or liquids, which are more likely to stop gamma rays. Also, low-energy alpha particles may be absorbed by the window of the Geiger counter and go undetected.

$$ {}^{1}_{0}\mathrm{n} + {}^{10}_{5}\mathrm{B} \longrightarrow {}^{7}_{3}\mathrm{Li} + {}^{4}_{2}\mathrm{He} $$

A **scintillation counter** (Figure 20.11) is *a device that detects nuclear radiation from flashes of light generated in a material by the radiation.* A *phosphor* is a substance that emits flashes of light when struck by radiation. Rutherford used zinc sulfide as a phosphor to detect alpha particles. A sodium iodide crystal containing thallium(I) iodide is used as a phosphor for gamma radiation. (Excited technetium-99

FIGURE 20.10

A Geiger counter
A particle of radiation enters the thin window and passes into the gas. Energy from the particle ionizes gas molecules, giving positive ions and electrons, which are accelerated to the electrodes. The electrons, which move faster, strike the wire anode and create a pulse of current. Pulses from radiation particles are counted.



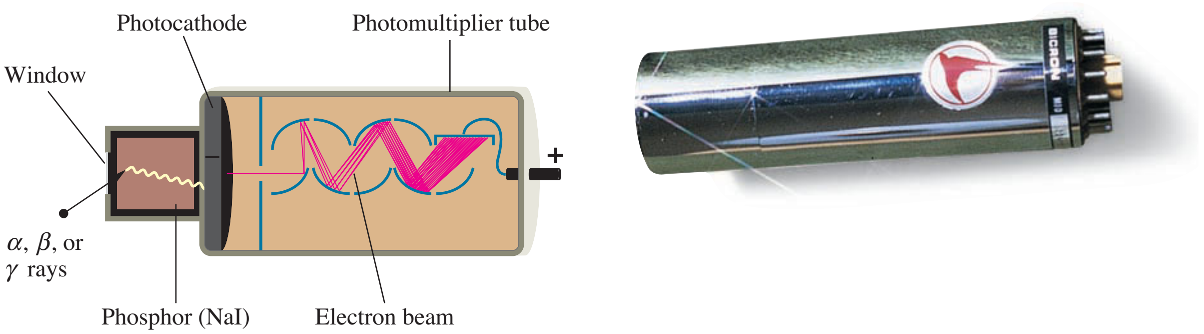


FIGURE 20.11

A scintillation counter probe

Left: Radiation passes through the window into a phosphor (here, NaI). Flashes of light from the phosphor fall on the photocathode, which ejects electrons by the photoelectric effect. The electrons are accelerated to electrodes of increasing positive voltage, each electrode ejecting more electrons, so that the original signal is magnified. *Right:* Photograph of a scintillation probe (the window is on the left).

emits gamma rays and is used for medical diagnostics. The gamma rays are detected by a scintillation counter.)

The flashes of light from the phosphor are detected by a *photomultiplier.* A photon of light from the phosphor hits a photoelectric-sensitive surface (the photocathode). < This emits an electron, which is accelerated by a positive voltage to another electrode, from which several electrons are emitted. These electrons are accelerated by a higher voltage to the next electrode, from which more electrons are emitted, and so forth. The result is that a single electron may produce a million electrons and therefore a detectable pulse of electric current.

The photoelectric effect was discussed in Section 7.2.

A radiation counter can be used to measure the rate of nuclear disintegrations in a radioactive material. The **activity of a radioactive source** is *the number of nuclear disintegrations per unit time occurring in a radioactive material.* A **curie (Ci)** is *a unit of activity equal to 3.700×10^{10} disintegrations per second.* < For example, a sample of technetium having an activity of 1.0×10^{-2} Ci is decaying at the rate of $(1.0 \times 10^{-2}) \times (3.7 \times 10^{10}) = 3.7 \times 10^{8}$ nuclei per second.

The curie was originally defined as the number of disintegrations per second from 1.0 g of radium-226.

Biological Effects and Radiation Dosage

Although the quantity of energy dissipated in a biological organism from a radiation dosage might be small, the effects can be quite damaging because important chemical bonds may be broken. DNA in the chromosomes of the cell is especially affected, which interferes with cell division (Figure 20.12). Cells that divide the fastest, such as those in the blood-forming tissue in bone marrow, are most affected by nuclear radiations.

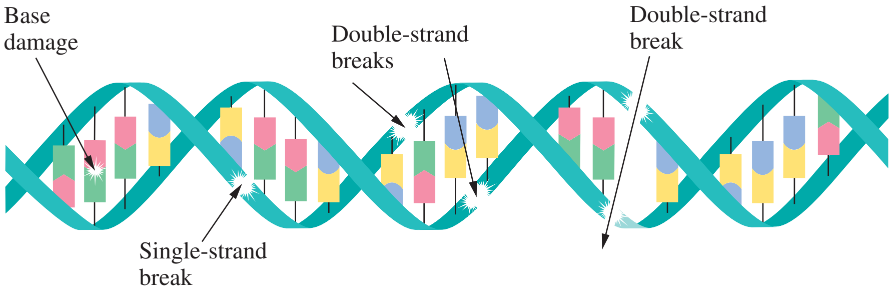
To monitor the effect of nuclear radiations on biological tissue, it is necessary to have a measure of radiation dosage. The **rad** (from *r*adiation *a*bsorbed *d*ose) is *the dosage of radiation that deposits 1×10^{-2} J of energy per kilogram of tissue.* However, the biological effect of radiation depends not only on the energy deposited in the tissue but also on the type of radiation. For example, neutrons are more destructive than gamma rays of the same radiation dosage measured in rads. A **rem** is *a unit of radiation dosage used to relate various kinds of radiation in terms of biological destruction. It equals the rad times a factor for the type of radiation, called the relative biological effectiveness (RBE).*

$$\text{rems} = \text{rads} \times \text{RBE}$$

FIGURE 20.12

Examples of damage to DNA from nuclear radiation

Damaged DNA can prevent cells from properly functioning and increase the likelihood of tumors.



Beta and gamma radiations have an RBE of about 1, whereas neutron radiation has an RBE of about 5 and alpha radiation an RBE of about 10. <

Sources of alpha radiation outside the body are relatively harmless, because the radiation is absorbed by the skin. Internal sources, however, are very destructive.

The effects of radiation on a person depend not only on the dosage but also on the length of time in which the dose was received. A series of small doses has less overall effect than these dosages given all at once. A single dose of about 500 rems is fatal to most people, and survival from a much smaller dose can be uncertain or leave the person chronically ill. Detectable effects are seen with doses as low as 30 rems. Continuous exposure to such low levels of radiation may result in cancer or leukemia. At even lower levels, whether the radiation dose is safe depends on the possible genetic effects of the radiation. Because radiation can cause chromosome damage, heritable defects are possible.

Safe limits for radiations are much debated. Although there may not be a strictly safe limit, it is important to have in mind the magnitude of the radiations humans may be subjected to. The background radiation we all receive results from cosmic rays (radiations from space) and natural radioactivity. This averages about 0.1 rem per year but varies considerably with location. Uranium and its decay products in the soil are an important source of background radiation. < Another source is potassium-40, a radioactive isotope with a natural abundance of 0.012%. In addition to natural background radiation, we may receive radiation from other fairly common sources. The most important of these are x rays used in medical diagnosis. The average person receives a radiation dose from this source that is about equal to that of the natural background. Very small radiation sources include consumer items such as television sets and luminous watches.

Soils contain varying amounts of uranium-238, which decays in several steps to radium-226, then to radon-222, a gas (see Figure 20.5). Some homes situated in areas of high uranium content have been found to accumulate radon gas. Radon has a half-life of 3.8 days, decaying by alpha emission to radioactive lead, bismuth, and polonium. These decay products can remain in the lungs and may lead to lung cancer.

The background radiation to which we are all subjected has increased slightly since the advent of nuclear technology. Fallout from atmospheric testing of nuclear weapons increased this background by several percent, but it has decreased since atmospheric testing was banned. The radiation contributed by nuclear power plants is only a fraction of a percent of the natural background.

Concept Check 20.2

If you are internally exposed to 10 rads of α, β, and γ radiation, which form of radiation will cause the greatest biological damage?

20.4 Rate of Radioactive Decay

Although technetium-99 is radioactive and decays by emitting beta particles (electrons), it is impossible to say when a particular nucleus will disintegrate. A sample of technetium-99 continues to give off beta rays for millions of years. Thus, a particular nucleus might disintegrate the next instant or several million years later. The rate of this radioactive decay cannot be changed by varying the temperature, the pressure, or the chemical environment of the technetium nucleus. Radioactivity, whether from technetium or some other nucleus, is not affected by the variables that affect the rate of a chemical reaction. In this section, we will look at how to express quantitatively the rate of radioactive decay.

Rate of Radioactive Decay and Half-Life

The rate of radioactive decay—that is, the number of nuclei disintegrating per unit time—is found to be proportional to the number of radioactive nuclei in the sample. You can express this rate mathematically as

$$\text{Rate} = kN_t$$

Here N_t is the number of radioactive nuclei at time t, and k is the **radioactive decay constant,** or *rate constant for radioactive decay.* This rate constant is a characteristic of the radioactive nuclide, each nuclide having a different value. <

The rate equation for radioactive decay has the same form as the rate law for a first-order chemical reaction. Indeed, radioactive decay is a first-order rate process, and the mathematical relationships used in Chapter 13 for first-order reactions apply here also.

You can obtain the decay constant for a radioactive nucleus by counting the nuclear disintegrations over a period of time. The original definition of the curie (now 3.7×10^{10} disintegrations per second) was the activity or decay rate of 1.0 g of radium-226. You can use this with the rate equation to obtain the decay constant of radium-226. Radium-226 has a molar mass of 226 g. A 1.0-g sample of radium-226 contains the following number of nuclei:

$$1.0\text{ g Ra-226} \times \frac{1\text{ mol Ra-226}}{226\text{ g Ra-226}} \times \frac{6.02 \times 10^{23}\text{ Ra-226 nuclei}}{1\text{ mol Ra-226}} = 2.7 \times 10^{21}\text{ Ra-226 nuclei}$$

This equals the value of N_t. When you solve Rate $= kN_t$ for k, you get

$$k = \frac{\text{rate}}{N_t}$$

Substituting into this gives

Recall from Chapter 7 that /s is equivalent to the unit s^{-1}.

$$k = \frac{3.7 \times 10^{10}\text{ nuclei/s}}{2.7 \times 10^{21}\text{ nuclei}} = 1.4 \times 10^{-11}\text{/s} <$$

Example 20.7 Calculating the Decay Constant from the Activity

A 1.0-mg sample of technetium-99 has an activity of 1.7×10^{-5} Ci (Ci = curies), decaying by beta emission. What is the decay constant for ${}^{99}_{43}\text{Tc}$?

Problem Strategy Solve the equation Rate $= kN_t$ for k; obtain Rate and N_t from values in the problem statement. The rate of decay (Rate) of Tc-99 equals the activity in curies expressed as nuclei decaying per second, noting that 1 Ci $= 3.7 \times 10^{10}$ nuclei/s. Obtain the number of Tc-99 nuclei, N_t, by converting 1.0×10^{-3} g of Tc-99 as follows:

$$\text{g Tc-99} \longrightarrow \text{mol Tc-99} \longrightarrow \text{number Tc-99 nuclei}$$

For the first conversion, note that the numerical value of the molar mass of Tc-99 is approximately equal to the mass number of Tc(99).

Solution The rate of decay in this sample is

$$\text{Rate} = 1.7 \times 10^{-5}\text{ Ci} \times \frac{3.7 \times 10^{10}\text{ nuclei/s}}{1.0\text{ Ci}} = 6.3 \times 10^{5}\text{ nuclei/s}$$

The number of nuclei in this sample of 1.0×10^{-3} g ${}^{99}_{43}\text{Tc}$ is

$$1.0 \times 10^{-3}\text{ g Tc-99} \times \frac{1\text{ mol Tc-99}}{99\text{ g Tc-99}} \times \frac{6.02 \times 10^{23}\text{ Tc-99 nuclei}}{1\text{ mol Tc-99}}$$
$$= 6.1 \times 10^{18}\text{ Tc-99 nuclei}$$

The decay constant is

$$k = \frac{\text{rate}}{N_t} = \frac{6.3 \times 10^{5}\text{ nuclei/s}}{6.1 \times 10^{18}\text{ nuclei}} = \mathbf{1.0 \times 10^{-13}/s}$$

Answer Check You should typically expect decay constants to range from 10^{-16}/s to 10^{-3}/s, so anything outside this range should be carefully checked.

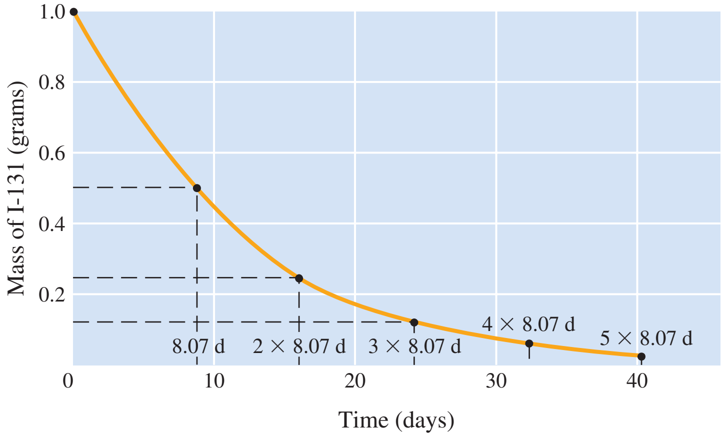
Exercise 20.7 The nucleus ${}^{99m}_{43}\text{Tc}$ is a metastable nucleus of technetium-99; it is used in medical diagnostic work. Technetium-99*m* decays by emitting gamma rays. A 2.5-μg (microgram) sample has an activity of 13 Ci. What is the decay constant (in units of /s)?

■ See Problems 20.57, 20.58, 20.59, and 20.60.

FIGURE 20.13

Radioactive decay of a 1.000-g sample of iodine-131

The sample decays by one-half in each half-life of 8.07 days.



The half-life of a reaction was discussed in Section 13.4.

Iodine is attracted to the thyroid gland, which incorporates the element into the growth hormone thyroxine. Radiation from iodine-131 kills cancer cells in the thyroid gland.

We define the **half-life** of a radioactive nucleus as *the time it takes for one-half of the nuclei in a sample to decay.* < The half-life is independent of the amount of sample. In some cases, you can find the half-life of a radioactive sample by directly observing how long it takes for one-half of the sample to decay. For example, you find that 1.000 g of iodine-131, an isotope used in treating thyroid cancer, decays to 0.500 g in 8.07 days. < Thus, its half-life is 8.07 days. In another 8.07 days, this sample would decay to one-half of 0.500 g, or 0.250 g, and so forth. Figure 20.13 shows this decay pattern.

Although you might be able to obtain the half-life of a radioactive nucleus by direct observation in some cases, this is impossible for many nuclei because they decay too quickly or too slowly. Uranium-238, for example, has a half-life of 4.51 billion years, much too long to be directly observed! The usual method of determining the half-life is by measuring decay rates and relating them to half-lives.

You relate the half-life for radioactive decay, $t_{1/2}$, to the decay constant k by the equation

$$t_{1/2} = \frac{0.693}{k}$$

The next example illustrates the use of this relation.

Example 20.8 Calculating the Half-Life from the Decay Constant

The decay constant for the beta decay of ${}^{99}_{43}\mathrm{Tc}$ was obtained in Example 20.7. We found that k equals 1.0×10^{-13}/s. What is the half-life of this isotope in years?

Problem Strategy Because the decay constant is given in the problem, the preceding equation can be used to calculate the half-life ($t_{1/2}$) from k.

Solution Substitute the value of k into the preceding equation.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.0 \times 10^{-13}/\text{s}} = 6.9 \times 10^{12}\ \text{s}$$

Then you convert this half-life in seconds to years.

$$6.9 \times 10^{12}\ \text{s} \times \frac{1\ \text{min}}{60\ \text{s}} \times \frac{1\ \text{h}}{60\ \text{min}} \times \frac{1\ \text{d}}{24\ \text{h}} \times \frac{1\ \text{y}}{365\ \text{d}} = \mathbf{2.2 \times 10^5\ y}$$

(*continued*)

(continued)

Answer Check Note the inverse relationship between the decay constant and the half-life; those compounds with very small decay constants have very long half-lives.

Exercise 20.8 Cobalt-60, used in cancer therapy, decays by beta and gamma emission. The decay constant is 4.18×10^{-9}/s. What is the half-life in years?

■ See Problems 20.61 and 20.62.

Tables of radioactive nuclei often list the half-life. When you want the decay constant or the activity of a sample, you can calculate them from the half-life. This calculation is illustrated in the next example.

Example 20.9 Calculating the Decay Constant and Activity from the Half-Life

Tritium, ${}^{3}_{1}\text{H}$, is a radioactive nucleus of hydrogen. It is used in luminous watch dials. Tritium decays by beta emission with a half-life of 12.3 years. What is the decay constant (in /s)? What is the activity (in Ci) of a sample containing 2.5 μg of tritium? The atomic mass of ${}^{3}_{1}\text{H}$ is 3.02 amu.

Problem Strategy First convert the half-life to its value in seconds and then calculate k. Then you can use the rate equation to find the rate of decay of the sample (in nuclei/s) and finally the activity.

Solution The conversion of the half-life to seconds gives

$$12.3 \text{ y} \times \frac{365 \text{ d}}{1 \text{ y}} \times \frac{24 \text{ h}}{1 \text{ d}} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{60 \text{ s}}{1 \text{ min}} = 3.88 \times 10^{8} \text{ s}$$

Because $t_{1/2} = 0.693/k$, you solve this for k and substitute the half-life in seconds.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3.88 \times 10^{8} \text{ s}} = \mathbf{1.79 \times 10^{-9}/s}$$

Before substituting into the rate equation, you need to know the number of tritium nuclei in a sample containing 2.5×10^{-6} g of tritium. You get

$$2.5 \times 10^{-6} \text{ g H-3} \times \frac{1 \text{ mol H-3}}{3.02 \text{ g H-3}} \times \frac{6.02 \times 10^{23} \text{ H-3 nuclei}}{1 \text{ mol H-3}} = 5.0 \times 10^{17} \text{ H-3 nuclei}$$

Now you substitute into the rate equation.

$$\text{Rate} = kN_t = 1.79 \times 10^{-9}/\text{s} \times 5.0 \times 10^{17} \text{ nuclei} = 9.0 \times 10^{8} \text{ nuclei/s}$$

You obtain the activity of the sample by converting the rate in disintegrations of nuclei per second to curies.

$$\text{Activity} = 9.0 \times 10^{8} \text{ nuclei/s} \times \frac{1.0 \text{ Ci}}{3.7 \times 10^{10} \text{ nuclei/s}} = \mathbf{0.024 \text{ Ci}}$$

Answer Check Note that the answer is a relatively small activity (0.024 Ci). If we consider the very small size of the sample of tritium (2.5 μg), we should expect an answer of this magnitude.

(continued)

(*continued*)

Exercise 20.9 Strontium-90, $^{90}_{38}Sr$, is a radioactive decay product of nuclear fallout from nuclear weapons testing. Because of its chemical similarity to calcium, it is incorporated into the bones if present in food. The half-life of strontium-90 is 28.1 y. What is the decay constant of this isotope? What is the activity of a sample containing 5.2 ng (5.2×10^{-9} g) of strontium-90?

■ See Problems 20.63, 20.64, 20.65, and 20.66.

Once you know the decay constant for a radioactive isotope, you can calculate the fraction of the radioactive nuclei that remains after a given period of time by the following equation. <

A similar equation is given in Chapter 13 for the reactant concentration at time t, $[A]_t$

$$\ln \frac{[A]_t}{[A]_o} = -kt$$

where $[A]_0$ is the concentration of A at t = 0.

$$\ln \frac{N_t}{N_0} = -kt$$

Here N_0 is the number of nuclei in the original sample ($t = 0$). After a period of time t, the number of nuclei decreases by decay to the number N_t. The fraction of nuclei remaining after time t is N_t/N_0. The next example illustrates the use of this equation.

Example 20.10 Determining the Fraction of Nuclei Remaining after a Specified Time

Phosphorus-32 is a radioactive isotope with a half-life of 14.3 d (d = days). A biochemist has a vial containing a compound of phosphorus-32. If the compound is used in an experiment 5.5 d after the compound was prepared, what fraction of the radioactive isotope originally present remains? Suppose the sample in the vial originally contained 0.28 g of phosphorus-32. How many grams remain after 5.5 d?

Problem Strategy In the first part of the problem, we are asked to determine what fractional amount of radioactive P-32 in a compound remains after 5.5 d. For this, we can use the preceding equation. Once we know the fractional amount of P-32 that remains, we can multiply this quantity by the original amount of compound (0.28 g) to find the mass of compound that remains after 5.5 d.

Solution If N_0 is the original number of P-32 nuclei in the vial and N_t is the number after 5.5 d, the fraction remaining is N_t/N_0. You can obtain this fraction from the equation

$$\ln \frac{N_t}{N_0} = -kt$$

You substitute $k = 0.693/t_{1/2}$.

$$\ln \frac{N_t}{N_0} = \frac{-0.693t}{t_{1/2}}$$

Because $t = 5.5$ d and $t_{1/2} = 14.3$ d, you obtain

$$\ln \frac{N_t}{N_0} = \frac{-0.693 \times 5.5\ \text{d}}{14.3\ \text{d}} = -0.267$$

(*continued*)

(*continued*)

(An additional digit has been retained for further calculation.) Hence,

$$\text{Fraction nuclei remaining} = \frac{N_t}{N_0} = e^{-0.267} = \mathbf{0.77}$$

(Note that 0.766 is rounded to two significant figures.) Thus, 77% of the nuclei remain. The mass of ${}^{32}_{15}P$ in the vial after 5.5 d is

$$0.28 \text{ g} \times 0.766 = \mathbf{0.21 \text{ g}}$$

Answer Check After one half-life of 14.3 days, only one-half of the sample would be left. Since only 5.5 days have elapsed, which is less than the half-life, you should expect less than half of the 0.28 g sample to have decayed. This means that there should be more than 0.14 g remaining, which is the case. For any problems of this type, this approach is an effective method for quickly checking your answers.

Exercise 20.10 A nuclear power plant emits into the atmosphere a very small amount of krypton-85, a radioactive isotope with a half-life of 10.76 y. What fraction of this krypton-85 remains after 25.0 y?

■ See Problems 20.69 and 20.70.

Radioactive Dating

Fixing the dates of relics and stone implements or pieces of charcoal from ancient campsites is an application based on radioactive decay rates. Because the rate of radioactive decay of a nuclide is constant, this rate can serve as a clock for dating very old rocks and human implements. Dating wood and similar carbon-containing objects that are several thousand to fifty thousand years old can be done with radioactive carbon, carbon-14, which has a half-life of 5730 y.

Carbon-14 is present in the atmosphere as a result of cosmic-ray bombardment of earth. Cosmic rays are radiations from space that consist of protons and alpha particles, as well as heavier ions. These radiations produce other kinds of particles, including neutrons, as they bombard the upper atmosphere. The collision of a neutron with a nitrogen-14 nucleus (the most abundant nitrogen nuclide) can produce a carbon-14 nucleus.

$${}^{14}_{7}N + {}^{1}_{0}n \longrightarrow {}^{14}_{6}C + {}^{1}_{1}H$$

Carbon dioxide containing carbon-14 mixes with the lower atmosphere. Because of the constant production of ${}^{14}_{6}C$ and its radioactive decay, a small, constant fractional abundance of carbon-14 is maintained in the atmosphere.

Living plants, which continuously use atmospheric carbon dioxide, also maintain a constant abundance of carbon-14. Similarly, living animals, by feeding on plants, have a constant fractional abundance of carbon-14. But once an organism dies, it is no longer in chemical equilibrium with atmospheric CO_2. The ratio of carbon-14 to carbon-12 begins to decrease by radioactive decay of carbon-14. In this way, this ratio of carbon isotopes becomes a clock measuring the time since the death of the organism.

If you assume that the ratio of carbon isotopes in the lower atmosphere has remained at the present level for the last 50,000 years (presently 1 out of 10^{12} carbon atoms is carbon-14), you can deduce the age of any dead organic object by measuring the level of beta emissions that arise from the radioactive decay of carbon-14. < This is the decay reaction:

Analyses of tree rings have shown that this assumption is not quite valid. Before 1000 B.C., the levels of carbon-14 were somewhat higher than they are today. Moreover, recent human activities (burning of fossil fuels and atmospheric nuclear testing) have changed the fraction of carbon-14 in atmospheric CO_2.

$${}^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e$$

In this way, bits of campfire charcoal, parchment, jawbones, and the like have been dated.

Example 20.11 Applying the Carbon-14 Dating Method

A piece of charcoal from a tree killed by the volcanic eruption that formed the crater in Crater Lake (in Oregon) gave 7.0 disintegrations of carbon-14 nuclei per minute per gram of total carbon. Present-day carbon (in living matter) gives 15.3 disintegrations per minute per gram of total carbon. Determine the date of the volcanic eruption. Recall that the half-life of carbon-14 is 5730 y.

Problem Strategy You substitute $k = 0.693/t_{1/2}$ into the equation for the number of nuclei in a sample after time t.

$$\ln\frac{N_t}{N_0} = -kt = \frac{-0.693t}{t_{1/2}}$$

Hence,

$$t = \frac{t_{1/2}}{0.693}\ln\frac{N_0}{N_t}$$

To get N_0/N_t, you assume that the ratio of $^{14}_{6}C$ to $^{12}_{6}C$ in the atmosphere has remained constant. Then you can say that 1.00 g of total carbon from the living tree gave 15.3 disintegrations per minute. The ratio of the number of $^{14}_{6}C$ nuclei originally present to the number that existed at the time of dating equals the ratio of rates of disintegration.

Solution The ratio of rates of disintegration is

$$\frac{N_0}{N_t} = \frac{15.3}{7.0} = 2.2$$

Substituting this value of N_0/N_t and $t_{1/2} = 5730$ y into the equation developed in the Problem Strategy gives

$$t = \frac{t_{1/2}}{0.693}\ln\frac{N_0}{N_t} = \frac{5730\text{ y}}{0.693}\ln 2.2 = 6.5 \times 10^3\text{ y}$$

Thus, the date of the eruption was about **4500 B.C.,** 6500 years ago.

Answer Check You can obtain a quick check by comparing the disintegration rate expected after various half-lives. For example, the original rate is 15.3 disintegrations per minute, whereas the rate after half the sample decays is one-half this, or 7.6 disintegrations per minute. (After two half-lives, the disintegration rate is one-half of 7.6, or 3.8 disintegrations per minute.) Thus, a rate of 7.0 disintegrations per minute is expected to occur at a time somewhat greater than the half-life of carbon-14 (that is, somewhat greater than 5730 y).

Exercise 20.11 A jawbone from the archaeological site at Folsom, New Mexico, was dated by analysis of its radioactive carbon. The activity of the carbon from the jawbone was 4.5 disintegrations per minute per gram of total carbon. What was the age of the jawbone? Carbon from living material gives 15.3 disintegrations per minute per gram of carbon.

■ See Problems 20.75 and 20.76.

For the age of rocks and meteorites, other, similar methods of dating have been used. One method depends on the radioactivity of naturally occurring potassium-40, which decays by positron emission and electron capture (as well as by beta emission).

$$^{40}_{19}K \longrightarrow {}^{40}_{18}Ar + {}^{0}_{1}e$$

$$^{40}_{19}K + {}^{0}_{-1}e \longrightarrow {}^{40}_{18}Ar$$

Potassium occurs in many rocks. Once such a rock forms by solidification of molten material, the argon from the decay of potassium-40 is trapped. To obtain the age of a rock, you first determine the number of $^{40}_{19}K$ atoms and the number of $^{40}_{18}Ar$ atoms in a sample. The number of $^{40}_{19}K$ atoms equals N_t. The number originally present, N_0, equals N_t plus the number of argon atoms, because each argon atom resulted from the decay of a $^{40}_{19}K$ nucleus. You then calculate the age of the rock from the ratio N_t/N_0.

The oldest rocks on earth have been dated at 3.8×10^9 y. The rocks at the earth's surface have been subjected to extensive weathering, so even older rocks may have existed. This age, 3.8×10^9 y, therefore represents the minimum possible age of the earth—the time since the solid crust first formed. Ages of meteorites, assumed to have solidified at the same time as other solid objects in the solar system, including earth, have been determined to be 4.4×10^9 y to 4.6×10^9 y. It is now believed from this and other evidence that the age of the earth is 4.6×10^9 y.

Concept Check 20.3

Why do you think that carbon-14 dating is limited to less than 50,000 years?

20.5 Applications of Radioactive Isotopes

We have already described two applications of nuclear chemistry. One was the preparation of elements not available naturally. We noted that the discovery of the transuranium elements clarified the position of the heavy elements in the periodic table. In the section just completed, we discussed the use of radioactivity in dating objects. We will discuss practical uses of nuclear energy later in the chapter. Here we will look at the applications of radioactive isotopes to chemical analysis and to medicine.

Chemical Analysis

A **radioactive tracer** is *a very small amount of radioactive isotope added to a chemical, biological, or physical system to study the system.* The advantage of a radioactive tracer is that it behaves chemically just as a nonradioactive isotope does, but it can be detected in exceedingly small amounts by measuring the radiations emitted.

As an illustration of the use of radioactive tracers, consider the problem of establishing that chemical equilibrium is a dynamic process. Let us look at the equilibrium of solid lead(II) iodide and its saturated solution, containing $Pb^{2+}(aq)$ and $I^-(aq)$. The equilibrium is

$$PbI_2(s) \xrightleftharpoons{H_2O} Pb^{2+}(aq) + 2I^-(aq)$$

In two separate beakers, you prepare saturated solutions of PbI_2 in contact with the solid. One beaker contains only natural iodine atoms with nonradioactive isotopes. The other beaker contains radioactive iodide ion, $^{131}I^-$. Some of the solution, but no solid, containing the radioactive iodide ion is now added to the beaker containing nonradioactive iodide ion. Both solutions are saturated, so the amount of solid in this beaker remains constant. Yet after a time the solid lead iodide, which was originally nonradioactive, becomes radioactive. This is evidence for a dynamic equilibrium, in which radioactive iodide ions in the solution substitute for nonradioactive iodide ions in the solid.

With only naturally occurring iodine available, it would have been impossible to detect the dynamic equilibrium. By using $^{131}I^-$ as a radioactive tracer, you can easily follow the substitution of radioactive iodine into the solid by measuring its increase in radioactivity.

Melvin Calvin received the Nobel Prize in Chemistry in 1961 for his work on photosynthesis.

A series of experiments using tracers was carried out in the late 1950s by Melvin Calvin at the University of California, Berkeley, to discover the mechanism of photosynthesis in plants. < The overall process of photosynthesis involves the reaction of CO_2 and H_2O to give glucose, $C_6H_{12}O_6$, and O_2. Energy for photosynthesis comes from the sun.

$$6CO_2(g) + 6H_2O(l) \xrightarrow{\text{sunlight}} C_6H_{12}O_6(aq) + 6O_2(g)$$

Chromatography was discussed in the essay at the end of Section 1.4.

This equation represents only the net result of photosynthesis. As Calvin was able to show, the actual process consists of many separate steps. In several experiments, algae (single-celled plants) were exposed to carbon dioxide containing much more radioactive carbon-14 than occurs naturally. Then the algae were extracted with a solution of alcohol and water. The various compounds in this solution were separated by chromatography and identified. < Compounds that contained radioactive carbon were produced in the different steps of photosynthesis. Eventually, Calvin was able to use tracers to show the main steps in photosynthesis.

Another example of the use of radioactive tracers in chemistry is **isotope dilution,** *a technique to determine the quantity of a substance in a mixture or of the total volume* *of solution by adding a known amount of an isotope to it.* After removal of a portion of the mixture, the fraction by which the isotope has been diluted provides a way of determining the quantity of substance or volume of solution.

As an example, suppose you wish to obtain the volume of water in a tank but are unable to drain the tank. You add 100 mL of water containing a radioactive isotope. After allowing this to mix completely with the water in the tank, you withdraw 100 mL of solution from the tank. You find that the activity of this solution in curies is 1/1000 that of the original radioactive solution. The isotope has been diluted by a factor of 1000, so the volume of the tank is 1000 × 100 mL = 100,000 mL (100 L).

A typical chemical example of isotope dilution is the determination of the amount of vitamin B_{12}, a cobalt-containing substance, in a sample of food. Although part of the vitamin in food can be obtained in pure form, not all of the vitamin can be separated. Therefore, you cannot precisely determine the quantity of vitamin B_{12} in a sample of food by separating the pure vitamin and weighing it. But you can determine the amount of vitamin B_{12} by isotope dilution. Suppose you add 2.0×10^{-7} g of vitamin B_{12} containing radioactive cobalt-60 to 125 g of food and mix well. You then separate 5.4×10^{-7} g of pure vitamin B_{12} from the food and find that the activity in curies of this quantity of the vitamin contains 5.6% of the activity added from the radioactive cobalt. This indicates that you have recovered 5.6% of the total amount of vitamin B_{12} in the sample. Therefore, the mass of vitamin B_{12} in the food, including the amount added (2.0×10^{-7} g), is

$$5.4 \times 10^{-7}\ \text{g} \times \frac{100}{5.6} = 9.6 \times 10^{-6}\ \text{g}$$

Subtracting the amount added in the analysis gives

$$9.6 \times 10^{-6}\ \text{g} - 2.0 \times 10^{-7}\ \text{g} = 9.4 \times 10^{-6}\ \text{g}$$

Neutron activation analysis is *an analysis of elements in a sample based on the conversion of stable isotopes to radioactive isotopes by bombarding a sample with neutrons.* Human hair contains trace amounts of many elements. By determining the exact amounts and the position of the elements in the hair shaft, you can identify whom the hair comes from (assuming you have a sample known to be that person's hair for comparison). Consider the analysis of human hair for arsenic, for example. When the natural isotope $^{75}_{33}\text{As}$ is bombarded with neutrons, a metastable nucleus $^{76m}_{33}\text{As}$ is obtained.

$$^{75}_{33}\text{As} + {}^{1}_{0}\text{n} \longrightarrow {}^{76m}_{33}\text{As}$$

A metastable nucleus is in an excited state. It decays, or undergoes a transition, to a lower state by emitting gamma rays. The frequencies, or energies, of the gamma rays emitted are characteristic of the element and serve to identify it. Also, the intensities of the gamma rays emitted are proportional to the amount of the element present. The method is very sensitive; it can identify as little as 10^{-9} g of arsenic. <

Neutron activation analysis has been used to authenticate oil paintings by giving an exact analysis of pigments used. Pigment compositions have changed, so it is possible to detect fraudulent paintings done with more modern pigments. The analysis can be done without affecting the painting.

Medical Therapy and Diagnosis

The use of radioactive isotopes has had a profound effect on the practice of medicine. Radioisotopes were first used in medicine in the treatment of cancer. This treatment is based on the fact that rapidly dividing cells, such as those in cancer, are more adversely affected by radiation from radioactive substances than are cells that divide more slowly. Radium-226 and its decay product radon-222 were used for cancer therapy a few years after the discovery of radioactivity. Today gamma radiation from cobalt-60 is more commonly used.

Cancer therapy is only one of the ways in which radioactive isotopes are used in medicine. The greatest advances in the use of radioactive isotopes have been in the diagnosis of disease. Radioactive isotopes are used for diagnosis in two ways. They are used to develop images of internal body organs so that their functioning can be

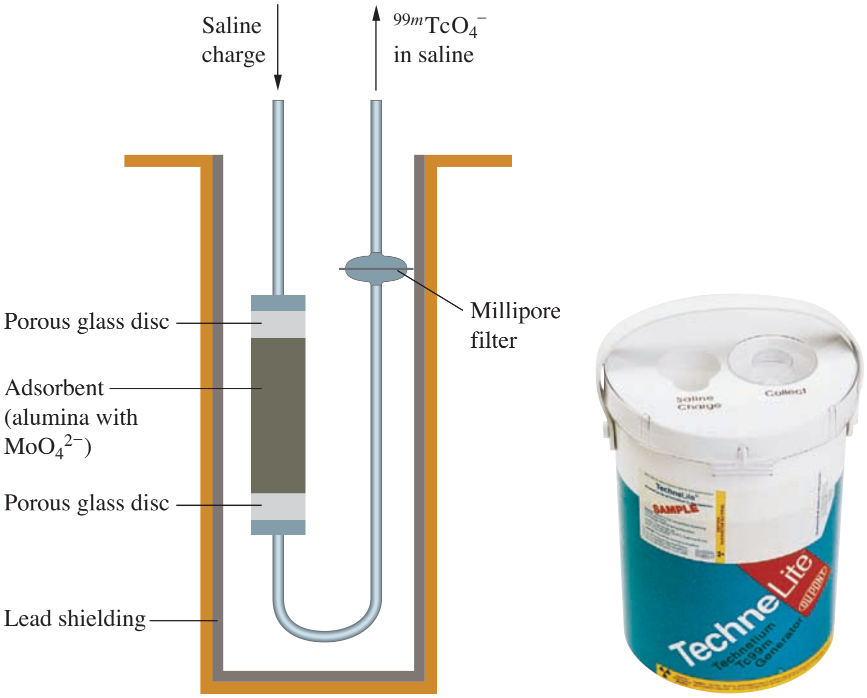


FIGURE 20.14

A technetium-99*m* generator
Left: A conceptual view of the generator. Molybdenum-99, in the form of MoO_4^{2-} ion adsorbed on alumina, decays to technetium-99*m*. The technetium is leached from the generator with a salt solution (saline charge) as TcO_4^-. *Right:* Photograph of a technetium-99*m* generator, with lead case and vials of saline charge.

examined. And they are used as tracers in the analysis of minute amounts of substances, such as a growth hormone in blood, to deduce possible disease conditions.

Technetium-99*m* is the radioactive isotope used most often to develop images (pictures) of internal body organs. It has a half-life of 6.02 h, decaying by gamma emission to technetium-99 in its nuclear ground state. The image is prepared by scanning part of the body for gamma rays with a scintillation detector. (Figure 20.1 shows the image of a person's skeleton obtained with technetium-99*m*.)

The technetium isotope is produced in a special container, or generator, shown in Figure 20.14. The generator contains radioactive molybdate ion, MoO_4^{2-}, adsorbed on alumina granules. Radioactive molybdenum-99 is produced from uranium-235 nuclear fission products (see Section 20.7). This radioactive molybdenum, adsorbed on alumina, is placed in the generator and sent to the hospital. Pertechnetate ion is obtained when the molybdenum-99 nucleus in MoO_4^{2-} decays. The nuclear equation is

$$^{99}_{42}\text{Mo} \longrightarrow {}^{99m}_{43}\text{Tc} + {}^{0}_{-1}\text{e}$$

Each day pertechnetate ion, TcO_4^-, is leached from the generator with a salt solution whose osmotic pressure is the same as that of blood. One use of this pertechnetate ion is in assessing the performance of a patient's heart. The physician injects tin(II) ion into a vein and, a few minutes later, administers a similar injection of the pertechnetate ion. In the presence of tin(II) ion, the pertechnetate ion binds to the red blood cells. The heart then becomes visible in gamma-ray imaging equipment, because of the quantity of blood in the heart. Technetium-99*m* pyrophosphate ($Tc_2P_2O_7$) is another technetium species useful for gamma-ray imaging. This compound binds especially strongly to recently damaged heart muscle, so these gamma-ray images can be used to assess the extent of damage from a heart attack.

Thallium-201 is a radioisotope used to determine whether a person has heart disease (caused by narrowing of the arteries to the heart). This isotope decays by electron capture and emits x rays and gamma rays, which can be used to obtain images similar to those obtained from technetium-99*m* (Figure 20.15). Thallium-201 injected into the blood binds particularly strongly to heart muscle. Diagnosis of heart disease depends on the fact that only tissue that receives sufficient blood flow binds thallium-201. When someone exercises strenuously, some part of the person's heart tissue may not receive

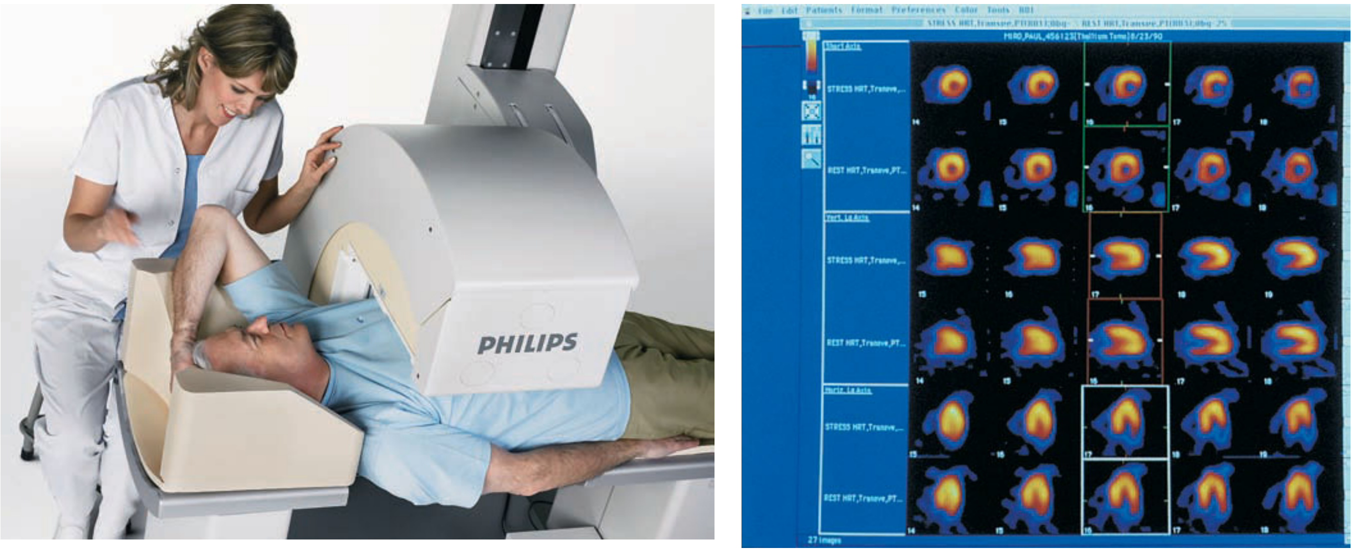


FIGURE 20.15

Using thallium-201 to diagnose heart disease
Left: A nuclear camera system used to detect the gamma emissions from thallium-201 or technetium-99*m* for cardiac studies. *Right:* A series of cross-sectional images of a patient's heart after exercise (labeled "stress") and then some time afterward (labeled "rest"). By comparing the stress and rest images, a physician can see if there is impaired blood flow to an area of the heart (the area is dark in the stress image but light in the rest image) or if the heart muscle has been damaged through a heart attack (the area is dark in both stress and rest images).

sufficient blood because of narrowed arteries. These areas do not bind thallium-201 and show up on an image as dark spots.

More than a hundred different radioactive isotopes have been used in medicine. Besides technetium-99*m* and thallium-201, other examples include iodine-131, used to measure thyroid activity; phosphorus-32, used to locate tumors; and iron-59, used to measure the rate of formation of red blood cells.

Radioimmunoassay is a technique for analyzing blood and other body fluids for very small quantities of biologically active substances. The technique depends on the reversible binding of the substance to an antibody. Antibodies are produced in animals as protection against foreign substances. They protect by binding to the substance and countering its biological activity. Consider, for example, the analysis for insulin in a sample of blood from a patient. Before the analysis, a solution of insulin-binding antibodies has been prepared from laboratory animals. This solution is combined with insulin containing a radioactive isotope, in which the antibodies bind with radioactive insulin. Now the blood sample containing an unknown amount of insulin is added to the antibody–radioactive insulin mixture. The nonradioactive insulin replaces some of the radioactive insulin bound to the antibody. As a result, the antibody loses some of its radioactivity. The loss in radioactivity can be related to the amount of insulin in the blood sample.

Energy of Nuclear Reactions

Nuclear reactions, like chemical reactions, involve changes of energy. However, the changes of energy in nuclear reactions are enormous by comparison with those in chemical reactions. The energy released by certain nuclear reactions is used in nuclear power reactors and to provide the energy for nuclear weapons. In the case of a power

A Chemist Looks at . . .

Positron Emission Tomography (PET)

Positron emission tomography (PET) is a technique for following biochemical processes within the organs (brain, heart, and so forth) of the human body. Like magnetic resonance imaging (see essay at the end of Section 8.1), a PET scan produces an image of a two-dimensional slice through a body organ of a patient. The image shows the distribution of some positron-emitting isotope present in a compound that was administered earlier by injection. By comparing the PET scan of the patient with that of a healthy subject, a physician can diagnose the presence or absence of disease (Figure 20.16). The PET scan of the brain of an Alzheimer's patient differs markedly from that of a healthy subject. Similarly, the PET scan of a patient with a heart damaged by a coronary attack clearly shows the damaged area. Moreover, the PET scan may help the physician assess the likelihood of success of by-pass surgery.

Some isotopes used in PET scans are carbon-11, nitrogen-13, oxygen-15, and fluorine-18. All have short half-lives, so the radiation dosage to the patient is minimal. However, because of the short half-life, a chemist must prepare the diagnostic compound containing the radioactive nucleus shortly before the physician administers it. The preparation of this compound requires a cyclotron, whose cost (several million dollars) is a major deterrent to the general use of PET scans.

Figure 20.17 shows a patient undergoing a PET scan of the brain. The instrument actually detects gamma radiation. When a nucleus emits a positron within the body, the positron travels only a few millimeters before it reacts with an electron. This reaction is an example of the annihilation of matter (an electron) by antimatter (a positron). Both the electron and the positron disappear and produce two gamma photons. The gamma photons easily pass through human tissue, so they can be recorded by scintillation detectors placed around the body. You can see the circular bank of detectors in Figure 20.17. The detectors record the distribution of gamma radiation, and from this information a computer constructs images that can be used by the physician.

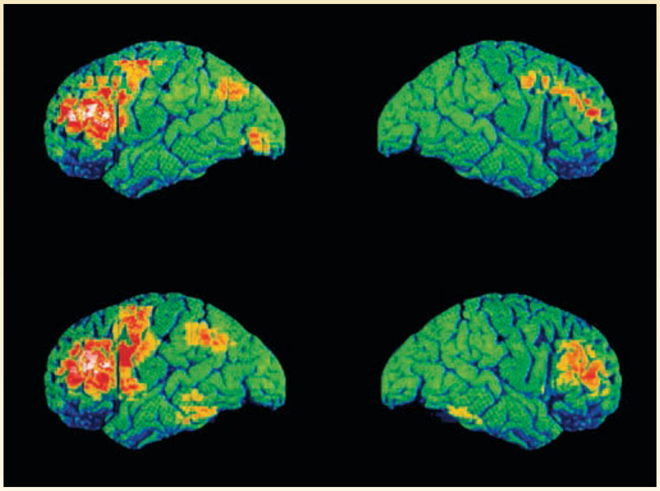


FIGURE 20.16 ▲

PET scans of normal and schizophrenic patients

Colored positron emission tomography (PET) brain scans of a schizophrenic (bottom) versus normal patient (top), speaking. The red/yellow highlighted areas are active when patients generate words. In the schizophrenic brain, there is additional brain activity not seen in normal subjects. Schizophrenic patients can suffer from delusions and depression.

FIGURE 20.17 ▲

A patient undergoing a PET scan of the brain

Note the circular bank of gamma-ray detectors.

■ See Problems 20.105 and 20.106.

plant, the energy from the reactions is released in controlled, small amounts by the fission of uranium-235. With a nuclear weapon, the objective is to release the energy as rapidly as possible and produce a nuclear explosion. Although the source of energy for nuclear power plants and weapons can be the same, a typical nuclear power plant does not contain enough fissionable material in high enough concentration to produce a nuclear explosion.

20.6 Mass–Energy Calculations

When nuclei decay, they form products of lower energy. The change of energy is related to changes of mass, according to the mass–energy equivalence relation derived by Albert Einstein in 1905. Using this relation, you can obtain the energies of nuclear reactions from mass changes.

Mass–Energy Equivalence

One of the conclusions from Einstein's theory of special relativity is that the mass of a particle changes with its speed: the greater the speed, the greater the mass. Or, because kinetic energy depends on speed, the greater the kinetic energy of a particle, the greater its mass. This result, according to Einstein, is even more general. Energy and mass are equivalent and are related by the equation

$$E = mc^2$$

Here c is the speed of light, 3.00×10^8 m/s.

The meaning of this equation is that for any mass there is an associated energy, or for any energy there is an associated mass. If a system loses energy, it must also lose mass. For example, when carbon burns in oxygen, it releases heat energy.

$$\mathrm{C(graphite)} + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g);\ \Delta H = -393.5\ \mathrm{kJ}$$

Because this chemical system loses energy, it should also lose mass. In principle, you could obtain ΔH for the reaction by measuring the change in mass and relating this by Einstein's equation to the change in energy. < However, weight measurements are of no practical value in determining heats of reaction—the changes in mass are simply too small to detect.

The change in mass gives the change in internal energy, ΔU. The enthalpy change, ΔH, equals ΔU + PΔV. For the reaction given in the text, PΔV is essentially zero.

Calculation of the mass change for a typical chemical reaction, the burning of carbon in oxygen, will show just how small this quantity is. When the energy changes by an amount ΔE, the mass changes by an amount Δm. You can write Einstein's equation in the form

$$\Delta E = (\Delta m)c^2$$

The change in energy when 1 mol of carbon reacts is -3.935×10^5 J, or -3.935×10^5 kg·m^2/s^2. Hence,

$$\Delta m = \frac{\Delta E}{c^2} = \frac{-3.935 \times 10^5\ \mathrm{kg{\cdot}\cancel{m^2}/\cancel{s^2}}}{(3.00 \times 10^8\ \mathrm{\cancel{m}/\cancel{s}})^2} = -4.37 \times 10^{-12}\ \mathrm{kg}$$

For comparison, a good analytical balance can detect a mass as small as 1×10^{-7} kg, but this is ten thousand times greater than the mass change caused by the release of heat during the combustion of 1 mol of carbon.

By contrast, the mass changes in nuclear reactions are approximately a million times larger per mole of reactant than those in chemical reactions. Consider the alpha decay of uranium-238 to thorium-234. The nuclear equation is

$$\underset{238.0003}{{}^{238}_{92}\mathrm{U}} \longrightarrow \underset{233.9942}{{}^{234}_{90}\mathrm{Th}} + \underset{4.00150\ \mathrm{amu}}{{}^{4}_{2}\mathrm{He}}$$

TABLE 20.3 Masses of Some Elements and Other Particles

Symbol	Z	A	Mass (amu)	Symbol	Z	A	Mass (amu)
e^-	−1	0	0.000549	Co	27	59	58.93320
n	0	1	1.008665	Ni	28	58	57.93534
p	1	1	1.00728		28	60	59.93079
H	1	1	1.00783	Pb	82	206	205.97444
	1	2	2.01400		82	207	206.97587
	1	3	3.01605		82	208	207.97663
He	2	3	3.01603	Po	84	208	207.98122
	2	4	4.00260		84	210	209.98285
Li	3	6	6.01512	Rn	86	222	222.01757
	3	7	7.01600	Ra	88	226	226.02540
Be	4	9	9.01218	Th	90	230	230.03313
B	5	10	10.01294		90	234	234.03660
	5	11	11.00931	Pa	91	234	234.04330
C	6	12	12.00000	U	92	233	233.03963
	6	13	13.00336		92	234	234.04095
O	8	16	15.99492		92	235	235.04392
Cr	24	52	51.94051		92	238	238.05078
Fe	26	56	55.93494	Pu	94	239	239.05216

Here we have written the nuclear mass (in amu) beneath each nuclide symbol. (Table 20.3 lists masses of some elements and other particles.) The change in mass for this nuclear reaction, starting with molar amounts, is

$$\Delta m = (233.9942 + 4.00150 - 238.0003)\ \text{g} = -0.0046\ \text{g}$$

As in calculating ΔH and similar quantities, you subtract the value for the reactant from the sum of the values for the products. The minus sign indicates a loss of mass. This loss of mass is clearly large enough to detect.

From a table of atomic masses, such as Table 20.3, you can use Einstein's equation to calculate the energy change for a nuclear reaction. This is illustrated in the next example. Recall from Section 20.2 that 1 eV $= 1.602 \times 10^{-19}$ J. Therefore, 1 MeV equals 1.602×10^{-13} J.

Example 20.12 Calculating the Energy Change for a Nuclear Reaction

a. Calculate the energy change in joules (four significant figures) for the following nuclear reaction per mole of ${}^{2}_{1}\text{H}$:

$${}^{2}_{1}\text{H} + {}^{3}_{2}\text{He} \longrightarrow {}^{4}_{2}\text{He} + {}^{1}_{1}\text{H}$$

Atomic and particle masses are given in Table 20.3; the speed of light is given on the inside back cover of this book.

b. What is the energy change in MeV for one ${}^{2}_{1}\text{H}$ nucleus?

Problem Strategy In order to calculate the energy changes for both parts of this problem, we will need to use Einstein's equation in the form $\Delta E = (\Delta m)c^2$. When using this

(*continued*)

(continued)

equation for this type of calculation, we will use the nuclear mass of the nuclides. For part a, we will need to determine the mass change (Δm) of the given nuclear reaction per mole of ${}^{2}_{1}\text{H}$. For part b, we calculate Δm for one ${}^{2}_{1}\text{H}$ nucleus. Finally, we convert our answer from joules to MeV.

Solution a. You need to write the *nuclear* masses below each nuclide symbol and then calculate Δm. Once you have Δm, you can obtain ΔE. The nuclear mass of a nuclide is the mass of the atom minus the mass of the electrons. For example, using mass information from Table 20.3, you calculate the nuclear mass of ${}^{4}_{1}\text{He}$ by starting with the atomic mass of ${}^{4}_{1}\text{He}$ and subtracting the mass of two electrons.

$$\text{Nuclear mass of } {}^{4}_{1}\text{He} = 4.00260 \text{ amu} - (2 \times 0.00549 \text{ amu}) = 4.001502 \text{ amu}$$

$$\underset{2.01345}{{}^{2}_{1}\text{H}} + \underset{3.01493}{{}^{3}_{2}\text{He}} \longrightarrow \underset{4.00150}{{}^{4}_{2}\text{He}} + \underset{1.00728 \text{ amu}}{{}^{1}_{1}\text{H}}$$

Hence,

$$\begin{aligned}\Delta m &= (4.00150 + 1.00728 - 2.01345 - 3.01493) \text{ amu} \\ &= -0.01960 \text{ amu}\end{aligned}$$

To obtain the energy change for molar amounts, note that the molar mass of an atom in grams is numerically equal to the mass of a single atom in amu. Therefore, the mass change for molar amounts in this nuclear reaction is -0.01960 g, or -1.960×10^{-5} kg. The energy change is

$$\begin{aligned}\Delta E &= (\Delta m)c^2 = (-1.960 \times 10^{-5} \text{ kg})(2.998 \times 10^{8} \text{ m/s})^2 \\ &= -1.762 \times 10^{12} \text{ kg}\cdot\text{m}^2/\text{s}^2 \qquad \text{or} \qquad \mathbf{-1.762 \times 10^{12}\ J}\end{aligned}$$

b. The mass change for the reaction of one ${}^{2}_{1}\text{H}$ atom is -0.01960 amu. First change this to grams. Recall that 1 amu equals 1/12 the mass of a ${}^{12}_{6}\text{C}$ atom, whose mass is 12 g/6.022 $\times$ 10^{23}. Thus, 1 amu = 1 g/6.022 $\times$ 10^{23}. Hence, the mass change in grams is

$$\begin{aligned}\Delta m &= -0.01960 \text{ amu} \times \frac{1 \text{ g}}{1 \text{ amu} \times 6.022 \times 10^{23}} \\ &= -3.255 \times 10^{-26} \text{ g} \qquad (\text{or } -3.255 \times 10^{-29} \text{ kg})\end{aligned}$$

Then,

$$\begin{aligned}\Delta E &= (\Delta m)c^2 = (-3.255 \times 10^{-29} \text{ kg})(2.998 \times 10^{8} \text{ m/s})^2 \\ &= -2.926 \times 10^{-12} \text{ J}\end{aligned}$$

Now convert this to MeV:

$$\Delta E = -2.926 \times 10^{-12} \text{ J} \times \frac{1 \text{ MeV}}{1.602 \times 10^{-13} \text{ J}} = \mathbf{-18.26\ MeV}$$

Answer Check When calculating mass changes for nuclear reactions, you should expect answers in the small magnitude shown in this example (10^{-26} g). Any mass change significantly larger than this value should be suspect.

Exercise 20.12 a. Calculate the energy change in joules when 1.00 g ${}^{234}_{90}\text{Th}$ decays to ${}^{234}_{91}\text{Pa}$ by beta emission.

b. What is the energy change in MeV when one ${}^{234}_{90}\text{Th}$ nucleus decays? Use Table 20.3 for these calculations.

■ See Problems 20.81 and 20.82.

Nuclear Binding Energy

The equivalence of mass and energy explains the otherwise puzzling fact that the mass of an atom is always less than the sum of the masses of its constituent particles. For example, the helium-4 atom consists of two protons, two neutrons, and two electrons, giving the following sum:

$$\begin{aligned} \text{Mass of 2 electrons} &= 2 \times 0.000549 \text{ amu} = 0.00110 \text{ amu} \\ \text{Mass of 2 protons} &= 2 \times 1.00728 \text{ amu} = 2.01456 \text{ amu} \\ \text{Mass of 2 neutrons} &= 2 \times 1.00867 \text{ amu} = \underline{2.01734 \text{ amu}} \\ \text{Total mass of particles} &= \phantom{2 \times 1.00867 \text{ amu} =} 4.03300 \text{ amu} \end{aligned}$$

The mass of the helium-4 atom is 4.00260 amu (see Table 20.3), so the mass difference is

$$\Delta m = (4.00260 - 4.03300) \text{ amu} = -0.03040 \text{ amu}$$

This mass difference is explained as follows. When the nucleons come together to form a nucleus, energy is released. (The nucleus has lower energy and is therefore more stable than the separate nucleons.) According to Einstein's equation, there must be an equivalent decrease in mass.

The **binding energy** of a nucleus is *the energy needed to break a nucleus into its individual protons and neutrons*. Thus, the binding energy of the helium-4 nucleus is the energy change for the reaction

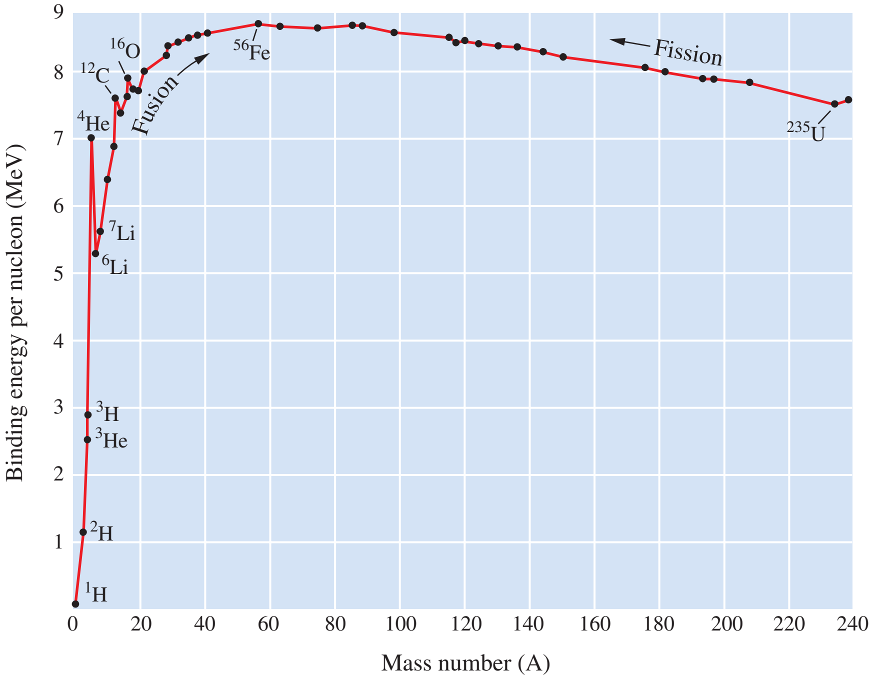
$${}^{4}_{2}\text{He}^{2+} \longrightarrow 2\,{}^{1}_{1}\text{p} + 2\,{}^{1}_{0}\text{n}$$

The **mass defect** of a nucleus is *the nucleon mass minus the atomic mass*. In the case of helium-4, the mass defect is 4.03300 amu − 4.00260 amu = 0.03040 amu. (This is the positive value of the mass difference we calculated earlier.) Both the binding energy and the corresponding mass defect are reflections of the stability of the nucleus.

To compare the stabilities of various nuclei, it is useful to compare binding energies per nucleon. Figure 20.18 shows values of this quantity (in MeV per nucleon) plotted against the mass number for various nuclides. Most of the points lie near the smooth curve drawn on the graph.

Note that nuclides near mass number 50 have the largest binding energies per nucleon. This means that a group of nucleons would tend to form those nuclides, because they would form nuclei of the lowest energy. For this reason, heavy nuclei

FIGURE 20.18



Plot of binding energy per nucleon versus mass number
The binding energy of each nuclide is divided by the number of nucleons (total of protons and neutrons), then plotted against the mass number of the nuclide. Note that nuclides near mass number 50 have the largest binding energies per nucleon. Thus, heavy nuclei are expected to undergo fission to approach this mass number, whereas light nuclei are expected to undergo fusion.

might be expected to split to give lighter nuclei, and light nuclei might be expected to react, or combine, to form heavier nuclei.

Nuclear fission is *a nuclear reaction in which a heavy nucleus splits into lighter nuclei and energy is released.* For example, californium-252 decays both by alpha emission (97%) and by spontaneous fission (3%). There are many possible ways in which the nucleus can split. One way is represented by the following equation:

$$^{252}_{98}\text{Cf} \longrightarrow {}^{142}_{56}\text{Ba} + {}^{106}_{42}\text{Mo} + 4\,^{1}_{0}\text{n}$$

In some cases, a nucleus can be induced to undergo fission by bombarding it with neutrons. An example is the nuclear fission of uranium-235. When a neutron strikes the $^{235}_{92}$U nucleus, the nucleus splits into roughly equal parts, giving off several neutrons. Three possible splittings are shown in the following equations:

$$^{1}_{0}\text{n} + {}^{235}_{92}\text{U} \begin{cases} \nearrow\ {}^{142}_{54}\text{Xe} + {}^{90}_{38}\text{Sr} + 4\,^{1}_{0}\text{n} \\ \longrightarrow\ {}^{139}_{56}\text{Ba} + {}^{94}_{36}\text{Kr} + 3\,^{1}_{0}\text{n} \\ \searrow\ {}^{144}_{55}\text{Cs} + {}^{90}_{37}\text{Rb} + 2\,^{1}_{0}\text{n} \end{cases}$$

Nuclear fission is discussed further in Section 20.7.

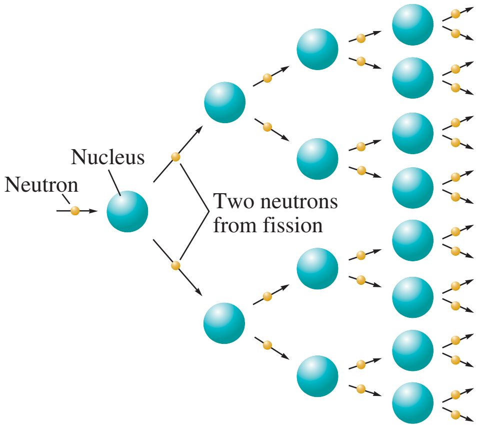
Nuclear fusion is *a nuclear reaction in which light nuclei combine to give a stabler, heavier nucleus plus possibly several neutrons, and energy is released.* An example of nuclear fusion is

$$^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + {}^{1}_{0}\text{n}$$

Even though a nuclear reaction is energetically favorable, the reaction may be imperceptibly slow unless the proper conditions are present (see Section 20.7).

20.7 Nuclear Fission and Nuclear Fusion

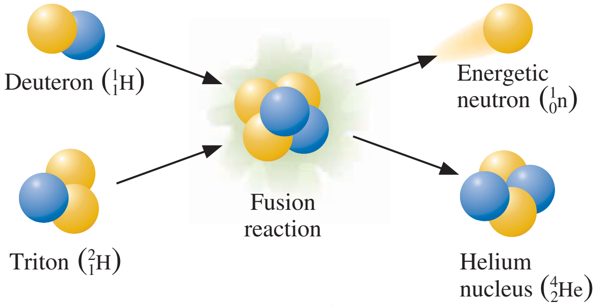
We have seen that the stablest nuclei are those of intermediate size (with mass numbers around 50). Nuclear fission and nuclear fusion are reactions in which nuclei attain sizes closer to this intermediate range. In doing so, these reactions release tremendous amounts of energy. Nuclear fission of uranium-235 is employed in nuclear power plants to generate electricity. Nuclear fusion may supply us with energy in the future.



Nuclear Fission

Nuclear Fission; Nuclear Reactors

Nuclear fission was discovered as a result of experiments to produce transuranium elements. Soon after the neutron was discovered in 1932, experimenters realized that this particle, being electrically neutral, should easily penetrate heavy nuclei. They began using neutrons in bombardment reactions, hoping to produce isotopes that would decay to new elements. In 1938, Otto Hahn, Lise Meitner, and Fritz Strassmann in Berlin identified barium in uranium samples that had been bombarded with neutrons. Soon afterward, the presence of barium was explained as a result of fission of the uranium-235 nucleus. When this nucleus is struck by a neutron, it splits into two nuclei. Fissions of uranium nuclei produce approximately 30 different elements of intermediate mass, including barium.



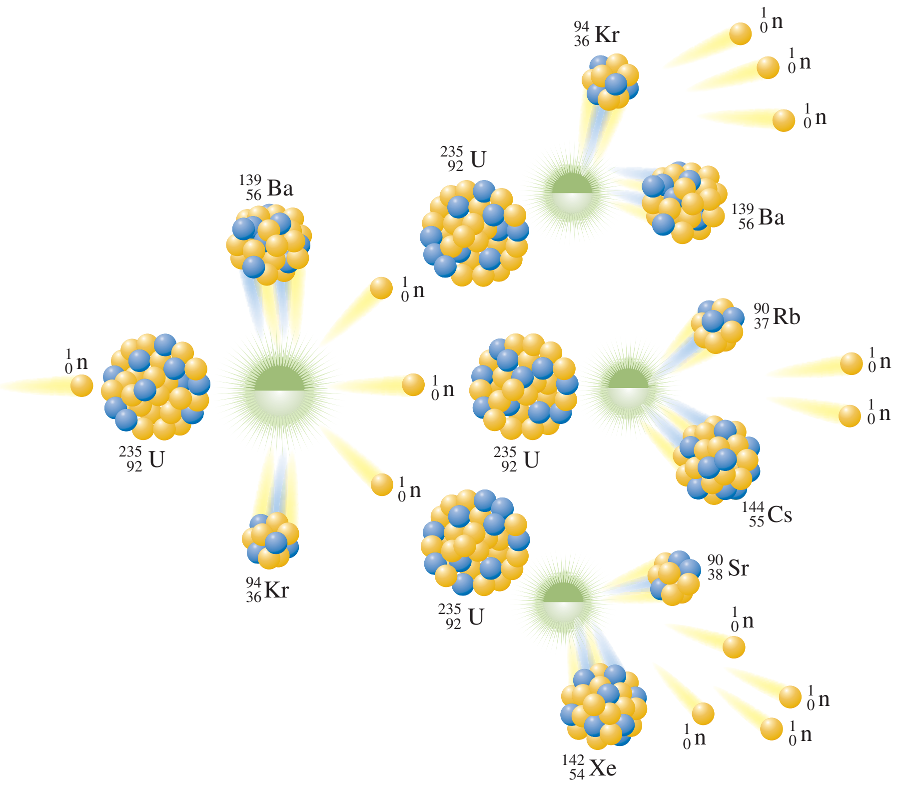
Nuclear Fusion

When the uranium-235 nucleus splits, approximately two or three neutrons are released. If the neutrons from each nuclear fission are absorbed by other uranium-235 nuclei, these nuclei split and release even more neutrons. In this way, a chain reaction can occur. A nuclear **chain reaction** is *a self-sustaining series of nuclear fissions caused by the absorption of neutrons released from previous nuclear fissions.* The numbers of nuclei that split quickly multiply as a result of the absorption of neutrons released

FIGURE 20.19

Representation of a chain reaction of nuclear fissions

Each nuclear fission produces two or more neutrons, which can in turn cause more nuclear fissions. At each stage, a greater number of neutrons are produced, so the number of nuclear fissions multiplies quickly. Such a chain reaction is the basis of nuclear power and nuclear weapons. The original nucleus splits into pieces of varying mass number.



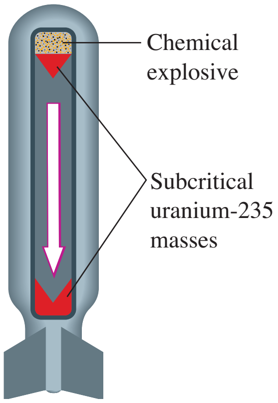


FIGURE 20.20

An atomic bomb

In the gun-type bomb, one piece of uranium-235 of subcritical mass is hurled into another piece by a chemical explosive. The two pieces together give a supercritical mass, and a nuclear explosion results. Bombs using plutonium-239 require an implosion technique, in which wedges of plutonium arranged on a spherical surface are pushed into the center of the sphere by a chemical explosive, where a supercritical mass of plutonium results in a nuclear explosion.

from previous nuclear fissions. Figure 20.19 shows how such a chain reaction occurs. The chain reaction of nuclear fissions is the basis of nuclear power and nuclear weapons.

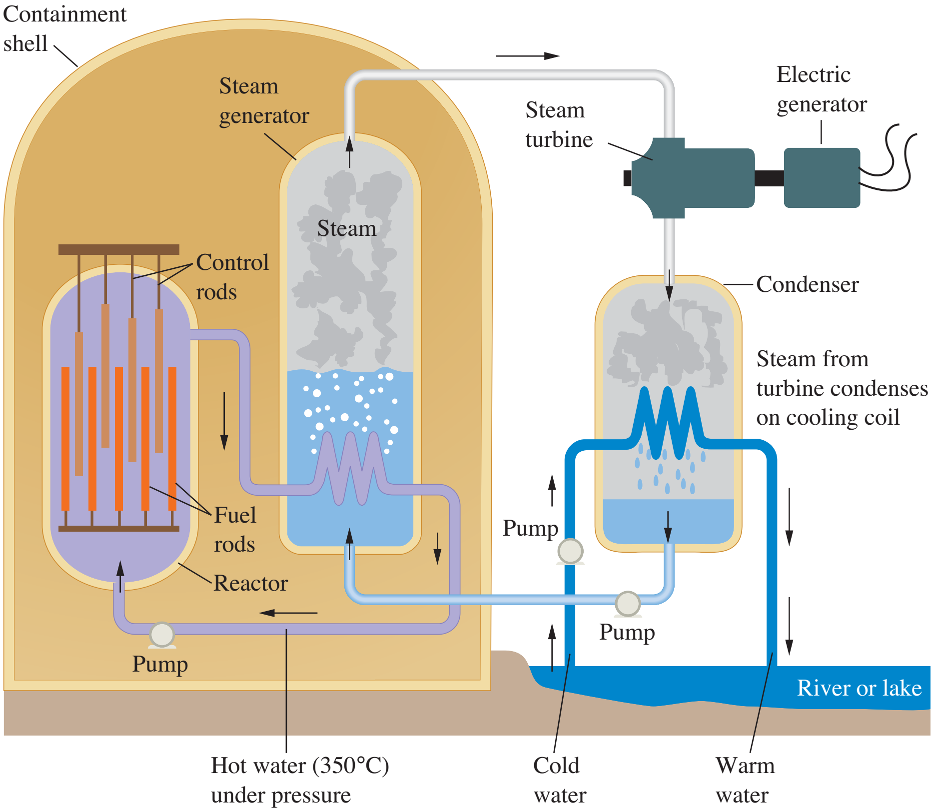
To sustain a chain reaction in a sample of fissionable material, a nucleus that splits must give an average of one neutron that results in the fission of another nucleus, and so on. If the sample is too small, many of the neutrons leave the sample before they have a chance to be absorbed. There is thus a **critical mass** for a particular fissionable material, which is *the smallest mass of fissionable material in which a chain reaction can be sustained.* If the mass is much larger than this (a *supercritical* mass), the numbers of nuclei that split multiply rapidly. An atomic bomb is detonated with a small amount of chemical explosive that pushes together two or more masses of fissionable material to get a supercritical mass (Figure 20.20). A rapid chain reaction results in the splitting of most of the fissionable nuclei—and in the explosive release of an enormous amount of energy.

A **nuclear fission reactor** is *a device that permits a controlled chain reaction of nuclear fissions.* In power plants, a nuclear reactor is used to produce heat, which in turn is used to produce steam to drive an electric generator. A nuclear reactor consists of fuel rods alternating with control rods contained within a vessel. The **fuel rods** are *the cylinders that contain fissionable material.* In the light-water (ordinary water) reactors commonly used in the United States (see Figure 20.21), these fuel rods contain uranium dioxide pellets in a zirconium alloy tube. Natural uranium contains only 0.72% uranium-235, which is the isotope that undergoes fission. The uranium used for fuel in these reactors is “enriched” so that it contains about 3% of the uranium-235 isotope. **Control rods** are *cylinders composed of substances that absorb neutrons, such as boron and cadmium, and can therefore slow the chain reaction.* By varying the depth of the control rods within the fuel-rod assembly (reactor core), one can increase or decrease the absorption of neutrons. If necessary, these rods can be dropped all the way into the fuel-rod assembly to stop the chain reaction.

FIGURE 20.21

Light-water nuclear reactor

The nuclear reactor consists of fuel rods with interspersed control rods. By raising or lowering the control rods, an operator can increase or decrease the rate of energy release from the fuel rods. Heat from the fuel rods raises the temperature of the liquid water in the reactor. A pump circulates the hot water to a steam generator, and the resulting steam passes through a turbine that operates an electric generator. The steam leaves the turbine and goes into the condenser, where it liquefies on the cooling coil. A nearby river or lake provides the cold water for the condenser.



A **moderator,** *a substance that slows down neutrons,* is required if uranium-235 is the fuel and this isotope is present as a small fraction of the total fuel. The neutrons that are released by the splitting of uranium-235 nuclei are absorbed more readily by uranium-238 than by other uranium-235 nuclei. However, when the neutrons are slowed down by a moderator, they are more readily absorbed by uranium-235, so it is possible to sustain a chain reaction with low fractional abundance of this isotope. Commonly used moderators are heavy water ($^2_1H_2O$), light water, and graphite.

In the light-water reactor, ordinary water acts as both a moderator and a coolant. Figure 20.21 shows a pressurized-water design of this type of reactor. Water in the reactor is maintained at about 350°C under high pressure (150 atm) so it does not boil. The hot water is circulated to a heat exchanger, where the heat is used to produce steam to run a turbine and generate electricity.

After a period of time, fission products that absorb neutrons accumulate in the fuel rods. This interferes with the chain reaction, so eventually the fuel rods must be replaced. Originally, the intention was to send these fuel rods to *reprocessing plants,* where fuel material could be chemically separated from the radioactive wastes. Opposition to constructing these plants has been intense, however. Plutonium-239 would be one of the fuel materials separated from the spent fuel rods. This isotope is produced during the operation of the reactor when uranium-238 is bombarded with neutrons. It is fissionable and can be used to construct atomic bombs. For this reason, many people believe that the availability of this element in large quantities would increase the chance that many countries and terrorist groups could divert enough plutonium to produce atomic bombs.

Whether or not the spent fuel rods are reprocessed, a pressing problem facing the nuclear power industry is how to dispose of radioactive wastes safely. One of many proposals is to encase the waste in a ceramic material and store the solids deep in the earth, perhaps in salt mines.

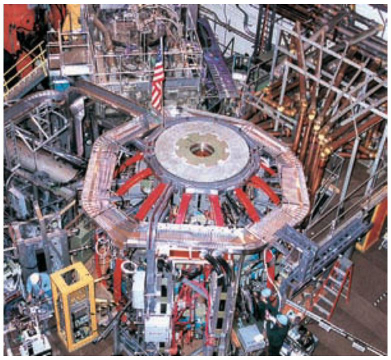


FIGURE 20.22

Torus Fusion Reactor
The National Spherical Torus Experiment at the Princeton Plasma Physics Laboratory uses this reactor to test an advanced magnetic field configuration to confine a compact, spherically shaped plasma.

Nuclear Fusion

As we noted in Section 20.6, energy can be obtained by combining light nuclei into a heavier nucleus by nuclear fusion. Such fusion reactions have been observed in the laboratory by means of bombardment using particle accelerators. Deuterons ($^{2}_{1}H$ nuclei), for example, can be accelerated toward targets containing deuterium ($^{2}_{1}H$ atoms) or tritium ($^{3}_{1}H$ atoms). The reactions are

$$^{2}_{1}H + ^{2}_{1}H \longrightarrow ^{3}_{2}He + ^{1}_{0}n$$

$$^{2}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n$$

To get the nuclei to react, the bombarding nucleus must have enough kinetic energy to overcome the repulsion of electric charges of the nuclei. The first reaction uses only deuterium, which is present in ordinary water. < It is therefore very attractive as a source of energy. But, as we will discuss, the second reaction is more likely to be used first.

Natural hydrogen contains 0.015% deuterium.

Energy cannot be obtained in a practical way using particle accelerators. Another way to give nuclei sufficient kinetic energy to react is by heating the nuclear materials to a sufficiently high temperature. The reaction of deuterium, $^{2}_{1}H$, and tritium, $^{3}_{1}H$, turns out to require the lowest temperature of any fusion reaction. For this reason it is likely to be the first fusion reaction developed as an energy source. For practical purposes, the temperature will have to be about 100 million °C. At this temperature, all atoms have been stripped of their electrons, so a plasma results. A **plasma** is *an electrically neutral gas of ions and electrons.* At 100 million °C, the plasma is essentially separate nuclei and electrons. Thus, the development of nuclear fusion requires study of the properties of plasmas at high temperatures.

It is now believed that the energy of stars, including our sun, where extremely high temperatures exist, derives from nuclear fusion. The hydrogen bomb also employs nuclear fusion for its destructive power. High temperature is first attained by a fission bomb. This then ignites fusion reactions in surrounding material of deuterium and tritium.

The main problem in developing controlled nuclear fusion is how to heat a plasma to high temperature and maintain those temperatures. When a plasma touches any material whatsoever, heat is quickly conducted away, and the plasma temperature quickly falls. < A *magnetic fusion reactor* uses a magnetic field to hold the plasma away from any material (see Figure 20.22). A *laser fusion reactor* employs a bank of lasers aimed at a single point. Pellets containing deuterium and tritium would drop into the reactor, where they would be heated to 100 million °C by bursts of laser light.

Even though the plasma is nearly 100 million °C above the melting point of any material, the total quantity of heat that could be transferred from the plasma is very small, because its concentration is extremely low. Therefore, if the plasma were to touch the walls of the reactor, the plasma would cool but the walls would not melt.

A Checklist for Review

Important Terms

radioactive decay (20.1)
nuclear bombardment reaction (20.1)
nuclear equation (20.1)
positron (20.1)
gamma photon (20.1)
nuclear force (20.1)
shell model of the nucleus (20.1)
magic number (20.1)
band of stability (20.1)
alpha emission (20.1)
beta emission (20.1)
positron emission (20.1)
electron capture (20.1)
gamma emission (20.1)
metastable nucleus (20.1)
spontaneous fission (20.1)
radioactive decay series (20.1)
transmutation (20.2)

particle accelerator (20.2)
electron volt (eV) (20.2)
cyclotron (20.2)
deuterons (20.2)
transuranium elements (20.2)
Geiger counter (20.3)
scintillation counter (20.3)
activity of a radioactive source (20.3)
curie (Ci) (20.3)
rad (20.3)
rem (20.3)
radioactive decay constant (20.4)
half-life (20.4)
radioactive tracer (20.5)
isotope dilution (20.5)
neutron activation analysis (20.5)
binding energy (20.6)
mass defect (20.6)
nuclear fission (20.6)
nuclear fusion (20.6)
chain reaction (20.7)
critical mass (20.7)
nuclear fission reactor (20.7)
fuel rods (20.7)
control rods (20.7)
moderator (20.7)
plasma (20.7)

Key Equations

$$\text{Rate} = kN_t$$

$$t_{1/2} = \frac{0.693}{k}$$

$$\ln\frac{N_t}{N_0} = -kt$$

$$\Delta E = (\Delta m)c^2$$

Summary of Facts and Concepts

Nuclear reactions are of two types, *radioactive decay* and *nuclear bombardment*. Such reactions are represented by nuclear equations, each nucleus being denoted by a nuclide symbol. The equations must be balanced in charge (subscripts) and in nucleons (superscripts).

According to the *nuclear shell model,* the nucleons are arranged in shells. *Magic numbers* are the numbers of nucleons in a completed shell of protons or neutrons. Nuclei with magic numbers of protons or neutrons are especially stable. Pairs of protons and pairs of neutrons are also especially stable. When placed on a plot of N versus Z, stable nuclei fall in a *band of stability.* Those radioactive nuclides that fall to the left of the band of stability in this plot usually decay by beta emission. Those radioactive nuclides that fall to the right of the band of stability usually decay by positron emission or electron capture. However, nuclides with $Z > 83$ often decay by alpha emission. Uranium-238 forms a *radioactive decay series.* In such series, one element decays to another, which decays to another, and so forth, until a stable isotope is reached (lead-206, in the case of the uranium-238 series).

Transmutation of elements has been carried out in the laboratory by bombarding nuclei with various atomic particles. Alpha particles from natural sources can be used as reactants with light nuclei. For heavier nuclei, positive ions such as alpha particles must first be accelerated in a *particle accelerator.* Many of the *transuranium elements* have been obtained by bombardment of elements with accelerated particles. For example, plutonium was first made by bombarding uranium-238 with deuterons ($^{2}_{1}$H nuclei) from a *cyclotron,* a type of particle accelerator.

Particles of radiation from nuclear processes can be counted by Geiger counters or scintillation counters. In a *Geiger counter,* the particle ionizes a gas, which then conducts a pulse of electricity between two electrodes. In a *scintillation counter,* the particle hits a phosphor, and this emits a flash of light that is detected by a photomultiplier tube. The activity of a radioactive source, or the number of nuclear disintegrations per unit time, is measured in units of *curies* (3.700×10^{10} disintegrations per second).

Radiation affects biological organisms by breaking chemical bonds. The *rad* is the measure of radiation dosage that deposits 1×10^{-2} J of energy per kilogram of tissue. A *rem* equals the number of rads times a factor to account for the relative biological effectiveness of the radiation.

Radioactive decay is a first-order rate process. The rate is characterized by the *decay constant,* k, or by the *half-life,* $t_{1/2}$. The quantities k and $t_{1/2}$ are related. Knowing one or the other, you can calculate how long it will take for a given radioactive sample to decay by a certain fraction. Methods of *radioactive dating* depend on determining the fraction of a radioactive isotope that has decayed and, from this, the time that has elapsed.

Radioactive isotopes are used as *radioactive tracers* in chemical analysis and medicine. *Isotope dilution* is one application of radioactive tracers in which the dilution of the tracer can be related to the original quantity of nonradioactive isotope. *Neutron activation analysis* is a method of analysis that depends on the conversion of elements to radioactive isotopes by neutron bombardment.

According to Einstein's *mass–energy equivalence,* mass is related to energy by the equation $E = mc^2$. A nucleus has less mass than the sum of the masses of the separate nucleons. The positive value of this mass difference is called the *mass defect;* it is equivalent to the *binding energy* of the nucleus. Nuclides having mass numbers near 50 have the largest binding energies per nucleon. It follows that heavy nuclei should tend to split, a process called *nuclear fission,* and that light nuclei should tend to combine, a process called *nuclear fusion*. Tremendous amounts of energy are released in both processes. Nuclear fission is used in conventional nuclear power reactors. Nuclear fusion reactors are in the experimental stage.

Media Summary

Visit the **student website at college.hmco.com/pic/ebbing9e** to help prepare for class, study for quizzes and exams, understand core concepts, and visualize molecular-level interactions. The following media activities are available for this chapter:

Prepare for Class

- **Video Lessons** *Mini lectures from chemistry experts*
  The Nature of Radioactivity
  The Stability of Atomic Nuclei
  Applications of Nuclear Chemistry
  Rates of Disintegration Reactions
  Radiochemical Dating
  Binding Energy
  Nuclear Fission
  Nuclear Fusion

Improve Your Grade

- **Visualizations** *Molecular-level animations and lab demonstration videos*
  Nuclear Particles
  Geiger Counter
  Half-Life of Nuclear Decay
  Nuclear Fission
  Nuclear Fusion
- **Flashcards** *Key terms and definitions*
  Online Flashcards
- **Self-Assessment Questions** *Additional questions with full worked-out solutions*
  6 Self-Assessment Questions

ACE the Test

Multiple-choice quizzes
3 ACE Practice Tests

Access these resources using the passkey available free with new texts or for purchase separately.

Learning Objectives

20.1 Radioactivity

- Define *radioactive decay* and *nuclear bombardment reaction.*
- Learn the nuclear symbols for *positron, gamma photon, electron, neutron, proton.*
- Write a nuclear equation. Example 20.1
- Deduce a product or reactant in a nuclear equation. Example 20.2
- Describe the *shell model of the nucleus.*
- Explain the *band of stability.*
- Predict the relative stabilities of nuclides. Example 20.3
- List the six types of radioactive decay.
- Predict the type of radioactive decay. Example 20.4
- Define *radioactive decay series.*

20.2 Nuclear Bombardment Reactions

- Define *transmutation.*
- Use the notation for a bombardment reaction. Example 20.5
- Locate the *transuranium elements* on the periodic table.
- Determine the product nucleus in a nuclear bombardment reaction. Example 20.6

20.3 Radiations and Matter: Detection and Biological Effects

- State the purposes of a *Geiger counter* and a *scintillation counter.*
- Define *activity of a radioactive source* and *curie* (*Ci*).
- State the relationship between a *rad* and a *rem.*

20.4 Rate of Radioactive Decay

- Define *radioactive decay constant.*
- Calculate the decay constant from activity. Example 20.7
- Define *half-life.*
- Draw a typical half-life decay curve of a radioactive element.
- Calculate the half-life from the decay constant. Example 20.8
- Calculate the decay constant and activity from half-life. Example 20.9
- Determine the fraction of nuclei remaining after a specified time. Example 20.10
- Apply the carbon-14 dating method. Example 20.11

20.5 Applications of Radioactive Isotopes

- State the ways in which radioactive isotopes are used for chemical analysis.
- Describe how isotopes are used for medical therapy and diagnosis.

20.6 Mass–Energy Calculations

- Calculate the energy change for a nuclear reaction. Example 20.12
- Define *nuclear binding energy* and *mass defect.*
- Compare and contrast *nuclear fission* and *nuclear fusion.*

20.7 Nuclear Fission and Nuclear Fusion

- Explain how a controlled *chain reaction* is applied in a *nuclear fission reactor* using a *critical mass* of fissionable material.
- Write the reaction of the nuclear fusion of deuterium and tritium.

Self-Assessment and Review Questions

20.1 What are the two types of nuclear reactions? Give an example of a nuclear equation for each type.

20.2 What are *magic numbers*? Give several examples of nuclei with magic numbers of protons.

20.3 List characteristics to look for in a nucleus to predict whether it is stable.

20.4 What are the six common types of radioactive decay? What condition usually leads to each type of decay?

20.5 What are the isotopes that begin each of the naturally occurring radioactive decay series?

20.6 Give equations for (a) the first transmutation of an element obtained in the laboratory by nuclear bombardment, and for (b) the reaction that produced the first artificial radioactive isotope.

20.7 What is a particle accelerator, and how does one operate? Why are they required for certain nuclear reactions?

20.8 In what major way has the discovery of transuranium elements affected the form of modern periodic tables?

20.9 Describe how a Geiger counter works. How does a scintillation counter work?

20.10 Define the units *curie, rad,* and *rem.*

20.11 The half-life of cesium-137 is 30.2y. How long will it take for a sample of cesium-137 to decay to 1/8 of its original mass?

20.12 What is the age of a rock that contains equal numbers of ${}^{40}_{19}\text{K}$ and ${}^{40}_{18}\text{Ar}$ nuclei? The half-life of ${}^{40}_{19}\text{K}$ is 1.28×10^{9}y.

20.13 What is a radioactive tracer? Give an example of the use of such a tracer in chemistry.

20.14 Isotope dilution has been used to obtain the volume of blood supply in a living animal. Explain how this could be done.

20.15 Briefly describe neutron activation analysis.

20.16 The deuteron, ${}^{2}_{1}\text{H}$, has a mass that is smaller than the sum of the masses of its constituents, the proton plus the neutron. Explain why this is so.

20.17 Certain stars obtain their energy from nuclear reactions such as

$${}^{12}_{6}\text{C} + {}^{12}_{6}\text{C} \longrightarrow {}^{23}_{11}\text{Na} + {}^{1}_{1}\text{H}$$

Explain in a sentence or two why this reaction might be expected to release energy.

20.18 Briefly describe how a nuclear fission reactor operates.

20.19 Polonium-216 decays to lead-212 by emission of an alpha particle. Which of the following is the nuclear equation for this radioactive decay?

a. ${}^{216}_{84}\text{Po} \longrightarrow {}^{212}_{82}\text{Pb} + {}^{0}_{-1}\text{e}$
b. ${}^{216}_{84}\text{Po} \longrightarrow {}^{212}_{82}\text{Pb} + {}^{4}_{2}\text{He}$
c. ${}^{216}_{84}\text{Po} + {}^{4}_{2}\text{He} \longrightarrow {}^{212}_{82}\text{Pb}$
d. ${}^{216}_{84}\text{Po} \longrightarrow {}^{212}_{82}\text{Pb} + {}^{0}_{1}\text{e}$
e. ${}^{216}_{84}\text{Po} + 2{}^{0}_{-1}\text{e} \longrightarrow {}^{212}_{82}\text{Pb} + 4{}^{1}_{0}\text{n}$

20.20 The half-life for the decay of carbon-14 is 5730 years. Present-day carbon (in living matter) gives 15.3 disintegrations of ${}^{14}\text{C}$ per minute per gram of total carbon. An archaeological sample containing carbon was dated by analysis of its radioactive carbon. The activity of the carbon from the sample was 5.4 disintegrations of ${}^{14}\text{C}$ per minute per gram of total carbon. What was the age of the sample?

a. 2.4×10^{-5} y
b. 1.2×10^{4} y
c. 3.7×10^{3} y
d. 7.2×10^{3} y
e. 8.6×10^{3} y

20.21 A radioactive isotope has a half-life of 56.6 days. What fraction of the isotope remains after 449 days?

a. 3.2×10^{-6}
b. 1.00
c. 0.92
d. 4.1×10^{-3}
e. 0.83

20.22 Neutron activation analysis is an analytical technique in which a sample of material is bombarded with neutrons from a fission reactor. When a 35.0-g aluminum can is irradiated, it has an initial activity of 40.0 curies (Ci). The safety office won't let you touch anything having an activity in excess of 0.100 Ci. Assuming all the radioactivity is from ${}^{28}\text{Al}$, which has an half-life of 2.28 min, how many minutes do you have to wait after bombardment before you can handle the can safely?

a. 17.0 min
b. 1.32×10^{3} min
c. 19.7 min
d. 478 min
e. 476 min

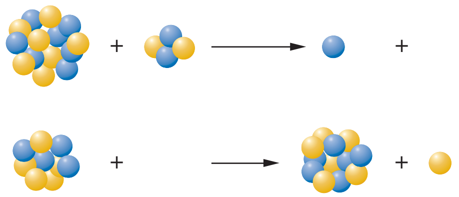
Conceptual Problems

20.23 When considering the lifetime of a radioactive species, a general rule of thumb is that after 10 half-lives have passed, the amount of radioactive material left in the sample is negligible. The disposal of some radioactive materials is based on this rule.

a. What percentage of the original material is left after 10 half-lives?

b. When would it be a bad idea to apply this rule?

20.24 Use drawings to complete the following nuclear reactions (orange circles represent neutrons and blue circles represent protons). Once you have completed the drawings, write the nuclide symbols under each reaction.



20.25 Sodium has only one naturally occurring isotope, sodium-23. Using the data presented in Table 20.3, explain how the molecular mass of sodium is 22.98976 amu and not the sum of the masses of the protons, neutrons, and electrons.

20.26 Identify each of the following reactions as fission, fusion, a transmutation, or radioactive decay.

a. $4\,^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,^{0}_{1}\mathrm{e}$

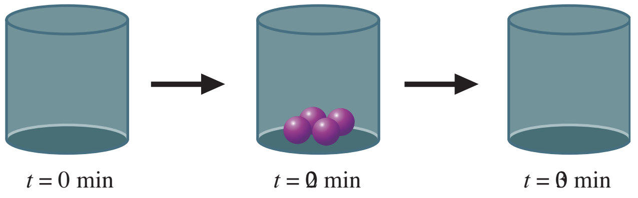
b. $^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e}$

c. $^{1}_{0}\mathrm{n} + {}^{235}_{92}\mathrm{U} \longrightarrow {}^{140}_{56}\mathrm{Ba} + {}^{93}_{36}\mathrm{Kr} + 3\,^{0}_{1}\mathrm{e}$

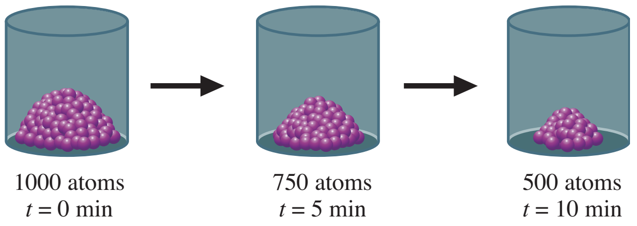
d. $^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}$

20.27 A radioactive sample with a half-life of 10 minutes is placed in a container.

a. Complete the pictures below depicting the amount of this sample at the beginning of the experiment (t = 0 min) and 30 minutes into the experiment (t = 30 min). Each sphere represents one radioactive nuclide of the sample.



b. A friend working with 1000 atoms of the same nuclide represents the amount of nuclide at three time intervals in the following manner.



Is his drawing correct? If not, explain where and why it is incorrect.

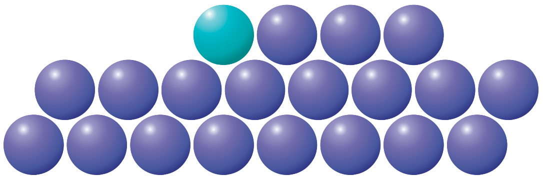
20.28 You have a mixture that contains 10 g of Pu-239 with a half-life of 2.4 × 10^4 years and 10 g of Np-239 with a half-life of 2.4 days. Estimate how much time must elapse before the quantity of radioactive material is reduced by 50%.

20.29 Come up with an explanation as to why α radiation is easily blocked by materials such as a piece of wood, whereas γ radiation easily passes through those same materials.

20.30 You have an acquaintance who tells you that he is going to reduce his radiation exposure to zero. What examples could you present that would illustrate this to be an impossible goal?

20.31 In Chapter 7 (A Chemist Looks At: Zapping Hamburger with Gamma Rays) there is a discussion of how gamma radiation is used to kill bacteria in food. As indicated in the feature, there is concern on the part of some people that the irradiated food is radioactive. Why is this not the case? If you wanted to make the food radioactive, what would you have to do?

20.32 You have a pile of I-131 atoms with a half-life of 8 days. A portion of the solid I-131 is represented below. Can you predict how many half-lives will occur before the green I-131 atom undergoes decay?



Practice Problems

Radioactivity

20.33 Rubidium-87, which forms about 28% of natural rubidium, is radioactive, decaying by the emission of a single beta particle to strontium-87. Write the nuclear equation for this decay of rubidium-87.

20.34 Write the nuclear equation for the decay of phosphorus-32 to sulfur-32 by beta emission. A phosphorus-32 nucleus emits a beta particle and gives a sulfur-32 nucleus.

20.35 Thorium is a naturally occurring radioactive element. Thorium-232 decays by emitting a single alpha particle to produce radium-228. Write the nuclear equation for this decay of thorium-232.

20.36 Radon is a radioactive noble gas formed in soil containing radium. Radium-226 decays by emitting a single alpha particle to produce radon-222. Write the nuclear equation for this decay of radium-226.

20.37 Fluorine-18 is an artificially produced radioactive isotope. It decays by emitting a single positron. Write the nuclear equation for this decay.

20.38 Scandium-41 is an artificially produced radioactive isotope. It decays by emitting a single positron. Write the nuclear equation for this decay.

20.39 Polonium was discovered in uranium ores by Marie and Pierre Curie. Polonium-210 decays by emitting a single alpha particle. Write the nuclear equation for this decay.

20.40 Actinium was discovered in uranium ore residues by André-Louis Debierne. Actinium-227 decays by emitting a single alpha particle. Write the nuclear equation for this decay.

20.41 From each of the following pairs, choose the nuclide that is radioactive. (One is known to be radioactive, the other stable.) Explain your choice.

a. ${}^{122}_{51}\text{Sb}$, ${}^{136}_{54}\text{Xe}$ **b.** ${}^{204}_{82}\text{Pb}$, ${}^{204}_{85}\text{At}$ **c.** ${}^{87}_{37}\text{Rb}$, ${}^{80}_{37}\text{Rb}$

20.42 From each of the following pairs, choose the nuclide that is radioactive. (One is known to be radioactive, the other stable.) Explain your choice.

a. ${}^{102}_{47}\text{Ag}$, ${}^{109}_{47}\text{Ag}$ **b.** ${}^{25}_{12}\text{Mg}$, ${}^{24}_{10}\text{Ne}$ **c.** ${}^{203}_{81}\text{Tl}$, ${}^{223}_{90}\text{Th}$

20.43 Predict the type of radioactive decay process that is likely for each of the following nuclides.

a. ${}^{228}_{92}\text{U}$ **b.** ${}^{8}_{5}\text{B}$ **c.** ${}^{68}_{29}\text{Cu}$

20.44 Predict the type of radioactive decay process that is likely for each of the following nuclides.

a. ${}^{60}_{30}\text{Zn}$ **b.** ${}^{10}_{6}\text{C}$ **c.** ${}^{241}_{93}\text{Np}$

20.45 Four radioactive decay series are known—three naturally occurring, and one beginning with the synthetic isotope ${}^{241}_{94}\text{Pu}$. To which of these decay series does the isotope ${}^{219}_{86}\text{Rn}$ belong? To which series does ${}^{220}_{86}\text{Rn}$ belong? Each isotope in these series decays by either alpha emission or beta emission. How do these decay processes affect the mass number?

20.46 Four radioactive decay series are known—three naturally occurring, and one beginning with the synthetic isotope ${}^{241}_{94}\text{Pu}$. To which of these decay series does the isotope ${}^{227}_{89}\text{Ac}$ belong? To which series does ${}^{225}_{89}\text{Ac}$ belong? Each isotope in these series decays by either alpha emission or beta emission. How do these decay processes affect the mass number?

Nuclear Bombardment Reactions

20.47 Write the abbreviated notations for the following bombardment reactions.

a. ${}^{26}_{12}\text{Mg} + {}^{2}_{1}\text{H} \longrightarrow {}^{24}_{11}\text{Na} + {}^{4}_{2}\text{He}$

b. ${}^{16}_{8}\text{O} + {}^{1}_{0}\text{n} \longrightarrow {}^{16}_{7}\text{N} + {}^{1}_{1}\text{p}$

20.48 Write abbreviated notations for the following bombardment reactions.

a. ${}^{14}_{7}\text{N} + {}^{1}_{0}\text{n} \longrightarrow {}^{14}_{6}\text{C} + {}^{1}_{1}\text{H}$

b. ${}^{63}_{29}\text{Cu} + {}^{4}_{2}\text{He} \longrightarrow {}^{66}_{31}\text{Ga} + {}^{1}_{0}\text{n}$

20.49 Write the nuclear equations for the following bombardment reactions.

a. ${}^{27}_{13}\text{Al}(d, \alpha){}^{25}_{12}\text{Mg}$ **b.** ${}^{10}_{5}\text{B}(\alpha, p){}^{13}_{6}\text{C}$

20.50 Write the nuclear equations for the following bombardment reactions.

a. ${}^{45}_{21}\text{Sc}(n, \alpha){}^{42}_{19}\text{K}$ **b.** ${}^{63}_{29}\text{Cu}(p, n){}^{63}_{30}\text{Zn}$

20.51 A proton is accelerated to 12.6 MeV per particle. What is this energy in kJ/mol?

20.52 An alpha particle is accelerated to 23.1 MeV per particle. What is this energy in kJ/mol?

20.53 Fill in the missing parts of the following reactions.

a. ${}^{6}_{3}\text{Li} + {}^{1}_{0}\text{n} \longrightarrow ? + {}^{3}_{1}\text{H}$

b. ${}^{232}_{90}\text{Th}(?, n){}^{235}_{92}\text{U}$

20.54 Fill in the missing parts of the following reactions.

a. ${}^{27}_{13}\text{Al} + {}^{3}_{1}\text{H} \longrightarrow {}^{27}_{12}\text{Mg} + ?$

b. ${}^{12}_{6}\text{C}({}^{3}_{1}\text{H}, ?){}^{14}_{6}\text{C}$

20.55 Curium was first synthesized by bombarding an element with alpha particles. The products were curium-242 and a neutron. What was the target element?

20.56 Californium was first synthesized by bombarding an element with alpha particles. The products were californium-245 and a neutron. What was the target element?

Rate of Radioactive Decay

20.57 Tritium, or hydrogen-3, is prepared by bombarding lithium-6 with neutrons. A 0.250-mg sample of tritium decays at the rate of 8.94×10^{10} disintegrations per second. What is the decay constant (in /s) of tritium, whose atomic mass is 3.02 amu?

20.58 The first isotope of plutonium discovered was plutonium-238. It is used to power batteries for heart pacemakers. A sample of plutonium-238 weighing 2.8×10^{-6} g decays at the rate of 1.8×10^{6} disintegrations per second. What is the decay constant of plutonium-238 in reciprocal seconds (/s)?

20.59 Sulfur-35 is a radioactive isotope used in chemical and medical research. A 0.48-mg sample of sulfur-35 has an activity of 20.4 Ci. What is the decay constant of sulfur-35 (in /s)?

20.60 Sodium-24 is used in medicine to study the circulatory system. A sample weighing 5.2×10^{-6} g has an activity of 45.3 Ci. What is the decay constant of sodium-24 (in /s)?

20.61 Tellurium-123 is a radioactive isotope occurring in natural tellurium. The decay constant is 1.7×10^{-21}/s. What is the half-life in years?

20.62 Neptunium-237 was the first isotope of a transuranium element to be discovered. The decay constant is 1.03×10^{-14}/s. What is the half-life in years?

20.63 Carbon-14 has been used to study the mechanisms of reactions that involve organic compounds. The half-life of carbon-14 is 5.73×10^{3} y. What is the decay constant (in /s)?

20.64 Promethium-147 has been used in luminous paint for dials. The half-life of this isotope is 2.5 y. What is the decay constant (in /s)?

20.65 Gold-198 has a half-life of 2.69 d. What is the activity (in curies) of a 0.86-mg sample?

20.66 Cesium-134 has a half-life of 2.05 y. What is the activity (in curies) of a 0.50-mg sample?

20.67 A sample of a phosphorus compound contains phosphorus-32. This sample of radioactive isotope is decaying at the rate of 6.0×10^{12} disintegrations per second. How many grams of ^{32}P are in the sample? The half-life of ^{32}P is 14.3d.

20.68 A sample of sodium thiosulfate, $Na_2S_2O_3$, contains sulfur-35. Determine the mass of ^{35}S in the sample from the decay rate, which was determined to be 7.7×10^{11} disintegrations per second. The half-life of ^{35}S is 88d.

20.69 A sample of sodium-24 was administered to a patient to test for faulty blood circulation by comparing the radioactivity reaching various parts of the body. What fraction of the sodium-24 nuclei would remain undecayed after 12.0 h? The half-life is 15.0h. If a sample contains 6.0 μg of ^{24}Na, how many micrograms remain after 12.0 h?

20.70 A solution of sodium iodide containing iodine-131 was given to a patient to test for malfunctioning of the thyroid gland. What fraction of the iodine-131 nuclei would remain undecayed after 7.0 d? If a sample contains 2.5 μg of ^{131}I, how many micrograms remain after 7.0 d? The half-life of I-131 is 8.07 d.

20.71 If 28.0% of a sample of nitrogen-17 decays in 1.97 s, what is the half-life of this isotope (in seconds)?

20.72 If 20.0% of a sample of zinc-65 decays in 69.9 d, what is the half-life of this isotope (in days)?

20.73 A sample of iron-59 initially registers 125 counts per second on a radiation counter. After 10.0 d, the sample registers 107 counts per second. What is the half-life (in days) of iron-59?

20.74 A sample of copper-64 gives a reading of 88 counts per second on a radiation counter. After 9.5 h, the sample gives a reading of 53 counts per second. What is the half-life (in hours) of copper-64?

20.75 Carbon from a cypress beam obtained from the tomb of Sneferu, a king of ancient Egypt, gave 8.1 disintegrations of ^{14}C per minute per gram of carbon. How old is the cypress beam? Carbon from living material gives 15.3 disintegrations of ^{14}C per minute per gram of carbon.

20.76 Carbon from the Dead Sea Scrolls, very old manuscripts found in Israel, gave 12.1 disintegrations of ^{14}C per minute per gram of carbon. How old are the manuscripts? Carbon from living material gives 15.3 disintegrations of ^{14}C per minute per gram of carbon.

20.77 Several hundred pairs of sandals found in a cave in Oregon were found by carbon-14 dating to be 9.0×10^3 years old. What must have been the activity of the carbon-14 in the sandals in disintegrations per minute per gram? Assume the original activity was 15.3 disintegrations per minute per gram.

20.78 Some mammoth bones found in Arizona were found by carbon-14 dating to be 1.13×10^4 years old. What must have been the activity of the carbon-14 in the bones in disintegrations per minute per gram? Assume the original activity was 15.3 disintegrations per minute per gram.

Mass-Energy Equivalence

20.79 Find the change of mass (in grams) resulting from the release of heat when 1 mol C reacts with 1 mol O_2.

$$C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -393.5\text{ kJ}$$

20.80 Find the change of mass (in grams) resulting from the release of heat when 1 mol SO_2 is formed from the elements.

$$S(s) + O_2(g) \longrightarrow SO_2(g);\ \Delta H = -297\text{ kJ}$$

20.81 Calculate the energy change for the following nuclear reaction (in joules per mole of ^2_1H).

$$^2_1H + ^3_1H \longrightarrow ^4_2He + ^1_0n$$

Give the energy change in MeV per ^2_1H nucleus. See Table 20.3.

20.82 Calculate the change in energy, in joules per mole of ^1_1H, for the following nuclear reaction.

$$^1_1H + ^1_1H \longrightarrow ^2_1H + ^0_1e$$

Give the energy change in MeV per ^1_1H nucleus. See Table 20.3.

20.83 Obtain the mass defect (in amu) and binding energy (in MeV) for the ^6_3Li nucleus. What is the binding energy (in MeV) per nucleon? See Table 20.3.

20.84 Obtain the mass defect (in amu) and binding energy (in MeV) for the $^{58}_{28}Ni$ nucleus. What is the binding energy (in MeV) per nucleon? See Table 20.3.

General Problems

20.85 Sodium-23 is the only stable isotope of sodium. Predict how sodium-20 will decay and how sodium-26 will decay.

20.86 Aluminum-27 is the only stable isotope of aluminum. Predict how aluminum-24 will decay and how aluminum-30 will decay.

20.87 A uranium-235 nucleus decays by a series of alpha and beta emissions until it reaches lead-207. How many alpha emissions and how many beta emissions occur in this series of decays?

20.88 A thorium-232 nucleus decays by a series of alpha and beta emissions until it reaches lead-208. How many alpha emissions and how many beta emissions occur in this series of decays?

20.89 A bismuth-209 nucleus reacts with an alpha particle to produce an astatine nucleus and two neutrons. Write the complete nuclear equation for this reaction.

20.90 A bismuth-209 nucleus reacts with a deuteron to produce a polonium nucleus and a neutron. Write the complete nuclear equation for this reaction.

20.91 Complete the following equation by filling in the blank.

$$^{238}_{92}\text{U} + ^{12}_{6}\text{C} \longrightarrow \_\_\_\_ + 4^{1}_{0}\text{n}$$

20.92 Complete the following equation by filling in the blank.

$$^{246}_{96}\text{Cm} + ^{12}_{6}\text{C} \longrightarrow \_\_\_\_ + 4^{1}_{0}\text{n}$$

20.93 Tritium, or hydrogen-3, is formed in the upper atmosphere by cosmic rays, similar to the formation of carbon-14. Tritium has been used to determine the age of wines. A certain wine that has been aged in a bottle has a tritium content only 70% of that in a similar wine of the same mass that has just been bottled. How long has the aged wine been in the bottle? The half-life of tritium is 12.3 y.

20.94 The naturally occurring isotope rubidium-87 decays by beta emission to strontium-87. This decay is the basis of a method for determining the ages of rocks. A sample of rock contains 102.1 μg ^{87}Rb and 5.3 μg ^{87}Sr. What is the age of the rock? The half-life of rubidium-87 is 4.8×10^{10} y.

20.95 When a positron and an electron collide, they are annihilated and two gamma photons of equal energy are emitted. Calculate the wavelength corresponding to this gamma emission.

20.96 When technetium-99*m* decays to technetium-99, a gamma photon corresponding to an energy of 0.143 MeV is emitted. What is the wavelength of this gamma emission? What is the difference in mass between Tc-99*m* and Tc-99?

20.97 Calculate the energy released when 5.00 kg of uranium-235 undergoes the following fission process.

$$^{1}_{0}\text{n} + ^{235}_{92}\text{U} \longrightarrow ^{136}_{53}\text{I} + ^{96}_{39}\text{Y} + 4^{1}_{0}\text{n}$$

The masses of $^{136}_{53}$I and $^{96}_{39}$Y nuclei are 135.8401 amu and 95.8629 amu, respectively. Other masses are given in Table 20.3. Compare this energy with the heat released when 5.00 kg C(graphite) burns to $CO_2(g)$.

20.98 Calculate the energy released when 1.00 kg of hydrogen-1 undergoes fusion to helium-4, according to the following reaction.

$$4^{1}_{1}\text{H} \longrightarrow ^{4}_{2}\text{He} + 2^{0}_{1}\text{e}$$

This reaction is one of the principal sources of energy from the sun. Compare the energy released by 1.00 kg of $^{1}_{1}$H in this reaction to the heat released when 1.00 kg of C(graphite) burns to $CO_2(g)$. See Table 20.3 for data.

20.99 The half-life of calcium-47 is 4.536 days and it decays by the emission of a beta particle.

a. Write a balanced equation for the decay of Ca-47.

b. If 10.0 μg of Ca-47 is needed for an experiment, what mass of $^{47}CaSO_4$ must be ordered if it takes 48 h for it to arrive from the supplier?

20.100 The radioactive isotope phosphorus-32 is often used in biochemical research. Its half-life is 14.28 days and it decays by beta emission.

a. Write a balanced equation for the decomposition of P-32.

b. If the original sample were 275 mg of $K_3{}^{32}PO_4$, what amount remains after 35.0 d? What percent of the sample has undergone decay?

20.101 The half-life of $^{82}_{35}$Br is 1.471 days. This isotope decays by the emission of a beta particle.

a. Gaseous HBr is made with Br-82. When the bromine isotope decays, the HBr produces H_2 and the bromine decay product. Write a balanced equation for the decay of Br-82. Now, write a balanced equation for the decomposition of $H^{82}Br$.

b. If a pure sample of 0.0150 mol of HBr made entirely with Br-82 is placed in an evacuated 1.00-L flask, how much HBr remains after 12.0 h? If the temperature is 22°C, what is the pressure in the flask?

20.102 The half-life of $^{132}_{52}$Te is 3.26 days. This isotope decays by beta emission to a highly unstable intermediate that decays rapidly to a stable product by beta emission.

a. What is the ultimate product obtained from Te-132? Write a balanced equation for this reaction.

b. Gaseous H_2Te is made with Te-132. When the tellurium isotope decays, the H_2Te produces H_2 and the ultimate decay product of Te-132. Write a balanced equation for the formation of stable products from $H_2{}^{132}Te$.

c. If a pure sample of 0.0125 mol of H_2Te made entirely of Te-132 is placed in an evacuated 1.50-L flask, how much H_2Te remains after 99.0 h? If the temperature is 25°C, what is the pressure in the flask?

20.103 How would you describe the structure of the alpha particle in terms of the shell model? Note that the protons and neutrons have their own shell structures. Why would you expect the alpha particle to be especially stable?

20.104 What are the next three energy levels following the 1*f* level (before spin-orbit coupling is accounted for)?

20.105 What is the purpose of a PET scan? What type of substance is administered to a person undergoing a PET scan?

20.106 The instrument for PET scans actually detects gamma rays. However, the radioactive substance emits another particle. Describe what is happening.

Strategy Problems

20.107 Complete the following nuclear reactions.

a. $^{31}_{14}\text{Si} \longrightarrow ^{31}_{15}\text{P} + ?$

b. $^{44}_{22}\text{Ti} + ? \longrightarrow ^{44}_{21}\text{Sc}$

c. $^{252}_{98}\text{Cf} \longrightarrow ^{142}_{56}\text{Ba} + ? + 4^{1}_{0}\text{n}$

20.108 What nuclide is formed when americium-241 undergoes alpha decay?

20.109 Radioisotope thermoelectric generators can be used by satellites to obtain power from radioactive decay of various isotopes, plutonium-238 being the preferred fuel. Plutonium-238 decays via alpha emission and has a half-life of 87.7 years.

a. Write the nuclear equation for the alpha decay of plutonium-238.

b. If you were to start with 250.0 g of Pu-238 to power a satellite, what mass would remain after 50 years?

20.110 Calculate the energy released, in joules per mole, when uranium-238 undergoes alpha decay. See Table 20.3.

20.111 Consider Rn-222.

a. Predict the type of radioactive decay that Rn-222 is most likely to undergo.

b. Write the equation for the decay process.

c. The half-life of Rn-222 is 3.82 days. If you start with a 150.0-g sample of Rn-222, how much remains after 15.0 days?

20.112 The gold-198 isotope is used in the treatment of brain, prostate, and ovarian cancer. Au-198 has a half-life of 2.69 d. If a hospital needs to have 15 mg of Au-198 on hand for treatments on a particular day, and shipping takes 72 h, what mass of Au-198 needs to be ordered?

20.113 The bromine isotope Br-75 is used for imaging in positron emission tomography. Br-75 has a half-life of 57 h. How much time must elapse for a given dose of Br-75 to drop to 25% of its initial amount?

20.114 The decay of Rb-87 ($t_{1/2} = 4.8 \times 10^{10}$ y) to Sr-87 has been used to determine the age of ancient rocks and minerals.

a. Write the balanced nuclear equation for this decay.

b. If a sample of rock is found to be 0.100% by mass Rb-87 and 0.00250% Sr-87, what is the age of the rock? Assume that there was no Sr-87 present when the rock formed.

20.115 You have two piles of different unknown radioactive substances: pile A with a mass of 200 g, and pile B with a mass of 100 g. Would it be possible for these two piles to have the same rate of radioactive decay? Explain.

20.116 Cobalt-60 has a half-life of 5.26 y. Gamma radiation from this isotope is used to treat malignant tumors. What mass of cobalt-60 is required to generate a 500-Ci gamma-ray source?

Cumulative-Skills Problems

20.117 A sample of sodium phosphate, Na_3PO_4, weighing 54.5 mg contains radioactive phosphorus-32 (with mass 32.0 amu). If 15.6% of the phosphorus atoms in the compound is phosphorus-32 (the remainder is naturally occurring phosphorus), how many disintegrations of this nucleus occur per second in this sample? Phosphorus-32 has a half-life of 14.3 d.

20.118 A sample of sodium thiosulfate, $Na_2S_2O_3$, weighing 38.1 mg contains radioactive sulfur-35 (with mass 35.0 amu). If 22.3% of the sulfur atoms in the compound is sulfur-35 (the remainder is naturally occurring sulfur), how many disintegrations of this nucleus occur per second in this sample? Sulfur-35 has a half-life of 87.9 d.

20.119 Polonium-210 has a half-life of 138.4 days, decaying by alpha emission. Suppose the helium gas originating from the alpha particles in this decay were collected. What volume of helium at 25°C and 735 mmHg could be obtained from 1.0000 g of polonium dioxide, PoO_2, in a period of 48.0 h?

20.120 Radium-226 decays by alpha emission to radon-222, a noble gas. What volume of pure radon-222 at 23°C and 785 mmHg could be obtained from 543.0 mg of radium bromide, $RaBr_2$, in a period of 37.5 y? The half-life of radium-226 is 1602 years.

20.121 What is the energy (in joules) evolved when 1 mol of helium-4 nuclei is produced from protons and neutrons? How many liters of ethane, $C_2H_6(g)$, at 25°C and 725 mmHg are needed to evolve the same quantity of energy when the ethane is burned in oxygen to $CO_2(g)$ and $H_2O(g)$? See Table 20.3 and Appendix C for data.

20.122 Plutonium-239 has been used as a power source for heart pacemakers. What is the energy obtained from the following decay of 215 mg of plutonium-239?

$$^{239}_{94}\mathrm{Pu} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{235}_{92}\mathrm{U}$$

Suppose the electric energy produced from this amount of plutonium-239 is 25.0% of this value. What is the minimum grams of zinc that would be needed for the standard voltaic cell $Zn|Zn^{2+}\|Cu^{2+}|Cu$ to obtain the same electric energy?