27. The surface tension and viscosity of water at several different temperatures are given in this table.

Water	Surface Tension (mN/m)	Viscosity (mPa s)
0 °C	75.6	1.79
20 °C	72.8	1.00
60 °C	66.2	0.47
100 °C	58.9	0.28

(a) As temperature increases, what happens to the surface tension of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.

(b) As temperature increases, what happens to the viscosity of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.

28. At 25 °C, how high will water rise in a glass capillary tube with an inner diameter of 0.63 mm? Refer to **Example 10.4** for the required information.

29. Water rises in a glass capillary tube to a height of 17 cm. What is the diameter of the capillary tube?

10.3 Phase Transitions

30. Heat is added to boiling water. Explain why the temperature of the boiling water does not change. What does change?

31. Heat is added to ice at 0 °C. Explain why the temperature of the ice does not change. What does change?

32. What feature characterizes the dynamic equilibrium between a liquid and its vapor in a closed container?

33. Identify two common observations indicating some liquids have sufficient vapor pressures to noticeably evaporate?

34. Identify two common observations indicating some solids, such as dry ice and mothballs, have vapor pressures sufficient to sublime?

35. What is the relationship between the intermolecular forces in a liquid and its vapor pressure?

36. What is the relationship between the intermolecular forces in a solid and its melting temperature?

37. Why does spilled gasoline evaporate more rapidly on a hot day than on a cold day?

38. Carbon tetrachloride, CCl_4, was once used as a dry cleaning solvent, but is no longer used because it is carcinogenic. At 57.8 °C, the vapor pressure of CCl_4 is 54.0 kPa, and its enthalpy of vaporization is 33.05 kJ/mol. Use this information to estimate the normal boiling point for CCl_4.

39. When is the boiling point of a liquid equal to its normal boiling point?

40. How does the boiling of a liquid differ from its evaporation?

41. Use the information in **Figure 10.24** to estimate the boiling point of water in Denver when the atmospheric pressure is 83.3 kPa.

42. A syringe at a temperature of 20 °C is filled with liquid ether in such a way that there is no space for any vapor. If the temperature is kept constant and the plunger is withdrawn to create a volume that can be occupied by vapor, what would be the approximate pressure of the vapor produced?

43. Explain the following observations:

(a) It takes longer to cook an egg in Ft. Davis, Texas (altitude, 5000 feet above sea level) than it does in Boston (at sea level).

(b) Perspiring is a mechanism for cooling the body.

44. The enthalpy of vaporization of water is larger than its enthalpy of fusion. Explain why.

45. Explain why the molar enthalpies of vaporization of the following substances increase in the order $CH_4 < C_2H_6 < C_3H_8$, even though the type of IMF (dispersion) is the same.

46. Explain why the enthalpies of vaporization of the following substances increase in the order $CH_4 < NH_3 < H_2O$, even though all three substances have approximately the same molar mass.

47. The enthalpy of vaporization of $CO_2(l)$ is 9.8 kJ/mol. Would you expect the enthalpy of vaporization of $CS_2(l)$ to be 28 kJ/mol, 9.8 kJ/mol, or −8.4 kJ/mol? Discuss the plausibility of each of these answers.

48. The hydrogen fluoride molecule, HF, is more polar than a water molecule, H_2O (for example, has a greater dipole moment), yet the molar enthalpy of vaporization for liquid hydrogen fluoride is lesser than that for water. Explain.

49. Ethyl chloride (boiling point, 13 °C) is used as a local anesthetic. When the liquid is sprayed on the skin, it cools the skin enough to freeze and numb it. Explain the cooling effect of liquid ethyl chloride.

50. Which contains the compounds listed correctly in order of increasing boiling points?

(a) $N_2 < CS_2 < H_2O < KCl$

(b) $H_2O < N_2 < CS_2 < KCl$

(c) $N_2 < KCl < CS_2 < H_2O$

(d) $CS_2 < N_2 < KCl < H_2O$

(e) $KCl < H_2O < CS_2 < N_2$

51. How much heat is required to convert 422 g of liquid H_2O at 23.5 °C into steam at 150 °C?

52. Evaporation of sweat requires energy and thus take excess heat away from the body. Some of the water that you drink may eventually be converted into sweat and evaporate. If you drink a 20-ounce bottle of water that had been in the refrigerator at 3.8 °C, how much heat is needed to convert all of that water into sweat and then to vapor? (Note: Your body temperature is 36.6 °C. For the purpose of solving this problem, assume that the thermal properties of sweat are the same as for water.)

53. Titanium tetrachloride, $TiCl_4$, has a melting point of −23.2 °C and has a $\Delta H_{\text{fusion}} = 9.37$ kJ/mol.

(a) How much energy is required to melt 263.1 g $TiCl_4$?

(b) For $TiCl_4$, which will likely have the larger magnitude: ΔH_{fusion} or $\Delta H_{\text{vaporization}}$? Explain your reasoning.

10.4 Phase Diagrams

54. From the phase diagram for water (**Figure 10.31**), determine the state of water at:

(a) 35 °C and 85 kPa

(b) −15 °C and 40 kPa

(c) −15 °C and 0.1 kPa

(d) 75 °C and 3 kPa

(e) 40 °C and 0.1 kPa

(f) 60 °C and 50 kPa

55. What phase changes will take place when water is subjected to varying pressure at a constant temperature of 0.005 °C? At 40 °C? At −40 °C?

56. Pressure cookers allow food to cook faster because the higher pressure inside the pressure cooker increases the boiling temperature of water. A particular pressure cooker has a safety valve that is set to vent steam if the pressure exceeds 3.4 atm. What is the approximate maximum temperature that can be reached inside this pressure cooker? Explain your reasoning.

57. From the phase diagram for carbon dioxide in **Figure 10.34**, determine the state of CO_2 at:

(a) 20 °C and 1000 kPa

(b) 10 °C and 2000 kPa

(c) 10 °C and 100 kPa

(d) −40 °C and 500 kPa

(e) −80 °C and 1500 kPa

(f) −80 °C and 10 kPa

58. Determine the phase changes that carbon dioxide undergoes as pressure is increased at a constant temperature of (a) −50 °C and (b) 50 °C. If the temperature is held at −40 °C? At 20 °C? (See the phase diagram in **Figure 10.34**.)

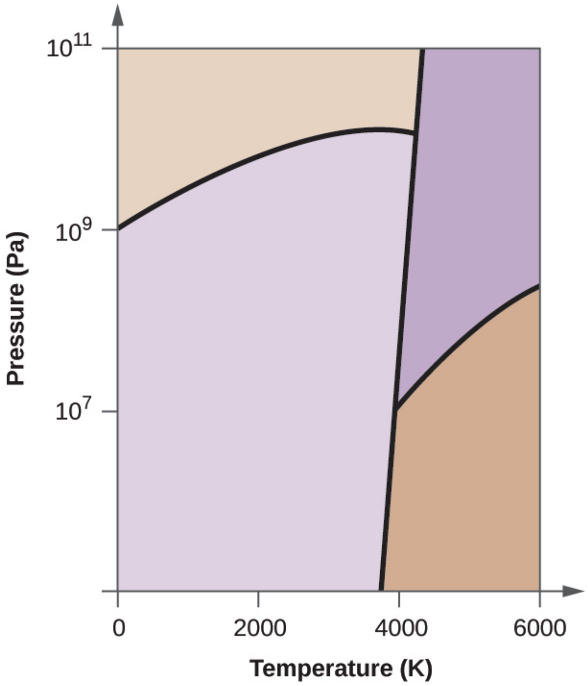
59. Consider a cylinder containing a mixture of liquid carbon dioxide in equilibrium with gaseous carbon dioxide at an initial pressure of 65 atm and a temperature of 20 °C. Sketch a plot depicting the change in the cylinder pressure with time as gaseous carbon dioxide is released at constant temperature.

60. Dry ice, $CO_2(s)$, does not melt at atmospheric pressure. It sublimes at a temperature of −78 °C. What is the lowest pressure at which $CO_2(s)$ will melt to give $CO_2(l)$? At approximately what temperature will this occur? (See **Figure 10.34** for the phase diagram.)

61. If a severe storm results in the loss of electricity, it may be necessary to use a clothesline to dry laundry. In many parts of the country in the dead of winter, the clothes will quickly freeze when they are hung on the line. If it does not snow, will they dry anyway? Explain your answer.

62. Is it possible to liquefy nitrogen at room temperature (about 25 °C)? Is it possible to liquefy sulfur dioxide at room temperature? Explain your answers.

63. Elemental carbon has one gas phase, one liquid phase, and two different solid phases, as shown in the phase diagram:



(a) On the phase diagram, label the gas and liquid regions.

(b) Graphite is the most stable phase of carbon at normal conditions. On the phase diagram, label the graphite phase.

(c) If graphite at normal conditions is heated to 2500 K while the pressure is increased to 10^{10} Pa, it is converted into diamond. Label the diamond phase.

(d) Circle each triple point on the phase diagram.

(e) In what phase does carbon exist at 5000 K and 10^8 Pa?

(f) If the temperature of a sample of carbon increases from 3000 K to 5000 K at a constant pressure of 10^6 Pa, which phase transition occurs, if any?

10.5 The Solid State of Matter

64. What types of liquids typically form amorphous solids?

65. At very low temperatures oxygen, O_2, freezes and forms a crystalline solid. Which best describes these crystals?

(a) ionic

(b) covalent network

(c) metallic

(d) amorphous

(e) molecular crystals

66. As it cools, olive oil slowly solidifies and forms a solid over a range of temperatures. Which best describes the solid?

(a) ionic

(b) covalent network

(c) metallic

(d) amorphous

(e) molecular crystals

67. Explain why ice, which is a crystalline solid, has a melting temperature of 0 °C, whereas butter, which is an amorphous solid, softens over a range of temperatures.

68. Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

(a) SiO_2

(b) KCl

(c) Cu

(d) CO_2

(e) C (diamond)

(f) $BaSO_4$

(g) NH_3

(h) NH_4F

(i) C_2H_5OH

69. Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

(a) $CaCl_2$

(b) SiC

(c) N_2

(d) Fe

(e) C (graphite)

(f) $CH_3CH_2CH_2CH_3$

(g) HCl

(h) NH_4NO_3

(i) K_3PO_4

70. Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	lustrous, malleable	1500 °C	high	insoluble
Y	soft, yellow	113 °C	none	insoluble
Z	hard, white	800 °C	only if melted/dissolved	soluble

71. Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	brittle, white	800 °C	only if melted/dissolved	soluble
Y	shiny, malleable	1100 °C	high	insoluble
Z	hard, colorless	3550 °C	none	insoluble

72. Identify the following substances as ionic, metallic, covalent network, or molecular solids:

Substance A is malleable, ductile, conducts electricity well, and has a melting point of 1135 °C. Substance B is brittle, does not conduct electricity as a solid but does when molten, and has a melting point of 2072 °C. Substance C is very hard, does not conduct electricity, and has a melting point of 3440 °C. Substance D is soft, does not conduct electricity, and has a melting point of 185 °C.

73. Substance A is shiny, conducts electricity well, and melts at 975 °C. Substance A is likely a(n):

(a) ionic solid

(b) metallic solid

(c) molecular solid

(d) covalent network solid

74. Substance B is hard, does not conduct electricity, and melts at 1200 °C. Substance B is likely a(n):

(a) ionic solid

(b) metallic solid

(c) molecular solid

(d) covalent network solid

10.6 Lattice Structures in Crystalline Solids

75. Describe the crystal structure of iron, which crystallizes with two equivalent metal atoms in a cubic unit cell.

76. Describe the crystal structure of Pt, which crystallizes with four equivalent metal atoms in a cubic unit cell.

77. What is the coordination number of a chromium atom in the body-centered cubic structure of chromium?

78. What is the coordination number of an aluminum atom in the face-centered cubic structure of aluminum?

79. Cobalt metal crystallizes in a hexagonal closest packed structure. What is the coordination number of a cobalt atom?

80. Nickel metal crystallizes in a cubic closest packed structure. What is the coordination number of a nickel atom?

81. Tungsten crystallizes in a body-centered cubic unit cell with an edge length of 3.165 Å.

(a) What is the atomic radius of tungsten in this structure?

(b) Calculate the density of tungsten.

82. Platinum (atomic radius = 1.38 Å) crystallizes in a cubic closely packed structure. Calculate the edge length of the face-centered cubic unit cell and the density of platinum.

83. Barium crystallizes in a body-centered cubic unit cell with an edge length of 5.025 Å

(a) What is the atomic radius of barium in this structure?

(b) Calculate the density of barium.

84. Aluminum (atomic radius = 1.43 Å) crystallizes in a cubic closely packed structure. Calculate the edge length of the face-centered cubic unit cell and the density of aluminum.

85. The density of aluminum is 2.7 g/cm^3; that of silicon is 2.3 g/cm^3. Explain why Si has the lower density even though it has heavier atoms.

86. The free space in a metal may be found by subtracting the volume of the atoms in a unit cell from the volume of the cell. Calculate the percentage of free space in each of the three cubic lattices if all atoms in each are of equal size and touch their nearest neighbors. Which of these structures represents the most efficient packing? That is, which packs with the least amount of unused space?

87. Cadmium sulfide, sometimes used as a yellow pigment by artists, crystallizes with cadmium, occupying one-half of the tetrahedral holes in a closest packed array of sulfide ions. What is the formula of cadmium sulfide? Explain your answer.

88. A compound of cadmium, tin, and phosphorus is used in the fabrication of some semiconductors. It crystallizes with cadmium occupying one-fourth of the tetrahedral holes and tin occupying one-fourth of the tetrahedral holes in a closest packed array of phosphide ions. What is the formula of the compound? Explain your answer.

89. What is the formula of the magnetic oxide of cobalt, used in recording tapes, that crystallizes with cobalt atoms occupying one-eighth of the tetrahedral holes and one-half of the octahedral holes in a closely packed array of oxide ions?

90. A compound containing zinc, aluminum, and sulfur crystallizes with a closest-packed array of sulfide ions. Zinc ions are found in one-eighth of the tetrahedral holes and aluminum ions in one-half of the octahedral holes. What is the empirical formula of the compound?

91. A compound of thallium and iodine crystallizes in a simple cubic array of iodide ions with thallium ions in all of the cubic holes. What is the formula of this iodide? Explain your answer.

92. Which of the following elements reacts with sulfur to form a solid in which the sulfur atoms form a closest-packed array with all of the octahedral holes occupied: Li, Na, Be, Ca, or Al?

93. What is the percent by mass of titanium in rutile, a mineral that contains titanium and oxygen, if structure can be described as a closest packed array of oxide ions with titanium ions in one-half of the octahedral holes? What is the oxidation number of titanium?

94. Explain why the chemically similar alkali metal chlorides NaCl and CsCl have different structures, whereas the chemically different NaCl and MnS have the same structure.

95. As minerals were formed from the molten magma, different ions occupied the same cites in the crystals. Lithium often occurs along with magnesium in minerals despite the difference in the charge on their ions. Suggest an explanation.

96. Rubidium iodide crystallizes with a cubic unit cell that contains iodide ions at the corners and a rubidium ion in the center. What is the formula of the compound?

97. One of the various manganese oxides crystallizes with a cubic unit cell that contains manganese ions at the corners and in the center. Oxide ions are located at the center of each edge of the unit cell. What is the formula of the compound?

98. NaH crystallizes with the same crystal structure as NaCl. The edge length of the cubic unit cell of NaH is 4.880 Å.

(a) Calculate the ionic radius of H^-. (The ionic radius of Li^+ is 0.0.95 Å.)

(b) Calculate the density of NaH.

99. Thallium(I) iodide crystallizes with the same structure as CsCl. The edge length of the unit cell of TlI is 4.20 Å. Calculate the ionic radius of TI^+. (The ionic radius of I^- is 2.16 Å.)

100. A cubic unit cell contains manganese ions at the corners and fluoride ions at the center of each edge.

(a) What is the empirical formula of this compound? Explain your answer.

(b) What is the coordination number of the Mn^{3+} ion?

(c) Calculate the edge length of the unit cell if the radius of a Mn^{3+} ion is 0.65 A.

(d) Calculate the density of the compound.

101. What is the spacing between crystal planes that diffract X-rays with a wavelength of 1.541 nm at an angle θ of 15.55° (first order reflection)?

102. A diffractometer using X-rays with a wavelength of 0.2287 nm produced first order diffraction peak for a crystal angle $\theta = 16.21°$. Determine the spacing between the diffracting planes in this crystal.

103. A metal with spacing between planes equal to 0.4164 nm diffracts X-rays with a wavelength of 0.2879 nm. What is the diffraction angle for the first order diffraction peak?

104. Gold crystallizes in a face-centered cubic unit cell. The second-order reflection ($n = 2$) of X-rays for the planes that make up the tops and bottoms of the unit cells is at $\theta = 22.20°$. The wavelength of the X-rays is 1.54 Å. What is the density of metallic gold?

105. When an electron in an excited molybdenum atom falls from the L to the K shell, an X-ray is emitted. These X-rays are diffracted at an angle of 7.75° by planes with a separation of 2.64 Å. What is the difference in energy between the K shell and the L shell in molybdenum assuming a first order diffraction?

Chapter 11

Solutions and Colloids

Figure 11.1 Coral reefs, such as this one at the Palmyra Atoll National Wildlife Refuge, are vital to the ecosystem of earth's oceans. The health of coral reefs and all marine life depends on the specific chemical composition of the complex mixture known as seawater. (credit: modification of work by "USFWS – Pacific Region"/Wikimedia Commons)

Chapter Outline

Introduction

Coral reefs are home to about 25% of all marine species. They are being threatened by climate change, oceanic acidification, and water pollution, all of which change the composition of the solution known as seawater. Dissolved oxygen in seawater is critical for sea creatures, but as the oceans warm, oxygen becomes less soluble. As the concentration of carbon dioxide in the atmosphere increases, the concentration of carbon dioxide in the oceans increases, contributing to oceanic acidification. Coral reefs are particularly sensitive to the acidification of the ocean, since the exoskeletons of the coral polyps are soluble in acidic solutions. Humans contribute to the changing of seawater composition by allowing agricultural runoff and other forms of pollution to affect our oceans.

Solutions are crucial to the processes that sustain life and to many other processes involving chemical reactions. This chapter considers the nature of solutions and examines factors that determine whether a solution will form and what properties it may have. The properties of colloids—mixtures containing dispersed particles larger than the molecules and ions of typical solutions—are also discussed.

11.1 The Dissolution Process

By the end of this section, you will be able to:

- Describe the basic properties of solutions and how they form
- Predict whether a given mixture will yield a solution based on molecular properties of its components
- Explain why some solutions either produce or absorb heat when they form

An earlier chapter of this text introduced *solutions*, defined as homogeneous mixtures of two or more substances. Often, one component of a solution is present at a significantly greater concentration, in which case it is called the *solvent*. The other components of the solution present in relatively lesser concentrations are called *solutes*. Sugar is a covalent solid composed of sucrose molecules, $C_{12}H_{22}O_{11}$. When this compound dissolves in water, its molecules become uniformly distributed among the molecules of water:

$$\mathrm{C_{12}H_{22}O_{11}}(s) \longrightarrow \mathrm{C_{12}H_{22}O_{11}}(aq)$$

The subscript "*aq*" in the equation signifies that the sucrose molecules are solutes and are therefore *individually dispersed* throughout the *aqueous solution* (water is the solvent). Although sucrose molecules are heavier than water molecules, they remain dispersed throughout the solution; gravity does not cause them to "settle out" over time.

Potassium dichromate, $K_2Cr_2O_7$, is an ionic compound composed of colorless potassium ions, K^+, and orange dichromate ions, $\mathrm{Cr_2O_7}^{2-}$. When a small amount of solid potassium dichromate is added to water, the compound dissolves and dissociates to yield potassium ions and dichromate ions uniformly distributed throughout the mixture (**Figure 11.2**), as indicated in this equation:

$$\mathrm{K_2Cr_2O_7}(s) \longrightarrow 2\mathrm{K}^+(aq) + \mathrm{Cr_2O_7}^{2-}(aq)$$

As with the mixture of sugar and water, this mixture is also an aqueous solution. Its solutes, potassium and dichromate ions, remain individually dispersed among the solvent (water) molecules.

Figure 11.2 When potassium dichromate ($K_2Cr_2O_7$) is mixed with water, it forms a homogeneous orange solution. (credit: modification of work by Mark Ott)

Link to Learning

Visit this **virtual lab (http://openstaxcollege.org/l/16Phetsugar)** to view simulations of the dissolution of common covalent and ionic substances (sugar and salt) in water.

Water is used so often as a solvent that the word solution has come to imply an aqueous solution to many people. However, almost any gas, liquid, or solid can act as a solvent. Many **alloys** are solid solutions of one metal dissolved in another; for example, US five-cent coins contain nickel dissolved in copper. Air is a gaseous solution, a homogeneous mixture of nitrogen, oxygen, and several other gases. Oxygen (a gas), alcohol (a liquid), and sugar (a solid) all dissolve in water (a liquid) to form liquid solutions. **Table 11.1** gives examples of several different solutions and the phases of the solutes and solvents.

Different Types of Solutions

Solution	Solute	Solvent
air	$O_2(g)$	$N_2(g)$
soft drinks[1]	$CO_2(g)$	$H_2O(l)$
hydrogen in palladium	$H_2(g)$	$Pd(s)$
rubbing alcohol	$H_2O(l)$	$C_3H_8O(l)$ (2-propanol)
saltwater	$NaCl(s)$	$H_2O(l)$
brass	$Zn(s)$	$Cu(s)$

Table 11.1

Solutions exhibit these defining traits:

- They are homogeneous; after a solution is mixed, it has the same composition at all points throughout (its composition is uniform).
- The physical state of a solution—solid, liquid, or gas—is typically the same as that of the solvent, as demonstrated by the examples in **Table 11.1**.
- The components of a solution are dispersed on a molecular scale; they consist of a mixture of separated solute particles (molecules, atoms, and/or ions) each closely surrounded by solvent species.
- The dissolved solute in a solution will not settle out or separate from the solvent.
- The composition of a solution, or the concentrations of its components, can be varied continuously (within limits determined by the *solubility* of the components, discussed in detail later in this chapter).

The Formation of Solutions

The formation of a solution is an example of a **spontaneous process**, a process that occurs under specified conditions without the requirement of energy from some external source. Sometimes a mixture is stirred to speed up the dissolution process, but this is not necessary; a homogeneous solution will form eventually. The topic of spontaneity is critically important to the study of chemical thermodynamics and is treated more thoroughly in a later chapter of this text. For purposes of this chapter's discussion, it will suffice to consider two criteria that *favor*, but do not guarantee, the spontaneous formation of a solution:

1. a decrease in the internal energy of the system (an exothermic change, as discussed in the previous chapter on thermochemistry)
2. an increased dispersal of matter in the system (which indicates an increase in the *entropy* of the system, as you will learn about in the later chapter on thermodynamics)

In the process of dissolution, an internal energy change often, but not always, occurs as heat is absorbed or evolved. An increase in matter dispersal always results when a solution forms from the uniform distribution of solute molecules throughout a solvent.

When the strengths of the intermolecular forces of attraction between solute and solvent species in a solution are no different than those present in the separated components, the solution is formed with no accompanying energy change. Such a solution is called an **ideal solution**. A mixture of ideal gases (or gases such as helium and argon, which closely approach ideal behavior) is an example of an ideal solution, since the entities comprising these gases experience no significant intermolecular attractions.

When containers of helium and argon are connected, the gases spontaneously mix due to diffusion and form a solution

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[1] If bubbles of gas are observed within the liquid, the mixture is not homogeneous and, thus, not a solution.

(**Figure 11.3**). The formation of this solution clearly involves an increase in matter dispersal, since the helium and argon atoms occupy a volume twice as large as that which each occupied before mixing.

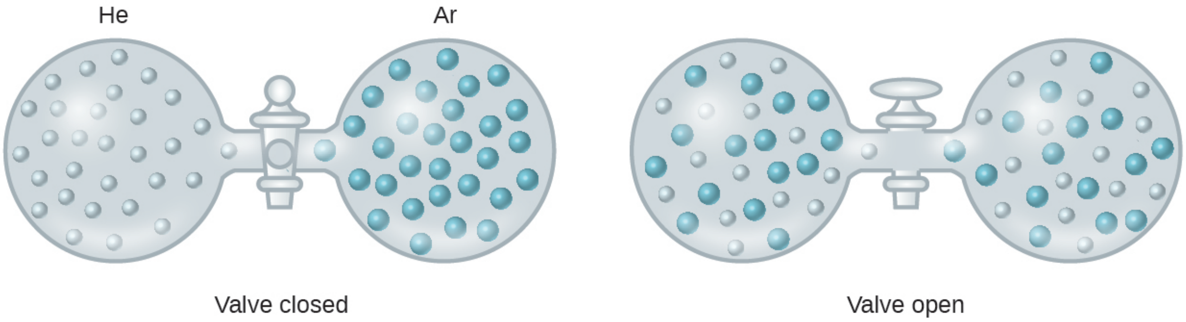


Figure 11.3 Samples of helium and argon spontaneously mix to give a solution.

Ideal solutions may also form when structurally similar liquids are mixed. For example, mixtures of the alcohols methanol (CH_3OH) and ethanol (C_2H_5OH) form ideal solutions, as do mixtures of the hydrocarbons pentane, C_5H_{12}, and hexane, C_6H_{14}. Placing methanol and ethanol, or pentane and hexane, in the bulbs shown in **Figure 11.3** will result in the same diffusion and subsequent mixing of these liquids as is observed for the He and Ar gases (although at a much slower rate), yielding solutions with no significant change in energy. Unlike a mixture of gases, however, the components of these liquid-liquid solutions do, indeed, experience intermolecular attractive forces. But since the molecules of the two substances being mixed are structurally very similar, the intermolecular attractive forces between like and unlike molecules are essentially the same, and the dissolution process, therefore, does not entail any appreciable increase or decrease in energy. These examples illustrate how increased matter dispersal alone can provide the driving force required to cause the spontaneous formation of a solution. In some cases, however, the relative magnitudes of intermolecular forces of attraction between solute and solvent species may prevent dissolution.

Three types of intermolecular attractive forces are relevant to the dissolution process: solute-solute, solvent-solvent, and solute-solvent. As illustrated in **Figure 11.4**, the formation of a solution may be viewed as a stepwise process in which energy is consumed to overcome solute-solute and solvent-solvent attractions (endothermic processes) and released when solute-solvent attractions are established (an exothermic process referred to as **solvation**). The relative magnitudes of the energy changes associated with these stepwise processes determine whether the dissolution process overall will release or absorb energy. In some cases, solutions do not form because the energy required to separate solute and solvent species is so much greater than the energy released by solvation.

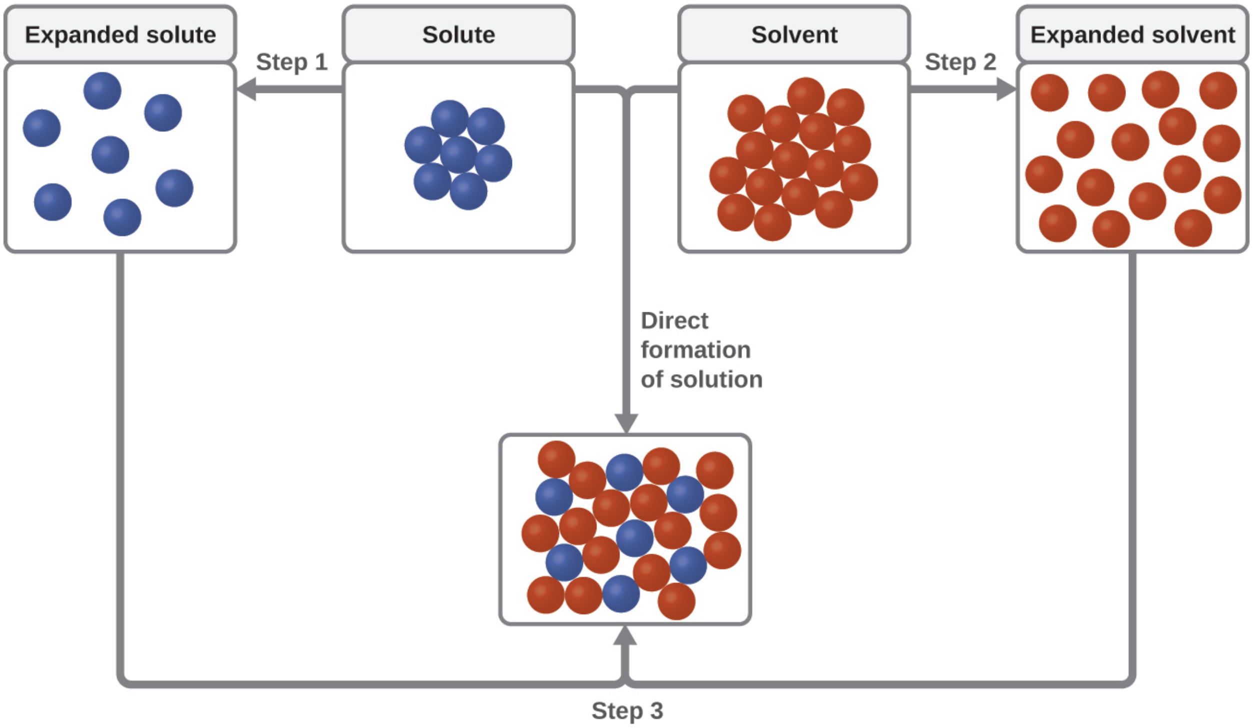


Figure 11.4 This schematic representation of dissolution shows a stepwise process involving the endothermic separation of solute and solvent species (Steps 1 and 2) and exothermic solvation (Step 3).

Consider the example of an ionic compound dissolving in water. Formation of the solution requires the electrostatic forces between the cations and anions of the compound (solute–solute) be overcome completely as attractive forces are established between these ions and water molecules (solute–solvent). Hydrogen bonding between a relatively small fraction of the water molecules must also be overcome to accommodate any dissolved solute. If the solute's electrostatic forces are significantly greater than the solvation forces, the dissolution process is significantly endothermic and the compound may not dissolve to an appreciable extent. Calcium carbonate, the major component of coral reefs, is one example of such an "insoluble" ionic compound (see **Figure 11.1**). On the other hand, if the solvation forces are much stronger than the compound's electrostatic forces, the dissolution is significantly exothermic and the compound may be highly soluble. A common example of this type of ionic compound is sodium chloride, commonly known as table salt.

As noted at the beginning of this module, spontaneous solution formation is favored, but not guaranteed, by exothermic dissolution processes. While many soluble compounds do, indeed, dissolve with the release of heat, some dissolve endothermically. Ammonium nitrate (NH_4NO_3) is one such example and is used to make instant cold packs for treating injuries like the one pictured in **Figure 11.5**. A thin-walled plastic bag of water is sealed inside a larger bag with solid NH_4NO_3. When the smaller bag is broken, a solution of NH_4NO_3 forms, absorbing heat from the surroundings (the injured area to which the pack is applied) and providing a cold compress that decreases swelling. Endothermic dissolutions such as this one require a greater energy input to separate the solute species than is recovered when the solutes are solvated, but they are spontaneous nonetheless due to the increase in disorder that accompanies formation of the solution.

Figure 11.5 An instant cold pack gets cold when certain salts, such as ammonium nitrate, dissolve in water—an endothermic process.

Link to Learning

Watch this brief **video (http://openstaxcollege.org/l/16endoexo)** illustrating endothermic and exothermic dissolution processes.

11.2 Electrolytes

By the end of this module, you will be able to:

- Define and give examples of electrolytes
- Distinguish between the physical and chemical changes that accompany dissolution of ionic and covalent electrolytes
- Relate electrolyte strength to solute-solvent attractive forces

When some substances are dissolved in water, they undergo either a physical or a chemical change that yields ions in solution. These substances constitute an important class of compounds called **electrolytes**. Substances that do not yield ions when dissolved are called **nonelectrolytes**. If the physical or chemical process that generates the ions is essentially 100% efficient (all of the dissolved compound yields ions), then the substance is known as a **strong electrolyte**. If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, it is called a **weak electrolyte**.

Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit (**Figure 11.6**).

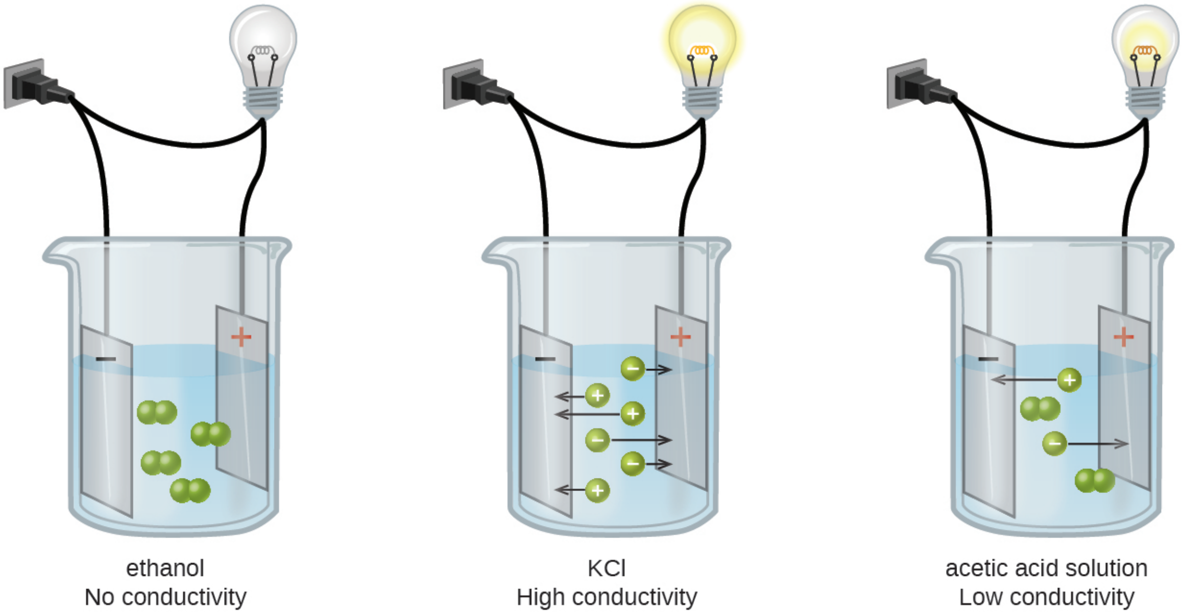


Figure 11.6 Solutions of nonelectrolytes such as ethanol do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte.

Ionic Electrolytes

Water and other polar molecules are attracted to ions, as shown in **Figure 11.7**. The electrostatic attraction between an ion and a molecule with a dipole is called an **ion-dipole attraction**. These attractions play an important role in the dissolution of ionic compounds in water.

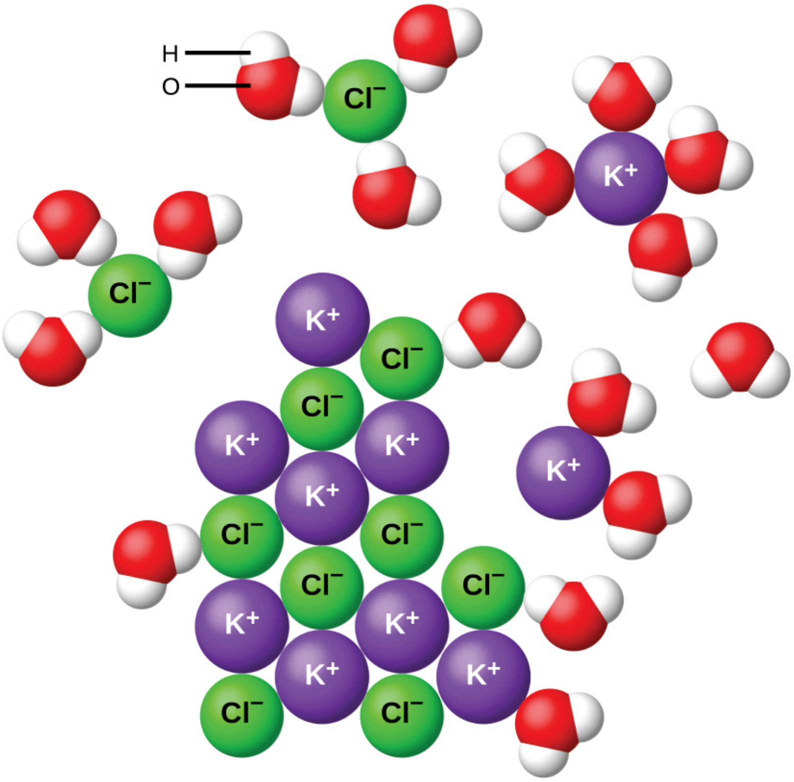


Figure 11.7 As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown.

When ionic compounds dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround and solvate the ions, reducing the strong electrostatic forces between them. This process represents a physical change known as **dissociation**. Under most conditions, ionic compounds will dissociate nearly completely when dissolved, and so they are classified as strong electrolytes. Even sparingly, soluble ionic compounds are strong electrolytes, since the small amount that does dissolve will dissociate completely.

Consider what happens at the microscopic level when solid KCl is added to water. Ion-dipole forces attract the positive (hydrogen) end of the polar water molecules to the negative chloride ions at the surface of the solid, and they attract the negative (oxygen) ends to the positive potassium ions. The water molecules surround individual K^+ and Cl^- ions, reducing the strong interionic forces that bind the ions together and letting them move off into solution as solvated ions, as **Figure 11.7** shows. Overcoming the electrostatic attraction permits the independent motion of each hydrated ion in a dilute solution as the ions transition from fixed positions in the undissolved compound to widely dispersed, solvated ions in solution.

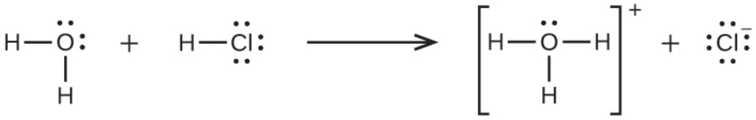
Covalent Electrolytes

Pure water is an extremely poor conductor of electricity because it is only very slightly ionized—only about two out of every 1 billion molecules ionize at 25 °C. Water ionizes when one molecule of water gives up a proton (H^+ ion) to another molecule of water, yielding hydronium and hydroxide ions.

$$\mathrm{H_2O}(l) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq)$$

In some cases, solutions prepared from covalent compounds conduct electricity because the solute molecules react chemically with the solvent to produce ions. For example, pure hydrogen chloride is a gas consisting of covalent HCl molecules. This gas contains no ions. However, an aqueous solution of HCl is a very good conductor, indicating that an appreciable concentration of ions exists within the solution.

Because HCl is an *acid*, its molecules react with water, transferring H^+ ions to form hydronium ions (H_3O^+) and chloride ions (Cl^-):



This reaction is essentially 100% complete for HCl (i.e., it is a *strong acid* and, consequently, a strong electrolyte). Likewise, weak acids and bases that only react partially generate relatively low concentrations of ions when dissolved in water and are classified as weak electrolytes. The reader may wish to review the discussion of strong and weak acids provided in the earlier chapter of this text on reaction classes and stoichiometry.

11.3 Solubility

By the end of this module, you will be able to:

- Describe the effects of temperature and pressure on solubility
- State Henry's law and use it in calculations involving the solubility of a gas in a liquid
- Explain the degrees of solubility possible for liquid-liquid solutions

Imagine adding a small amount of sugar to a glass of water, stirring until all the sugar has dissolved, and then adding a bit more. You can repeat this process until the sugar concentration of the solution reaches its natural limit, a limit determined primarily by the relative strengths of the solute-solute, solute-solvent, and solvent-solvent attractive forces discussed in the previous two modules of this chapter. You can be certain that you have reached this limit because, no matter how long you stir the solution, undissolved sugar remains. The concentration of sugar in the solution at this point is known as its solubility.

The **solubility** of a solute in a particular solvent is the maximum concentration that may be achieved under given conditions when the dissolution process is *at equilibrium*.

When a solute's concentration is equal to its solubility, the solution is said to be **saturated** with that solute. If the solute's concentration is less than its solubility, the solution is said to be **unsaturated**. A solution that contains a relatively low concentration of solute is called dilute, and one with a relatively high concentration is called concentrated.

Link to Learning

Use this **interactive simulation (http://openstaxcollege.org/l/16Phetsoluble)** to prepare various saturated solutions.

Solutions may be prepared in which a solute concentration *exceeds* its solubility. Such solutions are said to be **supersaturated**, and they are interesting examples of *nonequilibrium* states (a detailed treatment of this important concept is provided in the text chapters on equilibrium). For example, the carbonated beverage in an open container that has not yet "gone flat" is supersaturated with carbon dioxide gas; given time, the CO_2 concentration will decrease until it reaches its solubility.

Link to Learning

Watch this **impressive video (http://openstaxcollege.org/l/16NaAcetate)** showing the precipitation of sodium acetate from a supersaturated solution.

Solutions of Gases in Liquids

As for any solution, the solubility of a gas in a liquid is affected by the intermolecular attractive forces between solute and solvent species. Unlike solid and liquid solutes, however, there is no solute-solute intermolecular attraction to overcome when a gaseous solute dissolves in a liquid solvent (see **Figure 11.4**) since the atoms or molecules comprising a gas are far separated and experience negligible interactions. Consequently, solute-solvent interactions are the sole energetic factor affecting solubility. For example, the water solubility of oxygen is approximately three times greater than that of helium (there are greater dispersion forces between water and the larger oxygen molecules) but 100 times less than the solubility of chloromethane, $CHCl_3$ (polar chloromethane molecules experience dipole–dipole attraction to polar water molecules). Likewise note the solubility of oxygen in hexane, C_6H_{14}, is approximately 20 times greater than it is in water because greater dispersion forces exist between oxygen and the larger hexane molecules.

Temperature is another factor affecting solubility, with gas solubility typically decreasing as temperature increases (**Figure 11.8**). This inverse relation between temperature and dissolved gas concentration is responsible for one of the major impacts of thermal pollution in natural waters.

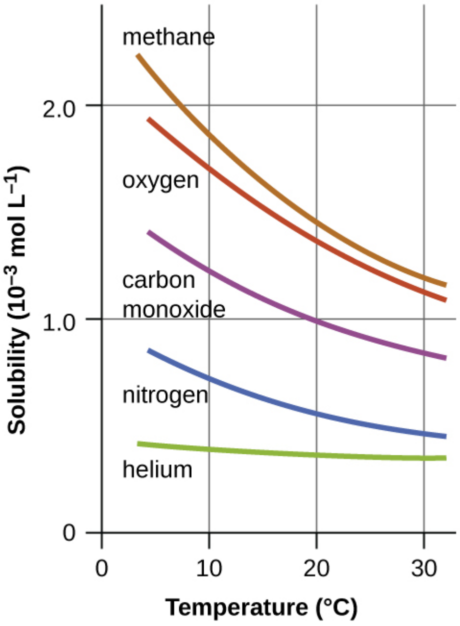


Figure 11.8 The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.

When the temperature of a river, lake, or stream is raised, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills (**Figure 11.9**).


(a) (b)

Figure 11.9 (a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (credit a: modification of work by Liz West; credit b: modification of work by U.S. Fish and Wildlife Service)

The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with CO_2 at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles (**Figure 11.10**). At this point, the beverage is *supersaturated* with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become “flat.”

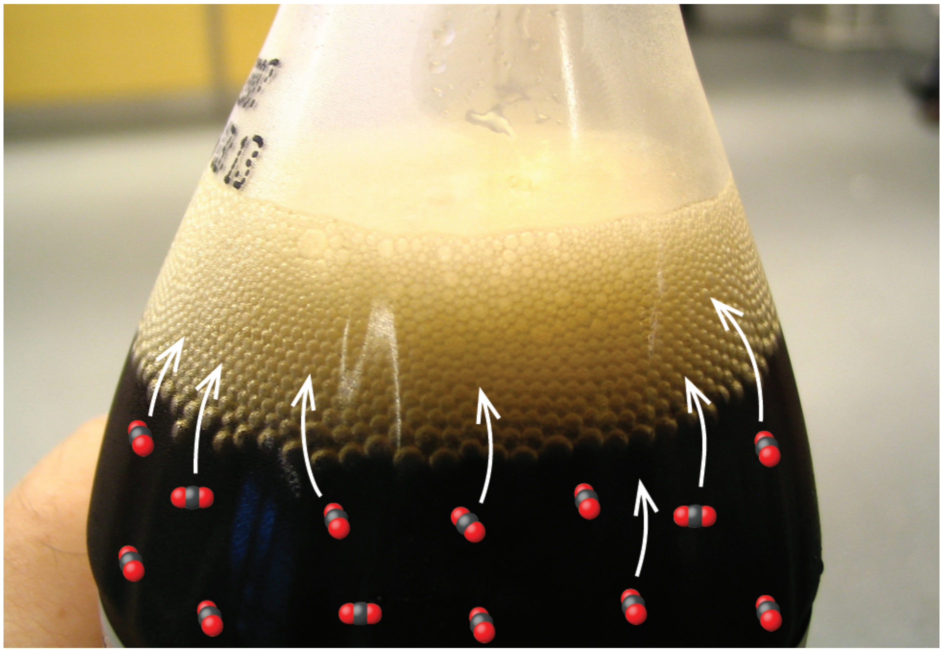


Figure 11.10 Opening the bottle of carbonated beverage reduces the pressure of the *gaseous* carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some *dissolved* carbon dioxide may be seen leaving the solution as small gas bubbles. (credit: modification of work by Derrick Coetzee)

For many gaseous solutes, the relation between solubility, C_g, and partial pressure, P_g, is a proportional one:

$$C_g = kP_g$$

where k is a proportionality constant that depends on the identities of the gaseous solute and solvent, and on the solution temperature. This is a mathematical statement of **Henry's law**: *The quantity of an ideal gas that dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.*

Example 11.1

Application of Henry's Law

At 20 °C, the concentration of dissolved oxygen in water exposed to gaseous oxygen at a partial pressure of 101.3 kPa is 1.38×10^{-3} mol L^{-1}. Use Henry's law to determine the solubility of oxygen when its partial pressure is 20.7 kPa, the approximate pressure of oxygen in earth's atmosphere.

Solution

According to Henry's law, for an ideal solution the solubility, C_g, of a gas (1.38×10^{-3} mol L^{-1}, in this case) is directly proportional to the pressure, P_g, of the undissolved gas above the solution (101.3 kPa in this case). Because both C_g and P_g are known, this relation can be rearragned and used to solve for k.

$$\begin{aligned} C_g &= kP_g \\ k &= \frac{C_g}{P_g} \\ &= \frac{1.38 \times 10^{-3}\ \text{mol L}^{-1}}{101.3\ \text{kPa}} \\ &= 1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \end{aligned}$$

Now, use k to find the solubility at the lower pressure.

$$\begin{aligned} C_g &= kP_g \\ & \quad 1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \times 20.7\ \text{kPa} \\ &= 2.82 \times 10^{-4}\ \text{mol L}^{-1} \end{aligned}$$

Note that various units may be used to express the quantities involved in these sorts of computations. Any combination of units that yield to the constraints of dimensional analysis are acceptable.

Check Your Learning

Exposing a 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 152 torr resulted in the dissolution of 1.45×10^{-3} g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 760 torr.

Answer: 7.25×10^{-3} in 100.0 mL or 0.0725 g/L

Example 11.2

Thermal Pollution and Oxygen Solubility

A certain species of freshwater trout requires a dissolved oxygen concentration of 7.5 mg/L. Could these fish thrive in a thermally polluted mountain stream (water temperature is 30.0 °C, partial pressure of atmospheric oxygen is 0.17 atm)?

Solution

First, compute the Henry's law constant for oxygen in water at the specified temperature of 30.0 °C (see

Figure 11.19).

$$k = \frac{C_g}{P_g} = 1.15 \times 10^{-3}\ \text{mol/L/1.00 atm} = 1.15 \times 10^{-3}\ \text{mol/L atm}$$

Then, use this k value to compute the oxygen solubility at the specified oxygen partial pressure, 0.17 atm.

$$C_g = kP_g = (1.15 \times 10^{-3}\ \text{mol/L atm})\,(0.17\ \text{atm}) = 1.95 \times 10^{-4}\ \text{mol/L}$$

Finally, convert this dissolved oxygen concentration from mol/L to mg/L.

$$(1.95 \times 10^{-4}\ \text{mol/L})\,(32.0\ \text{g/1 mol})\,(1000\ \text{mg/g}) = 6.2\ \text{mg/L}.$$

This concentration is lesser than the required minimum value of 7.5 mg/L, and so these trout would likely not thrive in the polluted stream.

Check Your Learning

What dissolved oxygen concentration is expected for the stream above when it returns to a normal summer time temperature of 15 °C?

Answer: 8.2 mg/L

Chemistry in Everyday Life

Decompression Sickness or “The Bends”

Decompression sickness (DCS), or “the bends,” is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver’s blood are proportionally higher per Henry’s law.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver’s blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventive measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers (**Figure 11.11**).

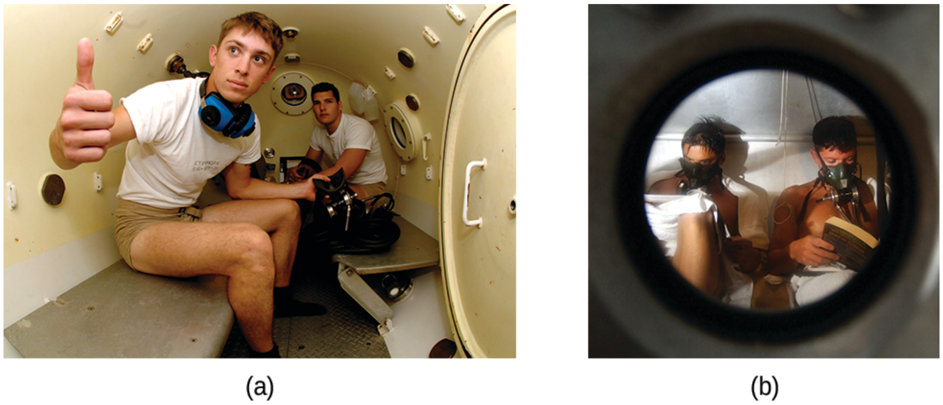
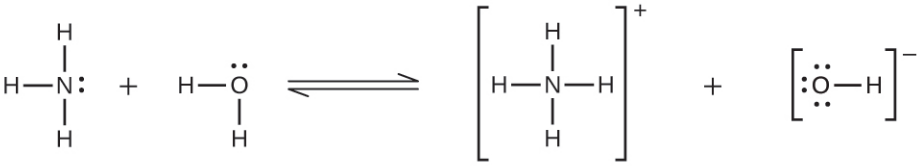

(a) (b)

Figure 11.11 (a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy.

Deviations from Henry's law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water increases more rapidly with increasing pressure than predicted by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.



Gases can form supersaturated solutions. If a solution of a gas in a liquid is prepared either at low temperature or under pressure (or both), then as the solution warms or as the gas pressure is reduced, the solution may become supersaturated. In 1986, more than 1700 people in Cameroon were killed when a cloud of gas, almost certainly carbon dioxide, bubbled from Lake Nyos (**Figure 11.12**), a deep lake in a volcanic crater. The water at the bottom of Lake Nyos is saturated with carbon dioxide by volcanic activity beneath the lake. It is believed that the lake underwent a turnover due to gradual heating from below the lake, and the warmer, less-dense water saturated with carbon dioxide reached the surface. Consequently, tremendous quantities of dissolved CO_2 were released, and the colorless gas, which is denser than air, flowed down the valley below the lake and suffocated humans and animals living in the valley.

Figure 11.12 (a) It is believed that the 1986 disaster that killed more than 1700 people near Lake Nyos in Cameroon resulted when a large volume of carbon dioxide gas was released from the lake. (b) A CO_2 vent has since been installed to help outgas the lake in a slow, controlled fashion and prevent a similar catastrophe from happening in the future. (credit a: modification of work by Jack Lockwood; credit b: modification of work by Bill Evans)

Solutions of Liquids in Liquids

Some liquids may be mixed in any proportions to yield solutions; in other words, they have infinite mutual solubility and are said to be **miscible**. Ethanol, sulfuric acid, and ethylene glycol (popular for use as antifreeze, pictured in **Figure 11.13**) are examples of liquids that are completely miscible with water. Two-cycle motor oil is miscible with gasoline, mixtures of which are used as lubricating fuels for various types of outdoor power equipment (chainsaws, leaf blowers, and so on).

Figure 11.13 Water and antifreeze are miscible; mixtures of the two are homogeneous in all proportions. (credit: “dno1967”/Wikimedia commons)

Miscible liquids are typically those with very similar polarities. Consider, for example, liquids that are polar or capable of hydrogen bonding. For such liquids, the dipole-dipole attractions (or hydrogen bonding) of the solute molecules with the solvent molecules are at least as strong as those between molecules in the pure solute or in the pure solvent. Hence, the two kinds of molecules mix easily. Likewise, nonpolar liquids are miscible with each other because there is no appreciable difference in the strengths of solute-solute, solvent-solvent, and solute-solvent intermolecular attractions. The solubility of polar molecules in polar solvents and of nonpolar molecules in nonpolar solvents is, again, an illustration of the chemical axiom “like dissolves like.”

Two liquids that do not mix to an appreciable extent are called **immiscible**. Separate layers are formed when immiscible liquids are poured into the same container. Gasoline, oil (**Figure 11.14**), benzene, carbon tetrachloride, some paints, and many other nonpolar liquids are immiscible with water. Relatively weak attractive forces between the polar water molecules and the nonpolar liquid molecules are not adequate to overcome much stronger hydrogen bonding between water molecules. The distinction between immiscibility and miscibility is really one of extent, so that miscible liquids are of infinite mutual solubility, while liquids said to be immiscible are of very low (though not zero) mutual solubility.

Figure 11.14 Water and oil are immiscible. Mixtures of these two substances will form two separate layers with the less dense oil floating on top of the water. (credit: “Yortw”/Flickr)

Two liquids, such as bromine and water, that are of *moderate* mutual solubility are said to be **partially miscible**. Two partially miscible liquids usually form two layers when mixed. In the case of the bromine and water mixture, the upper layer is water, saturated with bromine, and the lower layer is bromine saturated with water. Since bromine is nonpolar, and, thus, not very soluble in water, the water layer is only slightly discolored by the bright orange bromine dissolved in it. Since the solubility of water in bromine is very low, there is no noticeable effect on the dark color of the bromine layer (**Figure 11.15**).

Figure 11.15 Bromine (the deep orange liquid on the left) and water (the clear liquid in the middle) are partially miscible. The top layer in the mixture on the right is a saturated solution of bromine in water; the bottom layer is a saturated solution of water in bromine. (credit: Paul Flowers)

Solutions of Solids in Liquids

The dependence of solubility on temperature for a number of solids in water is shown by the solubility curves in **Figure 11.16**. Reviewing these data indicates a general trend of increasing solubility with temperature, although there are exceptions, as illustrated by the ionic compound cerium sulfate.

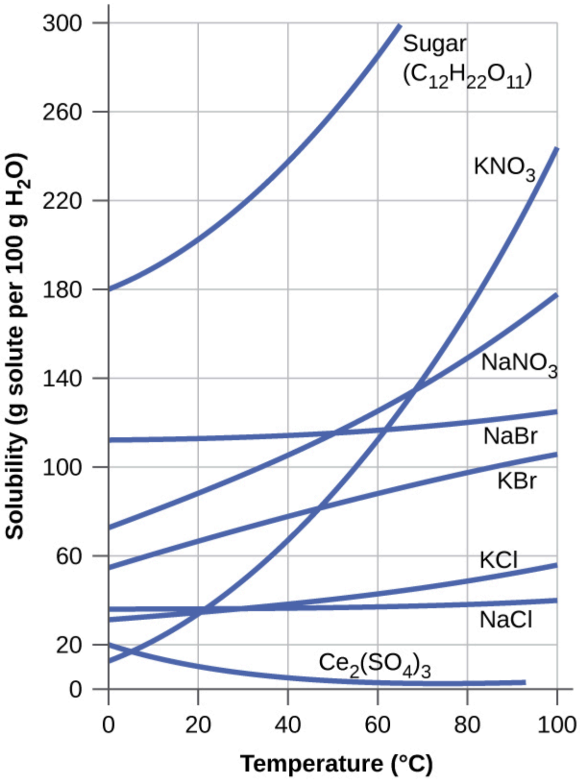


Figure 11.16 This graph shows how the solubility of several solids changes with temperature.

The temperature dependence of solubility can be exploited to prepare supersaturated solutions of certain compounds. A solution may be saturated with the compound at an elevated temperature (where the solute is more soluble) and subsequently cooled to a lower temperature without precipitating the solute. The resultant solution contains solute at a concentration greater than its equilibrium solubility at the lower temperature (i.e., it is supersaturated) and is relatively stable. Precipitation of the excess solute can be initiated by adding a seed crystal (see the video in the Link to Learning earlier in this module) or by mechanically agitating the solution. Some hand warmers, such as the one pictured in **Figure 11.17**, take advantage of this behavior.

Figure 11.17 This hand warmer produces heat when the sodium acetate in a supersaturated solution precipitates. Precipitation of the solute is initiated by a mechanical shockwave generated when the flexible metal disk within the solution is “clicked.” (credit: modification of work by “Velela”/Wikimedia Commons)

Link to Learning

This **video (http://openstaxcollege.org/l/16handwarmer)** shows the crystallization process occurring in a hand warmer.

11.4 Colligative Properties

By the end of this section, you will be able to:

- Express concentrations of solution components using mole fraction and molality
- Describe the effect of solute concentration on various solution properties (vapor pressure, boiling point, freezing point, and osmotic pressure)
- Perform calculations using the mathematical equations that describe these various colligative effects
- Describe the process of distillation and its practical applications
- Explain the process of osmosis and describe how it is applied industrially and in nature

The properties of a solution are different from those of either the pure solute(s) or solvent. Many solution properties are dependent upon the chemical identity of the solute. Compared to pure water, a solution of hydrogen chloride is more acidic, a solution of ammonia is more basic, a solution of sodium chloride is more dense, and a solution of sucrose is more viscous. There are a few solution properties, however, that depend *only* upon the total concentration of solute species, regardless of their identities. These **colligative properties** include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. This small set of properties is of central importance to many natural phenomena and technological applications, as will be described in this module.

Mole Fraction and Molality

Several units commonly used to express the concentrations of solution components were introduced in an earlier chapter of this text, each providing certain benefits for use in different applications. For example, molarity (M) is a convenient unit for use in stoichiometric calculations, since it is defined in terms of the molar amounts of solute species:

$$M = \frac{\text{mol solute}}{\text{L solution}}$$

Because solution volumes vary with temperature, molar concentrations will likewise vary. When expressed as molarity, the concentration of a solution with identical numbers of solute and solvent species will be different at different temperatures, due to the contraction/expansion of the solution. More appropriate for calculations involving many colligative properties are mole-based concentration units whose values are not dependent on temperature. Two such units are *mole fraction* (introduced in the previous chapter on gases) and *molality*.

The mole fraction, X, of a component is the ratio of its molar amount to the total number of moles of all solution components:

$$X_{\text{A}} = \frac{\text{mol A}}{\text{total mol of all components}}$$

By this definition, the sum of mole fractions for all solution components (the solvent and all solutes) is equal to one.

Molality is a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms:

$$m = \frac{\text{mol solute}}{\text{kg solvent}}$$

Since these units are computed using only masses and molar amounts, they do not vary with temperature and, thus, are better suited for applications requiring temperature-independent concentrations, including several colligative properties, as will be described in this chapter module.

Example 11.3

Calculating Mole Fraction and Molality

The antifreeze in most automobile radiators is a mixture of equal volumes of ethylene glycol and water, with minor amounts of other additives that prevent corrosion. What are the (a) mole fraction and (b) molality of ethylene glycol, $C_2H_4(OH)_2$, in a solution prepared from 2.22 × 10^3 g of ethylene glycol and 2.00 × 10^3 g of water (approximately 2 L of glycol and 2 L of water)?

Solution

(a) The mole fraction of ethylene glycol may be computed by first deriving molar amounts of both solution components and then substituting these amounts into the definition of mole fraction.

$$\text{mol } C_2H_4(OH)_2 = 2.22\times10^3 \text{ g} \times \frac{1 \text{ mol } C_2H_4(OH)_2}{62.07 \text{ g } C_2H_4(OH)_2} = 35.8 \text{ mol } C_2H_4(OH)_2$$

$$\text{mol } H_2O = 2.00\times10^3 \text{ g} \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 111 \text{ mol } H_2O$$

$$X_{\text{ethylene glycol}} = \frac{35.8 \text{ mol } C_2H_4(OH)_2}{(35.8 + 111) \text{ mol total}} = 0.244$$

Notice that mole fraction is a dimensionless property, being the ratio of properties with identical units (moles).

(b) Derive moles of solute and mass of solvent (in kg).

First, use the given mass of ethylene glycol and its molar mass to find the moles of solute:

$$2.22\times10^3 \text{ g } C_2H_4(OH)_2\left(\frac{\text{mol } C_2H_2(OH)_2}{62.07 \text{ g}}\right) = 35.8 \text{ mol } C_2H_4(OH)_2$$

Then, convert the mass of the water from grams to kilograms:

$$2.00\times10^3 \text{ g } H_2O\left(\frac{1 \text{ kg}}{1000 \text{ g}}\right) = 2.00 \text{ kg } H_2O$$

Finally, calculate molarity per its definition:

$$\text{molality} = \frac{\text{mol solute}}{\text{kg solvent}}$$

$$\text{molality} = \frac{35.8 \text{ mol } C_2H_4(OH)_2}{2 \text{ kg } H_2O}$$

$$\text{molality} = 17.9\, m$$

Check Your Learning

What are the mole fraction and molality of a solution that contains 0.850 g of ammonia, NH_3, dissolved in 125 g of water?

Answer: 7.14 × 10^{-3}; 0.399 *m*

Example 11.4

Converting Mole Fraction and Molal Concentrations

Calculate the mole fraction of solute and solvent in a 3.0 *m* solution of sodium chloride.

Solution

Converting from one concentration unit to another is accomplished by first comparing the two unit definitions. In this case, both units have the same numerator (moles of solute) but different denominators. The provided molal concentration may be written as:

$$\frac{3.0\text{ mol NaCl}}{1\text{ kg H}_2\text{O}}$$

The numerator for this solution's mole fraction is, therefore, 3.0 mol NaCl. The denominator may be computed by deriving the molar amount of water corresponding to 1.0 kg

$$1.0\text{ kg H}_2\text{O}\left(\frac{1000\text{ g}}{1\text{ kg}}\right)\left(\frac{\text{mol H}_2\text{O}}{18.02\text{ g}}\right) = 55\text{ mol H}_2\text{O}$$

and then substituting these molar amounts into the definition for mole fraction.

$$\begin{aligned}
X_{\text{H}_2\text{O}} &= \frac{\text{mol H}_2\text{O}}{\text{mol NaCl} + \text{mol H}_2\text{O}} \\
X_{\text{H}_2\text{O}} &= \frac{55\text{ mol H}_2\text{O}}{3.0\text{ mol NaCl} + 55\text{ mol H}_2\text{O}} \\
X_{\text{H}_2\text{O}} &= 0.95 \\
X_{\text{NaCl}} &= \frac{\text{mol NaCl}}{\text{mol NaCl} + \text{mol H}_2\text{O}} \\
X_{\text{NaCl}} &= \frac{3.0\text{ mol NaCl}}{3.0\text{ mol NaCl} + 55\text{ mol H}_2\text{O}} \\
X_{\text{NaCl}} &= 0.052
\end{aligned}$$

Check Your Learning

The mole fraction of iodine, I_2, dissolved in dichloromethane, CH_2Cl_2, is 0.115. What is the molal concentration, *m*, of iodine in this solution?

Answer: 1.50 *m*

Example 11.5

Molality and Molarity Conversions

Intravenous infusion of a 0.556 *M* aqueous solution of glucose (density of 1.04 g/mL) is part of some post-operative recovery therapies. What is the molal concentration of glucose in this solution?

Solution

The provided molal concentration may be explicitly written as:

$$M = 0.556\text{ mol glucose/1 L solution}$$

Consider the definition of molality:

$$m = \text{mol solute/kg solvent}$$

The amount of glucose in 1-L of this solution is 0.556 mol, so the mass of water in this volume of solution is needed.

First, compute the mass of 1.00 L of the solution:

$$(1.0\text{ L soln})(1.04\text{ g/mL})(1000\text{ mL/1L})(1\text{ kg/1000 g}) = 1.04\text{ kg soln}$$

This is the mass of both the water and its solute, glucose, and so the mass of glucose must be subtracted. Compute the mass of glucose from its molar amount:

$$(0.556\text{ mol glucose})(180.2\text{ g/1 mol}) = 100.2\text{ g or }0.1002\text{ kg}$$

Subtracting the mass of glucose yields the mass of water in the solution:

$$1.02\text{ kg solution} - 0.1002\text{ kg glucose} = 0.92\text{ kg water}$$

Finally, the molality of glucose in this solution is computed as:

$$m = 0.556\text{ mol glucose/0.92 kg water} = 0.60\text{ m}$$

Check Your Learning

Nitric acid, HNO_3*(aq)*, is commercially available as a 33.7 m aqueous solution (density = 1.35 g/mL). What is the molarity of this solution?

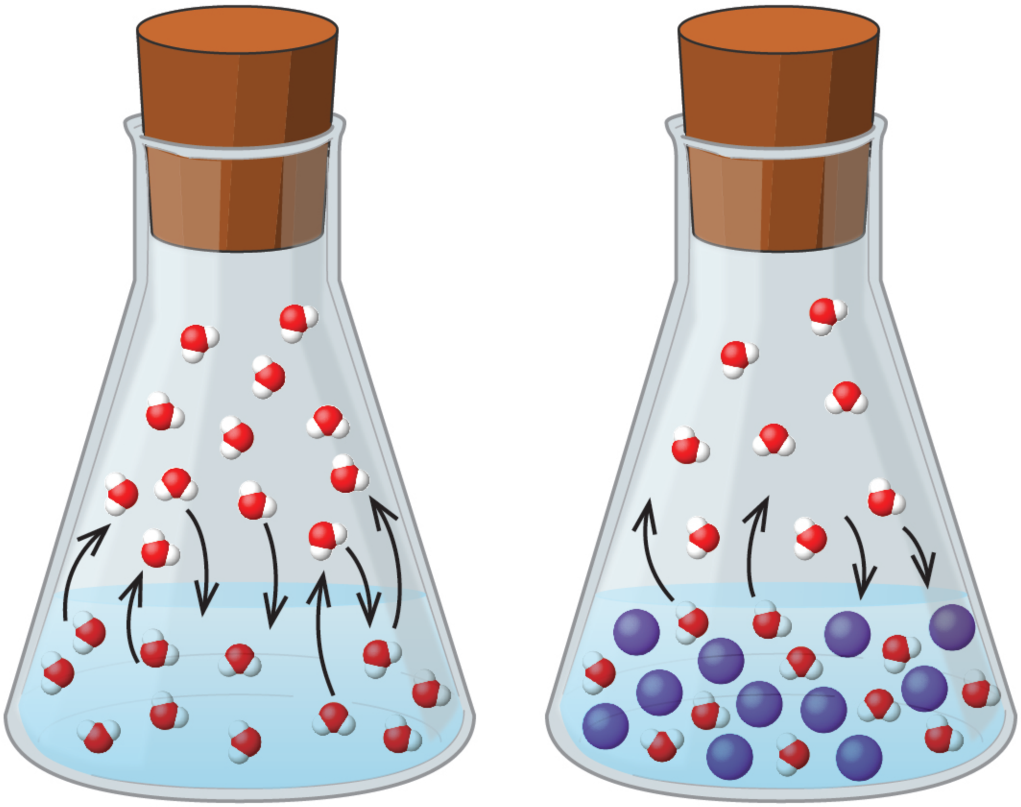
Answer: 14.6 M

Vapor Pressure Lowering

As described in the chapter on liquids and solids, the equilibrium vapor pressure of a liquid is the pressure exerted by its gaseous phase when vaporization and condensation are occurring at equal rates:

$$\text{liquid} \rightleftharpoons \text{gas}$$

Dissolving a nonvolatile substance in a volatile liquid results in a lowering of the liquid's vapor pressure. This phenomenon can be rationalized by considering the effect of added solute molecules on the liquid's vaporization and condensation processes. To vaporize, solvent molecules must be present at the surface of the solution. The presence of solute decreases the surface area available to solvent molecules and thereby reduces the rate of solvent vaporization. Since the rate of condensation is unaffected by the presence of solute, the net result is that the vaporization-condensation equilibrium is achieved with fewer solvent molecules in the vapor phase (i.e., at a lower vapor pressure) (**Figure 11.18**). While this interpretation is useful, it does not account for several important aspects of the colligative nature of vapor pressure lowering. A more rigorous explanation involves the property of *entropy*, a topic of discussion in a later text chapter on thermodynamics. For purposes of understanding the lowering of a liquid's vapor pressure, it is adequate to note that the more dispersed nature of matter in a solution, compared to separate solvent and solute phases, serves to effectively stabilize the solvent molecules and hinder their vaporization. A lower vapor pressure results, and a correspondingly higher boiling point as described in the next section of this module.



(a) Pure water (b) Aqueous solution

Figure 11.18 The presence of nonvolatile solutes lowers the vapor pressure of a solution by impeding the evaporation of solvent molecules.

The relationship between the vapor pressures of solution components and the concentrations of those components is described by **Raoult's law**: *The partial pressure exerted by any component of an ideal solution is equal to the vapor pressure of the pure component multiplied by its mole fraction in the solution.*

$$P_A = X_A P_A^*$$

where P_A is the partial pressure exerted by component A in the solution, P_A^* is the vapor pressure of pure A, and X_A is the mole fraction of A in the solution.

Recalling that the total pressure of a gaseous mixture is equal to the sum of partial pressures for all its components (Dalton's law of partial pressures), the total vapor pressure exerted by a solution containing i components is

$$P_{\text{solution}} = \sum_i P_i = \sum_i X_i P_i^*$$

A nonvolatile substance is one whose vapor pressure is negligible ($P^* \approx 0$), and so the vapor pressure above a solution containing only nonvolatile solutes is due only to the solvent:

$$P_{\text{solution}} = X_{\text{solvent}} P^{*}_{\text{solvent}}$$

Example 11.6

Calculation of a Vapor Pressure

Compute the vapor pressure of an ideal solution containing 92.1 g of glycerin, $C_3H_5(OH)_3$, and 184.4 g of ethanol, C_2H_5OH, at 40 °C. The vapor pressure of pure ethanol is 0.178 atm at 40 °C. Glycerin is essentially nonvolatile at this temperature.

Solution

Since the solvent is the only volatile component of this solution, its vapor pressure may be computed per Raoult's law as:

$$P_{\text{solution}} = X_{\text{solvent}} P^{*}_{\text{solvent}}$$

First, calculate the molar amounts of each solution component using the provided mass data.

$$92.1\ \cancel{\text{g C}_3\text{H}_5(\text{OH})_3} \times \frac{1\ \text{mol C}_3\text{H}_5(\text{OH})_3}{92.094\ \cancel{\text{g C}_3\text{H}_5(\text{OH})_3}} = 1.00\ \text{mol C}_3\text{H}_5(\text{OH})_3$$

$$184.4\ \cancel{\text{g C}_2\text{H}_5\text{OH}} \times \frac{1\ \text{mol C}_2\text{H}_5\text{OH}}{46.069\ \cancel{\text{g C}_2\text{H}_5\text{OH}}} = 4.000\ \text{mol C}_2\text{H}_5\text{OH}$$

Next, calculate the mole fraction of the solvent (ethanol) and use Raoult's law to compute the solution's vapor pressure.

$$X_{\text{C}_2\text{H}_5\text{OH}} = \frac{4.000\ \text{mol}}{(1.00\ \text{mol} + 4.000\ \text{mol})} = 0.800$$

$$P_{\text{solv}} = X_{\text{solv}} P^{*}_{\text{solv}} = 0.800 \times 0.178\ \text{atm} = 0.142\ \text{atm}$$

Check Your Learning

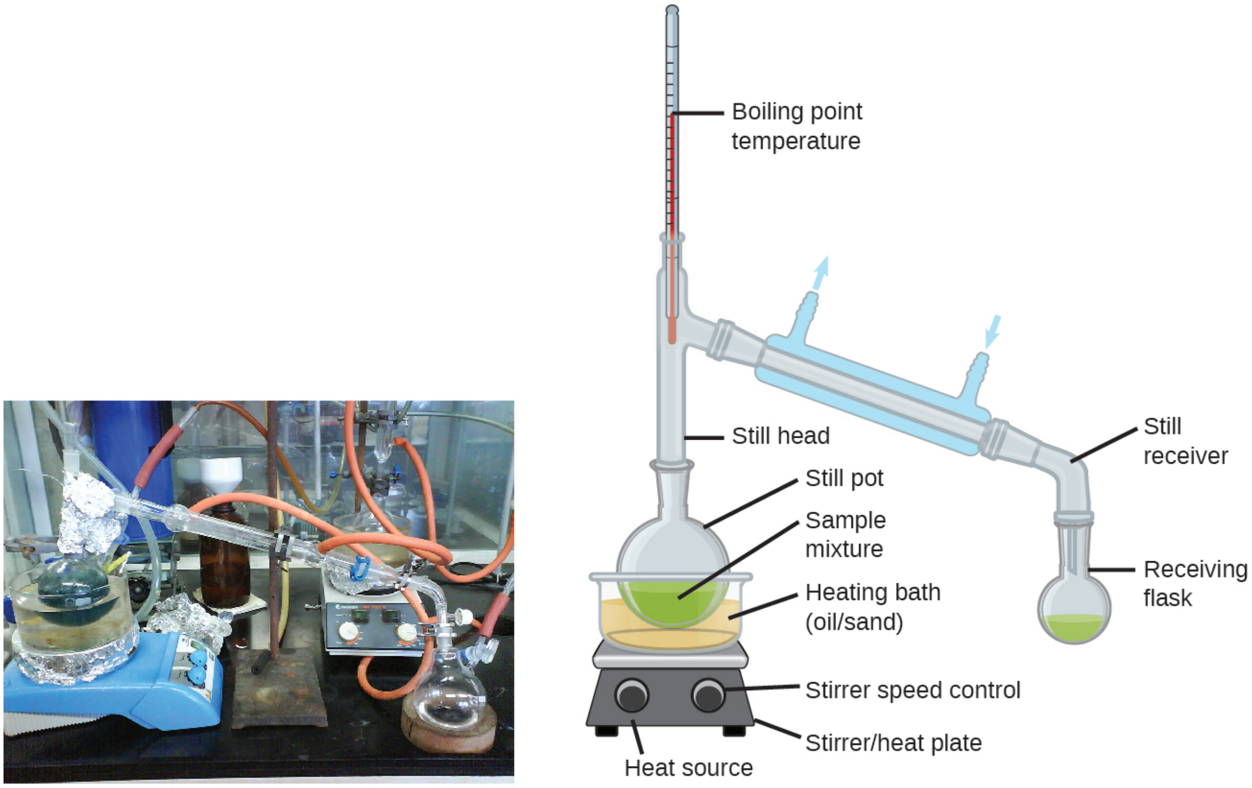
A solution contains 5.00 g of urea, $CO(NH_2)_2$ (a nonvolatile solute) and 0.100 kg of water. If the vapor pressure of pure water at 25 °C is 23.7 torr, what is the vapor pressure of the solution assuming ideal behavior?

Answer: 23.4 torr

Distillation of Solutions

Solutions whose components have significantly different vapor pressures may be separated by a selective vaporization process known as distillation. Consider the simple case of a mixture of two volatile liquids, A and B, with A being the more volatile liquid. Raoult's law can be used to show that the vapor above the solution is enriched in component A, that is, the mole fraction of A in the vapor is greater than the mole fraction of A in the liquid (see end-of-chapter Exercise 65). By appropriately heating the mixture, component A may be vaporized, condensed, and collected—effectively separating it from component B.

Distillation is widely applied in both laboratory and industrial settings, being used to refine petroleum, to isolate fermentation products, and to purify water. A typical apparatus for laboratory-scale distillations is shown in **Figure 11.19**.



(a) (b)

Figure 11.19 A typical laboratory distillation unit is shown in (a) a photograph and (b) a schematic diagram of the components. (credit a: modification of work by “Rifleman82”/Wikimedia commons; credit b: modification of work by “Slashme”/Wikimedia Commons)

Oil refineries use large-scale *fractional distillation* to separate the components of crude oil. The crude oil is heated to high temperatures at the base of a tall *fractionating column*, vaporizing many of the components that rise within the column. As vaporized components reach adequately cool zones during their ascent, they condense and are collected. The collected liquids are simpler mixtures of hydrocarbons and other petroleum compounds that are of appropriate composition for various applications (e.g., diesel fuel, kerosene, gasoline), as depicted in **Figure 11.20**.

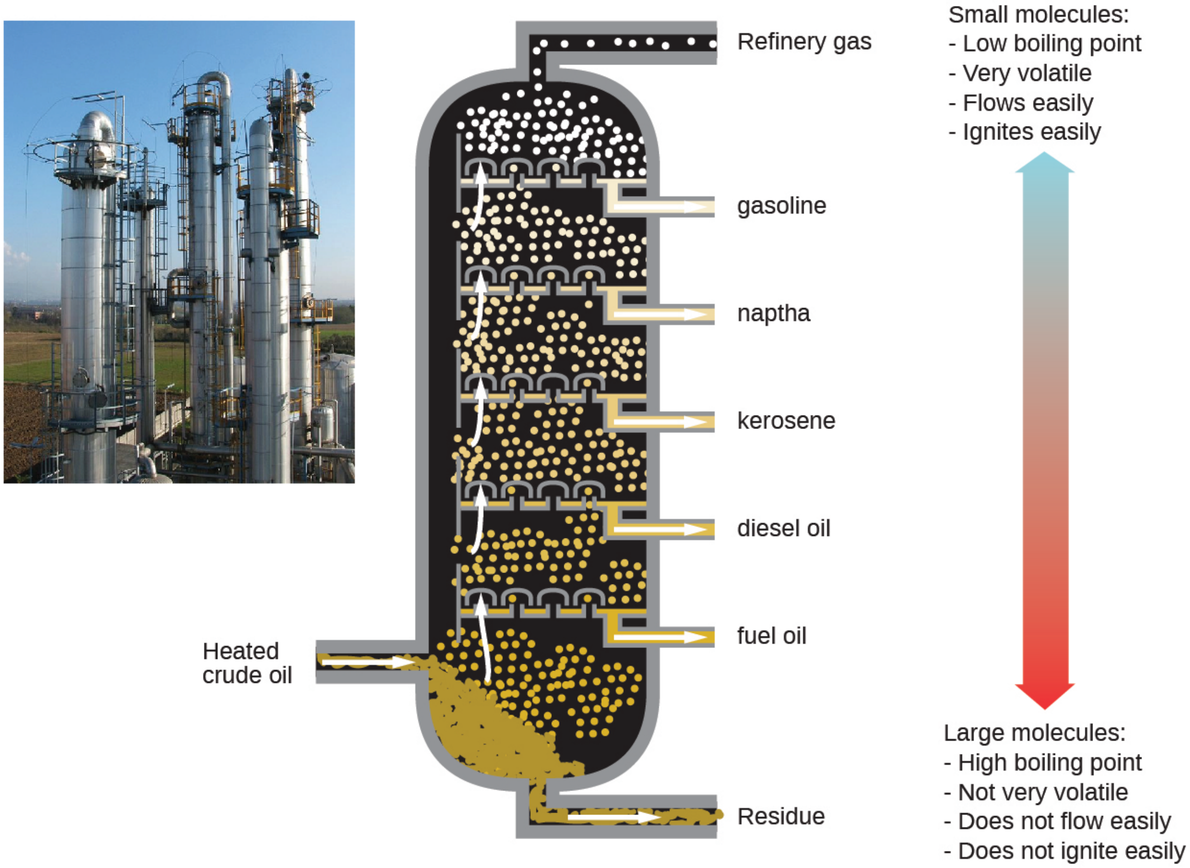


Figure 11.20 Crude oil is a complex mixture that is separated by large-scale fractional distillation to isolate various simpler mixtures.

Boiling Point Elevation

As described in the chapter on liquids and solids, the *boiling point* of a liquid is the temperature at which its vapor pressure is equal to ambient atmospheric pressure. Since the vapor pressure of a solution is lowered due to the presence of nonvolatile solutes, it stands to reason that the solution’s boiling point will subsequently be increased. Vapor pressure increases with temperature, and so a solution will require a higher temperature than will pure solvent to achieve any given vapor pressure, including one equivalent to that of the surrounding atmosphere. The increase in boiling point observed when nonvolatile solute is dissolved in a solvent, ΔT_b, is called **boiling point elevation** and is directly proportional to the molal concentration of solute species:

$$\Delta T_b = K_b m$$

where K_b is the **boiling point elevation constant**, or the *ebullioscopic constant* and m is the molal concentration (molality) of all solute species.

Boiling point elevation constants are characteristic properties that depend on the identity of the solvent. Values of K_b for several solvents are listed in **Table 11.2**.

Boiling Point Elevation and Freezing Point Depression Constants for Several Solvents

Solvent	Boiling Point (°C at 1 atm)	K_b (°Cm^{-1})	Freezing Point (°C at 1 atm)	K_f (°Cm^{-1})
water	100.0	0.512	0.0	1.86
hydrogen acetate	118.1	3.07	16.6	3.9
benzene	80.1	2.53	5.5	5.12
chloroform	61.26	3.63	−63.5	4.68
nitrobenzene	210.9	5.24	5.67	8.1

Table 11.2

The extent to which the vapor pressure of a solvent is lowered and the boiling point is elevated depends on the total number of solute particles present in a given amount of solvent, not on the mass or size or chemical identities of the particles. A 1 *m* aqueous solution of sucrose (342 g/mol) and a 1 *m* aqueous solution of ethylene glycol (62 g/mol) will exhibit the same boiling point because each solution has one mole of solute particles (molecules) per kilogram of solvent.

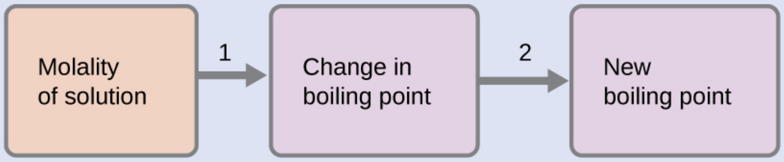
Example 11.7

Calculating the Boiling Point of a Solution

Assuming ideal solution behavior, what is the boiling point of a 0.33 *m* solution of a nonvolatile solute in benzene?

Solution

Use the equation relating boiling point elevation to solute molality to solve this problem in two steps.



Step 1. *Calculate the change in boiling point.*

$$\Delta T_b = K_b m = 2.53\ ^\circ\text{C}\ m^{-1} \times 0.33\ m = 0.83\ ^\circ\text{C}$$

Step 2. *Add the boiling point elevation to the pure solvent's boiling point.*

$$\text{Boiling temperature} = 80.1\ ^\circ\text{C} + 0.83\ ^\circ\text{C} = 80.9\ ^\circ\text{C}$$

Check Your Learning

Assuming ideal solution behavior, what is the boiling point of the antifreeze described in **Example 11.3**?

Answer: 109.2 °C

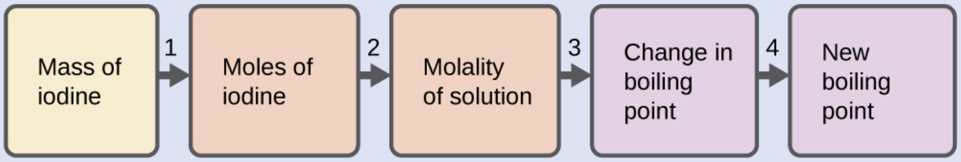
Example 11.8

The Boiling Point of an Iodine Solution

Find the boiling point of a solution of 92.1 g of iodine, I_2, in 800.0 g of chloroform, $CHCl_3$, assuming that the iodine is nonvolatile and that the solution is ideal.

Solution

A four-step approach to solving this problem is outlined below.



Step 1. *Convert from grams to moles of* I_2 *using the molar mass of* I_2 *in the unit conversion factor.*
Result: 0.363 mol
Step 2. *Determine the molality of the solution from the number of moles of solute and the mass of solvent, in kilograms.*
Result: 0.454 *m*
Step 3. *Use the direct proportionality between the change in boiling point and molal concentration to determine how much the boiling point changes.*
Result: 1.65 °C
Step 4. *Determine the new boiling point from the boiling point of the pure solvent and the change.*
Result: 62.91 °C
Check each result as a self-assessment.

Check Your Learning

What is the boiling point of a solution of 1.0 g of glycerin, $C_3H_5(OH)_3$, in 47.8 g of water? Assume an ideal solution.

Answer: 100.12 °C

Freezing Point Depression

Solutions freeze at lower temperatures than pure liquids. This phenomenon is exploited in “de-icing” schemes that use salt (**Figure 11.21**), calcium chloride, or urea to melt ice on roads and sidewalks, and in the use of ethylene glycol as an “antifreeze” in automobile radiators. Seawater freezes at a lower temperature than fresh water, and so the Arctic and Antarctic oceans remain unfrozen even at temperatures below 0 °C (as do the body fluids of fish and other cold-blooded sea animals that live in these oceans).

Figure 11.21 Rock salt (NaCl), calcium chloride ($CaCl_2$), or a mixture of the two are used to melt ice. (credit: modification of work by Eddie Welker)

The decrease in freezing point of a dilute solution compared to that of the pure solvent, ΔT_f, is called the **freezing point depression** and is directly proportional to the molal concentration of the solute

$$\Delta T_f = K_f m$$

where m is the molal concentration of the solute and K_f is called the **freezing point depression constant** (or *cryoscopic constant*). Just as for boiling point elevation constants, these are characteristic properties whose values depend on the chemical identity of the solvent. Values of K_f for several solvents are listed in **Table 11.2**.

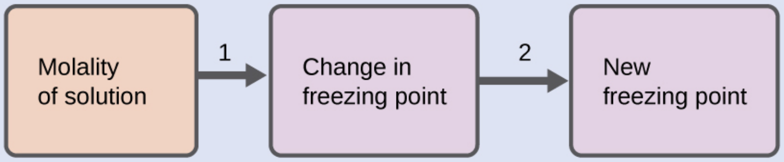
Example 11.9

Calculation of the Freezing Point of a Solution

Assuming ideal solution behavior, what is the freezing point of the 0.33 m solution of a nonvolatile nonelectrolyte solute in benzene described in **Example 11.4**?

Solution

Use the equation relating freezing point depression to solute molality to solve this problem in two steps.



Step 1. *Calculate the change in freezing point.*

$$\Delta T_f = K_f m = 5.12\ °\text{C}\ m^{-1} \times 0.33\ m = 1.7\ °\text{C}$$

Step 2. *Subtract the freezing point change observed from the pure solvent's freezing point.*

$$\text{Freezing Temperature} = 5.5\ °\text{C} - 1.7\ °\text{C} = 3.8\ °\text{C}$$

Check Your Learning

Assuming ideal solution behavior, what is the freezing point of a 1.85 m solution of a nonvolatile nonelectrolyte solute in nitrobenzene?

Answer: −9.3 °C

Chemistry in Everyday Life

Colligative Properties and De-Icing

Sodium chloride and its group 2 analogs calcium and magnesium chloride are often used to de-ice roadways and sidewalks, due to the fact that a solution of any one of these salts will have a freezing point lower than 0 °C, the freezing point of pure water. The group 2 metal salts are frequently mixed with the cheaper and more readily available sodium chloride (“rock salt”) for use on roads, since they tend to be somewhat less corrosive than the NaCl, and they provide a larger depression of the freezing point, since they dissociate to yield three particles per formula unit, rather than two particles like the sodium chloride.

Because these ionic compounds tend to hasten the corrosion of metal, they would not be a wise choice to use in antifreeze for the radiator in your car or to de-ice a plane prior to takeoff. For these applications, covalent compounds, such as ethylene or propylene glycol, are often used. The glycols used in radiator fluid not only lower the freezing point of the liquid, but they elevate the boiling point, making the fluid useful in both winter and summer. Heated glycols are often sprayed onto the surface of airplanes prior to takeoff in inclement weather in the winter to remove ice that has already formed and prevent the formation of more ice, which would be particularly dangerous if formed on the control surfaces of the aircraft (**Figure 11.22**).

Figure 11.22 Freezing point depression is exploited to remove ice from (a) roadways and (b) the control surfaces of aircraft.

Phase Diagram for a Solution

The colligative effects on vapor pressure, boiling point, and freezing point described in the previous section are conveniently summarized by comparing the phase diagrams for a pure liquid and a solution derived from that liquid (**Figure 11.23**).

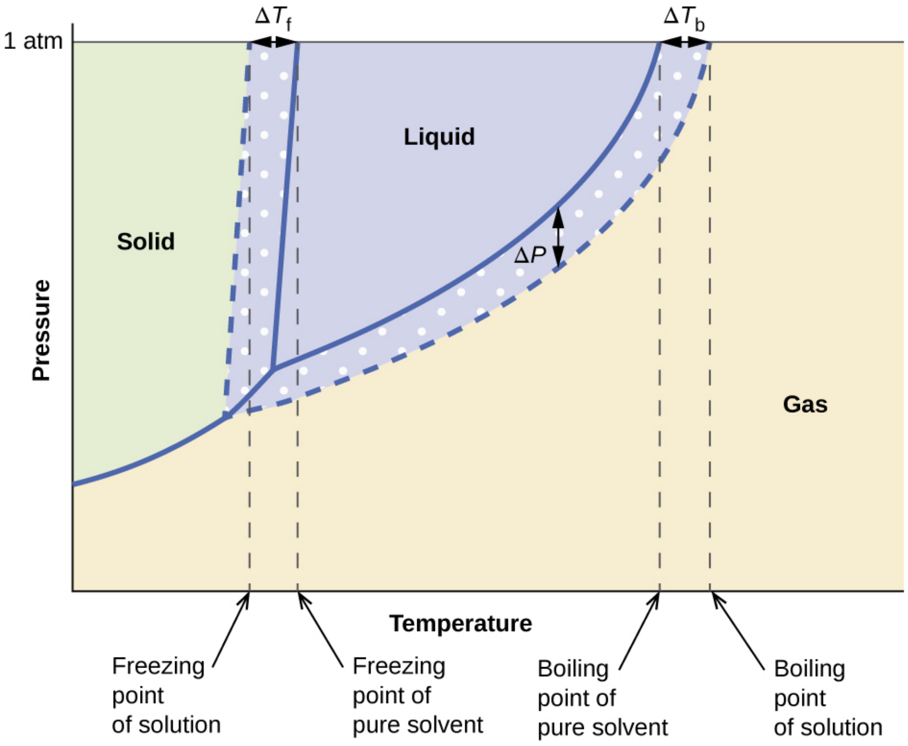


Figure 11.23 Phase diagrams for a pure solvent (solid curves) and a solution formed by dissolving nonvolatile solute in the solvent (dashed curves).

The liquid-vapor curve for the solution is located *beneath* the corresponding curve for the solvent, depicting the vapor pressure *lowering*, Δ*P*, that results from the dissolution of nonvolatile solute. Consequently, at any given pressure, the solution's boiling point is observed at a higher temperature than that for the pure solvent, reflecting the boiling point elevation, ΔT_b, associated with the presence of nonvolatile solute. The solid-liquid curve for the solution is displaced left of that for the pure solvent, representing the freezing point depression, ΔT_f, that accompanies solution formation. Finally, notice that the solid-gas curves for the solvent and its solution are identical. This is the case for many solutions comprising liquid solvents and nonvolatile solutes. Just as for vaporization, when a solution of this sort is frozen, it is actually just the *solvent* molecules that undergo the liquid-to-solid transition, forming pure solid solvent that excludes solute species. The solid and gaseous phases, therefore, are composed of solvent only, and so transitions between these phases are not subject to colligative effects.

Osmosis and Osmotic Pressure of Solutions

A number of natural and synthetic materials exhibit *selective permeation*, meaning that only molecules or ions of a certain size, shape, polarity, charge, and so forth, are capable of passing through (permeating) the material. Biological cell membranes provide elegant examples of selective permeation in nature, while dialysis tubing used to remove metabolic wastes from blood is a more simplistic technological example. Regardless of how they may be fabricated, these materials are generally referred to as **semipermeable membranes**.

Consider the apparatus illustrated in **Figure 11.24**, in which samples of pure solvent and a solution are separated by a membrane that only solvent molecules may permeate. Solvent molecules will diffuse across the membrane in both directions. Since the concentration of *solvent* is greater in the pure solvent than the solution, these molecules will diffuse from the solvent side of the membrane to the solution side at a faster rate than they will in the reverse direction. The result is a net transfer of solvent molecules from the pure solvent to the solution. Diffusion-driven transfer of solvent molecules through a semipermeable membrane is a process known as **osmosis**.

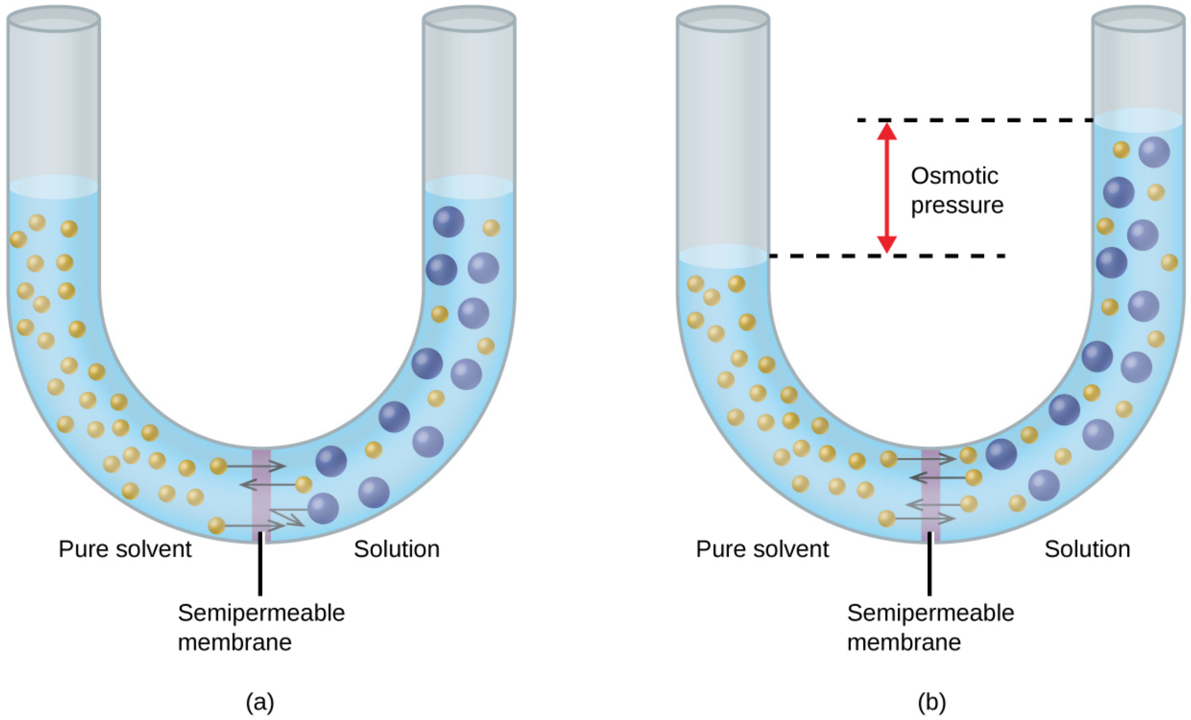


Figure 11.24 (a) A solution and pure solvent are initially separated by an osmotic membrane. (b) Net transfer of solvent molecules to the solution occurs until its osmotic pressure yields equal rates of transfer in both directions.

When osmosis is carried out in an apparatus like that shown in **Figure 11.24**, the volume of the solution increases as it becomes diluted by accumulation of solvent. This causes the level of the solution to rise, increasing its hydrostatic pressure (due to the weight of the column of solution in the tube) and resulting in a faster transfer of solvent molecules back to the pure solvent side. When the pressure reaches a value that yields a reverse solvent transfer rate equal to the osmosis rate, bulk transfer of solvent ceases. This pressure is called the **osmotic pressure (Π)** of the solution. The osmotic pressure of a dilute solution is related to its solute molarity, M, and absolute temperature, T, according to the equation

$$\Pi = MRT$$

where R is the universal gas constant.

Example 11.10

Calculation of Osmotic Pressure

Assuming ideal solution behavior, what is the osmotic pressure (atm) of a 0.30 M solution of glucose in water that is used for intravenous infusion at body temperature, 37 °C?

Solution

Find the osmotic pressure, Π, using the formula $\Pi = MRT$, where T is on the Kelvin scale (310 K) and the value of R is expressed in appropriate units (0.08206 L atm/mol K).

$$\begin{aligned}\Pi &= MRT \\ &= 0.03\ \text{mol/L} \times 0.08206\ \text{L atm/mol K} \times 310\ \text{K} \\ &= 7.6\ \text{atm}\end{aligned}$$

Check Your Learning

Assuming ideal solution behavior, what is the osmotic pressure (atm) a solution with a volume of 0.750 L that contains 5.0 g of methanol, CH_3OH, in water at 37 °C?

Answer: 5.3 atm

If a solution is placed in an apparatus like the one shown in **Figure 11.25**, applying pressure greater than the osmotic pressure of the solution reverses the osmosis and pushes solvent molecules from the solution into the pure solvent. This technique of reverse osmosis is used for large-scale desalination of seawater and on smaller scales to produce high-purity tap water for drinking.

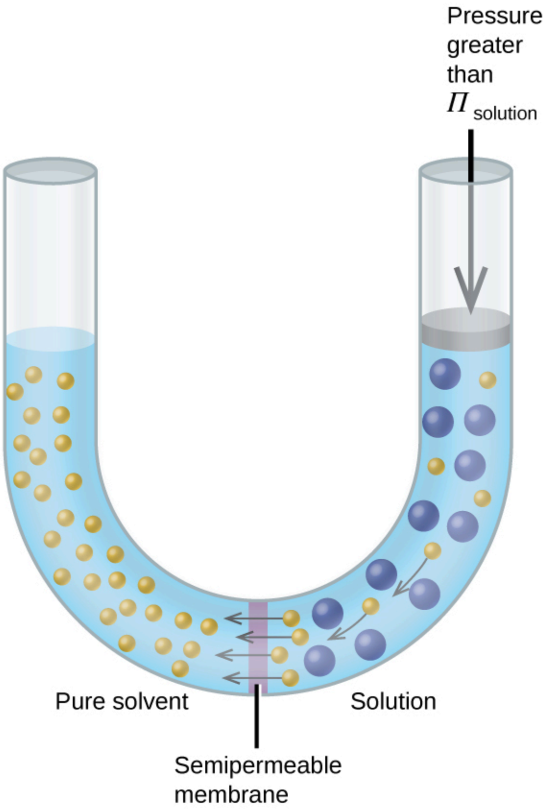


Figure 11.25 Applying a pressure greater than the osmotic pressure of a solution will reverse osmosis. Solvent molecules from the solution are pushed into the pure solvent.

Chemistry in Everyday Life

Reverse Osmosis Water Purification

In the process of osmosis, diffusion serves to move water through a semipermeable membrane from a less concentrated solution to a more concentrated solution. Osmotic pressure is the amount of pressure that must be applied to the more concentrated solution to cause osmosis to stop. If greater pressure is applied, the water will go from the more concentrated solution to a less concentrated (more pure) solution. This is called reverse osmosis. Reverse osmosis (RO) is used to purify water in many applications, from desalination plants in coastal cities, to water-purifying machines in grocery stores (**Figure 11.26**), and smaller reverse-osmosis household units. With a hand-operated pump, small RO units can be used in third-world countries, disaster areas, and in lifeboats. Our military forces have a variety of generator-operated RO units that can be transported in vehicles to remote locations.

(a) (b)

Figure 11.26 Reverse osmosis systems for purifying drinking water are shown here on (a) small and (b) large scales. (credit a: modification of work by Jerry Kirkhart; credit b: modification of work by Willard J. Lathrop)

Examples of osmosis are evident in many biological systems because cells are surrounded by semipermeable membranes. Carrots and celery that have become limp because they have lost water can be made crisp again by placing them in water. Water moves into the carrot or celery cells by osmosis. A cucumber placed in a concentrated salt solution loses water by osmosis and absorbs some salt to become a pickle. Osmosis can also affect animal cells. Solute concentrations are particularly important when solutions are injected into the body. Solutes in body cell fluids and blood serum give these solutions an osmotic pressure of approximately 7.7 atm. Solutions injected into the body must have the same osmotic pressure as blood serum; that is, they should be **isotonic** with blood serum. If a less concentrated solution, a **hypotonic** solution, is injected in sufficient quantity to dilute the blood serum, water from the diluted serum passes into the blood cells by osmosis, causing the cells to expand and rupture. This process is called **hemolysis**. When a more concentrated solution, a **hypertonic** solution, is injected, the cells lose water to the more concentrated solution, shrivel, and possibly die in a process called **crenation**. These effects are illustrated in **Figure 11.27**.

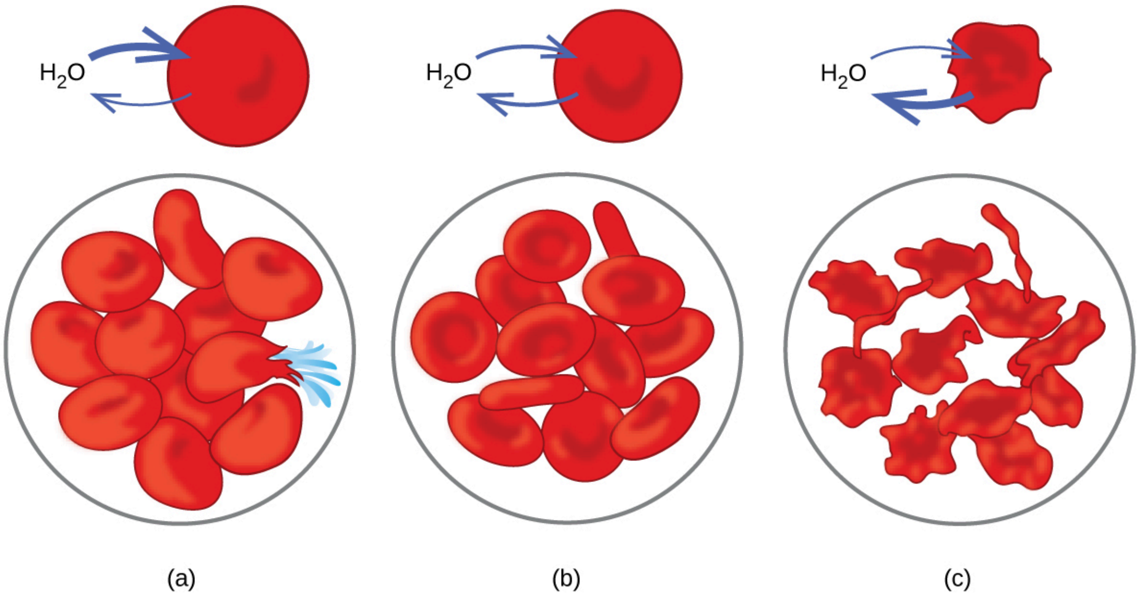


Figure 11.27 Red blood cell membranes are water permeable and will (a) swell and possibly rupture in a hypotonic solution; (b) maintain normal volume and shape in an isotonic solution; and (c) shrivel and possibly die in a hypertonic solution. (credit a/b/c: modifications of work by “LadyofHats”/Wikimedia commons)

Determination of Molar Masses

Osmotic pressure and changes in freezing point, boiling point, and vapor pressure are directly proportional to the number of solute species present in a given amount of solution. Consequently, measuring one of these properties for a solution prepared using a known mass of solute permits determination of the solute’s molar mass.

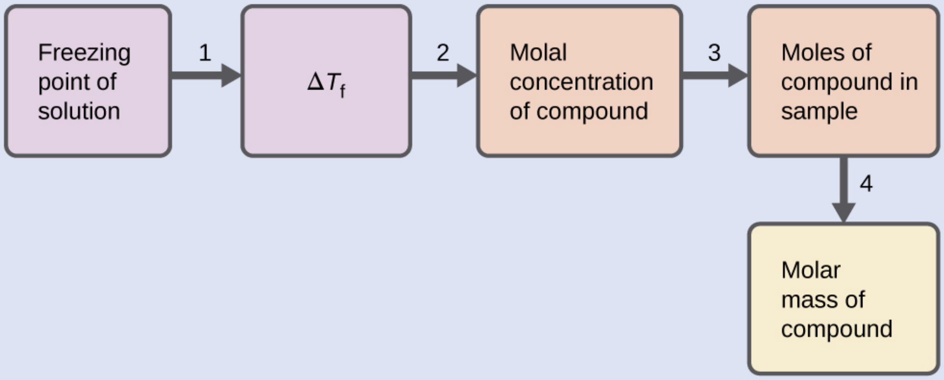
Example 11.11

Determination of a Molar Mass from a Freezing Point Depression

A solution of 4.00 g of a nonelectrolyte dissolved in 55.0 g of benzene is found to freeze at 2.32 °C. Assuming ideal solution behavior, what is the molar mass of this compound?

Solution

Solve this problem using the following steps.



Step 1. *Determine the change in freezing point from the observed freezing point and the freezing*

point of pure benzene (**Table 11.2**).

$$\Delta T_f = 5.5\ °\text{C} - 2.32\ °\text{C} = 3.2\ °\text{C}$$

Step 2. *Determine the molal concentration from* K_f, *the freezing point depression constant for benzene* (**Table 11.2**), *and* ΔT_f.

$$\Delta T_f = K_f m$$

$$m = \frac{\Delta T_f}{K_f} = \frac{3.2\ °\text{C}}{5.12\ °\text{C}\ m^{-1}} = 0.63\ m$$

Step 3. *Determine the number of moles of compound in the solution from the molal concentration and the mass of solvent used to make the solution.*

$$\text{Moles of solute} = \frac{0.63\ \text{mol solute}}{1.00\ \cancel{\text{kg solvent}}} \times 0.0550\ \cancel{\text{kg solvent}} = 0.035\ \text{mol}$$

Step 4. *Determine the molar mass from the mass of the solute and the number of moles in that mass.*

$$\text{Molar mass} = \frac{4.00\ \text{g}}{0.035\ \text{mol}} = 1.1 \times 10^2\ \text{g/mol}$$

Check Your Learning

A solution of 35.7 g of a nonelectrolyte in 220.0 g of chloroform has a boiling point of 64.5 °C. Assuming ideal solution behavior, what is the molar mass of this compound?

Answer: 1.8×10^2 g/mol

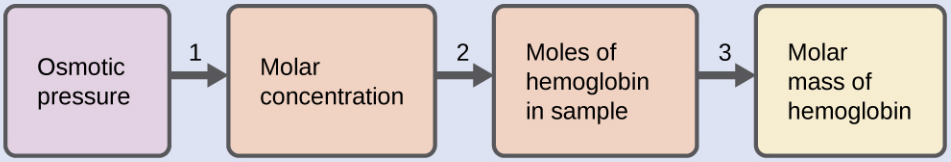
Example 11.12

Determination of a Molar Mass from Osmotic Pressure

A 0.500 L sample of an aqueous solution containing 10.0 g of hemoglobin has an osmotic pressure of 5.9 torr at 22 °C. Assuming ideal solution behavior, what is the molar mass of hemoglobin?

Solution

Here is one set of steps that can be used to solve the problem:



Step 1. *Convert the osmotic pressure to atmospheres, then determine the molar concentration from the osmotic pressure.*

$$\Pi = \frac{5.9\ \text{torr} \times 1\ \text{atm}}{760\ \text{torr}} = 7.8 \times 10^{-3}\ \text{atm}$$

$$\Pi = MRT$$

$$M = \frac{\Pi}{RT} = \frac{7.8 \times 10^{-3}\ \text{atm}}{(0.08206\ \text{L atm/mol K})(295\ \text{K})} = 3.2 \times 10^{-4}\ \text{M}$$

Step 2. *Determine the number of moles of hemoglobin in the solution from the concentration and the volume of the solution.*

$$\text{moles of hemoglobin} = \frac{3.2 \times 10^{-4}\ \text{mol}}{1\ \cancel{\text{L solution}}} \times 0.500\ \cancel{\text{L solution}} = 1.6 \times 10^{-4}\ \text{mol}$$

Step 3. *Determine the molar mass from the mass of hemoglobin and the number of moles in that mass.*

$$\text{molar mass} = \frac{10.0\ \text{g}}{1.6 \times 10^{-4}\ \text{mol}} = 6.2 \times 10^4\ \text{g/mol}$$

Check Your Learning

Assuming ideal solution behavior, what is the molar mass of a protein if a solution of 0.02 g of the protein in 25.0 mL of solution has an osmotic pressure of 0.56 torr at 25 °C?

Answer: 3×10^4 g/mol

Colligative Properties of Electrolytes

As noted previously in this module, the colligative properties of a solution depend only on the number, not on the identity, of solute species dissolved. The concentration terms in the equations for various colligative properties (freezing point depression, boiling point elevation, osmotic pressure) pertain to *all solute species present in the solution*. For the solutions considered thus far in this chapter, the solutes have been nonelectrolytes that dissolve physically without dissociation or any other accompanying process. Each molecule that dissolves yields one dissolved solute molecule. The dissolution of an electroyte, however, is not this simple, as illustrated by the two common examples below:

$$\begin{array}{ll} \textit{dissociation} & \text{NaCl}(s) \longrightarrow \text{Na}_{+}(aq) + \text{Cl}_{-}(aq) \\ \textit{ionization} & \text{HCl}(aq) + \text{H}_2\text{O}(l) \longrightarrow \text{Cl}_{-}(aq) + \text{H}_3\text{O}_{+}(aq) \end{array}$$

Considering the first of these examples, and assuming complete dissociation, a 1.0 *m* aqueous solution of NaCl contains 2.0 mole of ions (1.0 mol Na^+ and 1.0 mol Cl^-) per each kilogram of water, and its freezing point depression is expected to be

$$\Delta T_\text{f} = 2.0 \text{ mol ions/kg water} \times 1.86 \text{ °C kg water/mol ion} = 3.7 \text{ °C}.$$

When this solution is actually prepared and its freezing point depression measured, however, a value of 3.4 °C is obtained. Similar discrepancies are observed for other ionic compounds, and the differences between the measured and expected colligative property values typically become more significant as solute concentrations increase. These observations suggest that the ions of sodium chloride (and other strong electrolytes) are not completely dissociated in solution.

To account for this and avoid the errors accompanying the assumption of total dissociation, an experimentally measured parameter named in honor of Nobel Prize-winning German chemist Jacobus Henricus van't Hoff is used. The **van't Hoff factor (*i*)** is defined as the ratio of solute particles in solution to the number of formula units dissolved:

$$i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}}$$

Values for measured van't Hoff factors for several solutes, along with predicted values assuming complete dissociation, are shown in **Table 11.3**.

Predicated and Measured van't Hoff Factors for Several 0.050 *m* Aqueous Solutions

Formula unit	Classification	Dissolution products	*i* (predicted)	*i* (measured)
$C_{12}H_{22}O_{11}$ (glucose)	Nonelectrolyte	$C_{12}H_{22}O_{11}$	1	1.0
NaCl	Strong electrolyte	Na^+, Cl^-	2	1.9
HCl	Strong electrolyte (acid)	H_3O^+, Cl^-	2	1.9
$MgSO_4$	Strong electrolyte	Mg^{2+}, $SO_4{}^{2-}$,	2	1.3
$MgCl_2$	Strong electrolyte	Mg^{2+}, $2Cl^-$	3	2.7
$FeCl_3$	Strong electrolyte	Fe^{3+}, $3Cl^-$	4	3.4

Table 11.3

In 1923, the chemists Peter Debye and Erich Hückel proposed a theory to explain the apparent incomplete ionization of strong electrolytes. They suggested that although interionic attraction in an aqueous solution is very greatly reduced by solvation of the ions and the insulating action of the polar solvent, it is not completely nullified. The residual attractions prevent the ions from behaving as totally independent particles (**Figure 11.28**). In some cases, a positive and negative ion may actually touch, giving a solvated unit called an ion pair. Thus, the **activity**, or the effective concentration, of any particular kind of ion is less than that indicated by the actual concentration. Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less and less. Thus, in extremely dilute solutions, the effective concentrations of the ions (their activities) are essentially equal to the actual concentrations. Note that the van't Hoff factors for the electrolytes in **Table 11.3** are for 0.05 *m* solutions, at which concentration the value of *i* for NaCl is 1.9, as opposed to an ideal value of 2.

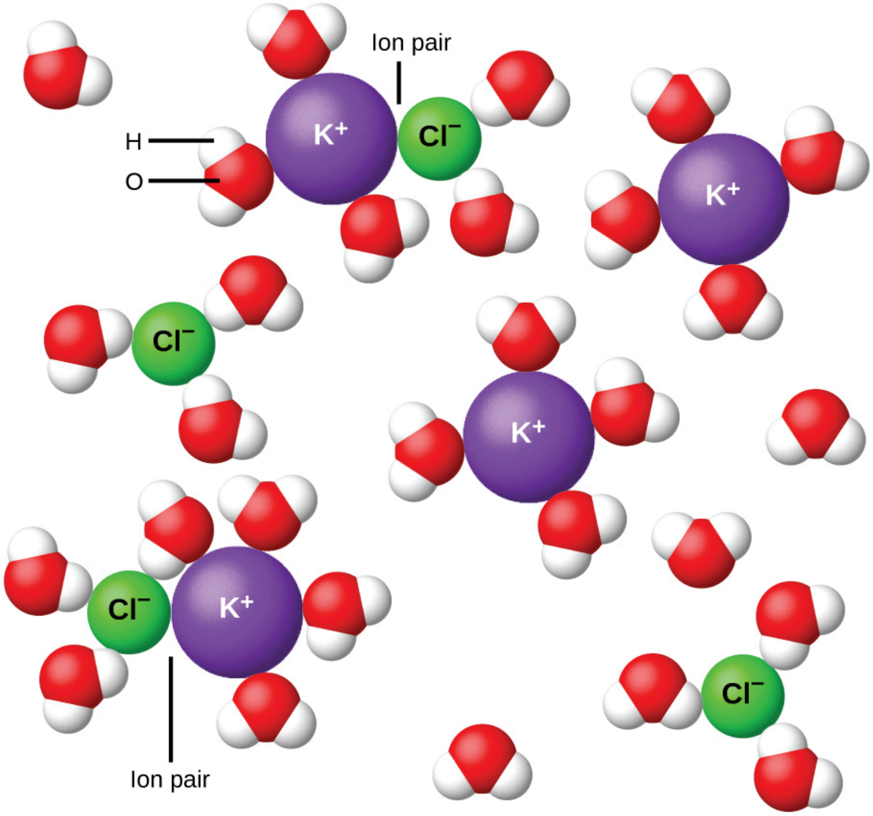


Figure 11.28 Dissociation of ionic compounds in water is not always complete due to the formation of ion pairs.

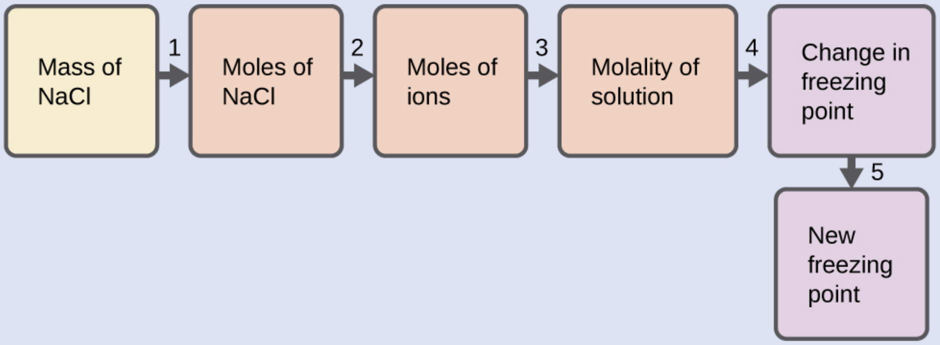
Example 11.13

The Freezing Point of a Solution of an Electrolyte

The concentration of ions in seawater is approximately the same as that in a solution containing 4.2 g of NaCl dissolved in 125 g of water. Use this information and a predicted value for the van't Hoff factor (**Table 11.3**) to determine the freezing temperature the solution (assume ideal solution behavior).

Solution

Solve this problem using the following series of steps.



Step 1. *Convert from grams to moles of NaCl using the molar mass of NaCl in the unit conversion factor.*
Result: 0.072 mol NaCl
Step 2. *Determine the number of moles of ions present in the solution using the number of moles of ions in 1 mole of NaCl as the conversion factor (2 mol ions/1 mol NaCl).*
Result: 0.14 mol ions
Step 3. *Determine the molality of the ions in the solution from the number of moles of ions and the mass of solvent, in kilograms.*
Result: 1.2 *m*
Step 4. *Use the direct proportionality between the change in freezing point and molal concentration to determine how much the freezing point changes.*
Result: 2.1 °C
Step 5. *Determine the new freezing point from the freezing point of the pure solvent and the change.*
Result: −2.1 °C
Check each result as a self-assessment, taking care to avoid rounding errors by retaining guard digits in each step's result for computing the next step's result.

Check Your Learning

Assuming complete dissociation and ideal solution behavior, calculate the freezing point of a solution of 0.724 g of $CaCl_2$ in 175 g of water.

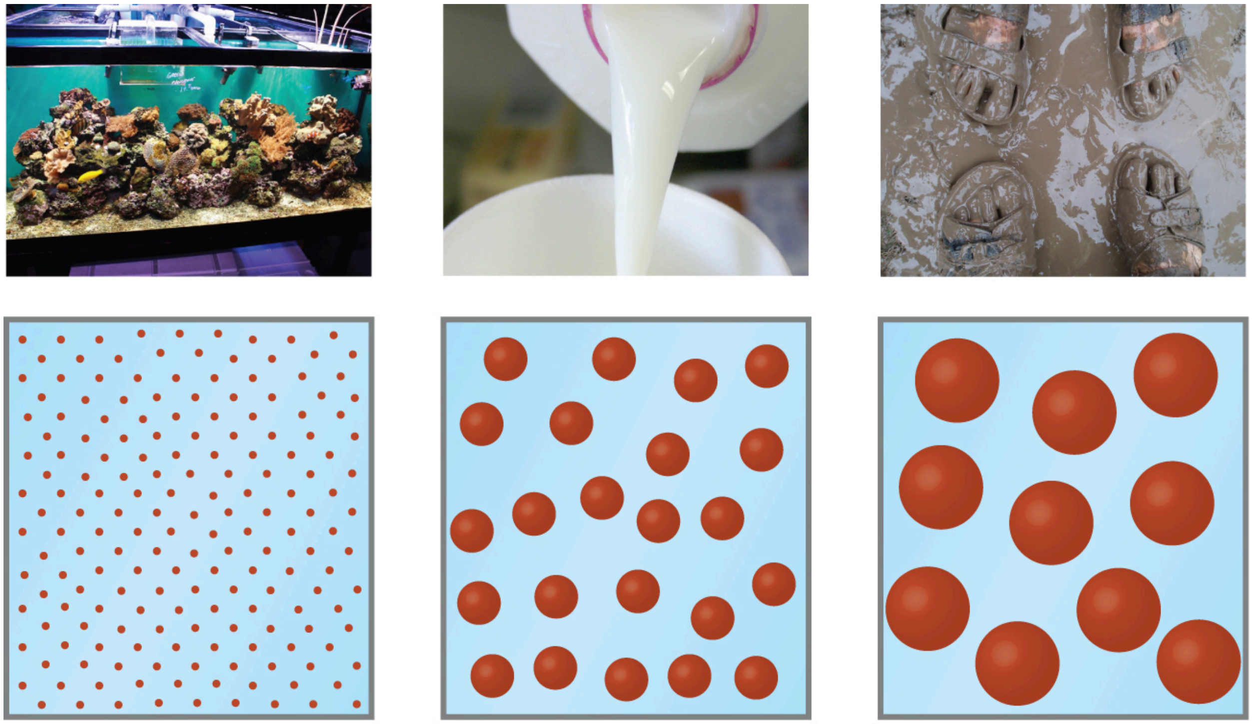
Answer: −0.208 °C

11.5 Colloids

By the end of this section, you will be able to:

- Describe the composition and properties of colloidal dispersions
- List and explain several technological applications of colloids

As a child, you may have made suspensions such as mixtures of mud and water, flour and water, or a suspension of solid pigments in water, known as tempera paint. These **suspensions** are heterogeneous mixtures composed of relatively large particles that are visible (or that can be seen with a magnifying glass). They are cloudy, and the suspended particles settle out after mixing. On the other hand, a solution is a homogeneous mixture in which no settling occurs and in which the dissolved species are molecules or ions. Solutions exhibit completely different behavior from suspensions. A solution may be colored, but it is transparent, the molecules or ions are invisible, and they do not settle out on standing. Another class of mixtures called **colloids** (or **colloidal dispersions**) exhibit properties intermediate between those of suspensions and solutions (Figure 11.29). The particles in a colloid are larger than most simple molecules; however, colloidal particles are small enough that they do not settle out upon standing.



(a) (b) (c)

Figure 11.29 (a) A solution is a homogeneous mixture that appears clear, such as the saltwater in this aquarium. (b) In a colloid, such as milk, the particles are much larger but remain dispersed and do not settle. (c) A suspension, such as mud, is a heterogeneous mixture of suspended particles that appears cloudy and in which the particles can settle. (credit a photo: modification of work by Adam Wimsatt; credit b photo: modification of work by Melissa Wiese; credit c photo: modification of work by Peter Burgess)

The particles in a colloid are large enough to scatter light, a phenomenon called the **Tyndall effect**. This can make colloidal mixtures appear cloudy or opaque, such as the searchlight beams shown in **Figure 11.30**. Clouds are colloidal mixtures. They are composed of water droplets that are much larger than molecules, but that are small enough that they do not settle out.

Figure 11.30 The paths of searchlight beams are made visible when light is scattered by colloidal-size particles in the air (fog, smoke, etc.). (credit: “Bahman”/Wikimedia Commons)

The term “colloid”—from the Greek words *kolla*, meaning “glue,” and *eidos*, meaning “like”—was first used in 1861 by Thomas Graham to classify mixtures such as starch in water and gelatin. Many colloidal particles are aggregates of hundreds or thousands of molecules, but others (such as proteins and polymer molecules) consist of a single extremely large molecule. The protein and synthetic polymer molecules that form colloids may have molecular masses ranging from a few thousand to many million atomic mass units.

Analogous to the identification of solution components as “solute” and “solvent,” the components of a colloid are likewise classified according to their relative amounts. The particulate component typically present in a relatively minor amount is called the **dispersed phase** and the substance or solution throughout which the particulate is dispersed is called the **dispersion medium**. Colloids may involve virtually any combination of physical states (gas in liquid, liquid in solid, solid in gas, etc.), as illustrated by the examples of colloidal systems given in Table 11.4.

Examples of Colloidal Systems

Dispersed Phase	Dispersion Medium	Common Examples	Name
solid	gas	smoke, dust	—
solid	liquid	starch in water, some inks, paints, milk of magnesia	sol
solid	solid	some colored gems, some alloys	—
liquid	gas	clouds, fogs, mists, sprays	aerosol
liquid	liquid	milk, mayonnaise, butter	emulsion
liquid	solid	jellies, gels, pearl, opal (H_2O in SiO_2)	gel
gas	liquid	foams, whipped cream, beaten egg whites	foam

Table 11.4

Examples of Colloidal Systems

Dispersed Phase	Dispersion Medium	Common Examples	Name
gas	solid	pumice, floating soaps	—

Table 11.4

Preparation of Colloidal Systems

Colloids are prepared by producing particles of colloidal dimensions and distributing these particles throughout a dispersion medium. Particles of colloidal size are formed by two methods:

1. Dispersion methods: breaking down larger particles. For example, paint pigments are produced by dispersing large particles by grinding in special mills.
2. Condensation methods: growth from smaller units, such as molecules or ions. For example, clouds form when water molecules condense and form very small droplets.

A few solid substances, when brought into contact with water, disperse spontaneously and form colloidal systems. Gelatin, glue, starch, and dehydrated milk powder behave in this manner. The particles are already of colloidal size; the water simply disperses them. Powdered milk particles of colloidal size are produced by dehydrating milk spray. Some atomizers produce colloidal dispersions of a liquid in air.

An **emulsion** may be prepared by shaking together or blending two immiscible liquids. This breaks one liquid into droplets of colloidal size, which then disperse throughout the other liquid. Oil spills in the ocean may be difficult to clean up, partly because wave action can cause the oil and water to form an emulsion. In many emulsions, however, the dispersed phase tends to coalesce, form large drops, and separate. Therefore, emulsions are usually stabilized by an **emulsifying agent**, a substance that inhibits the coalescence of the dispersed liquid. For example, a little soap will stabilize an emulsion of kerosene in water. Milk is an emulsion of butterfat in water, with the protein casein serving as the emulsifying agent. Mayonnaise is an emulsion of oil in vinegar, with egg yolk components as the emulsifying agents.

Condensation methods form colloidal particles by aggregation of molecules or ions. If the particles grow beyond the colloidal size range, drops or precipitates form, and no colloidal system results. Clouds form when water molecules aggregate and form colloid-sized particles. If these water particles coalesce to form adequately large water drops of liquid water or crystals of solid water, they settle from the sky as rain, sleet, or snow. Many condensation methods involve chemical reactions. A red colloidal suspension of iron(III) hydroxide may be prepared by mixing a concentrated solution of iron(III) chloride with hot water:

$$\text{Fe}^{3+}(\text{aq}) + 3\text{Cl}^-(\text{aq}) + 6\text{H}_2\text{O}(l) \longrightarrow \text{Fe(OH)}_3(s) + \text{H}_3\text{O}^+(aq) + 3\text{Cl}^-(aq).$$

A colloidal gold sol results from the reduction of a very dilute solution of gold(III) chloride by a reducing agent such as formaldehyde, tin(II) chloride, or iron(II) sulfate:

$$\text{Au}^{3+} + 3\text{e}^- \longrightarrow \text{Au}$$

Some gold sols prepared in 1857 are still intact (the particles have not coalesced and settled), illustrating the long-term stability of many colloids.

Soaps and Detergents

Pioneers made soap by boiling fats with a strongly basic solution made by leaching potassium carbonate, K_2CO_3, from wood ashes with hot water. Animal fats contain polyesters of fatty acids (long-chain carboxylic acids). When animal fats are treated with a base like potassium carbonate or sodium hydroxide, glycerol and salts of fatty acids such as palmitic, oleic, and stearic acid are formed. The salts of fatty acids are called *soaps*. The sodium salt of stearic acid, sodium stearate, has the formula $C_{17}H_{35}CO_2Na$ and contains an uncharged nonpolar hydrocarbon chain, the

$C_{17}H_{35}$— unit, and an ionic carboxylate group, the $—CO_2^-$ unit (**Figure 11.31**).

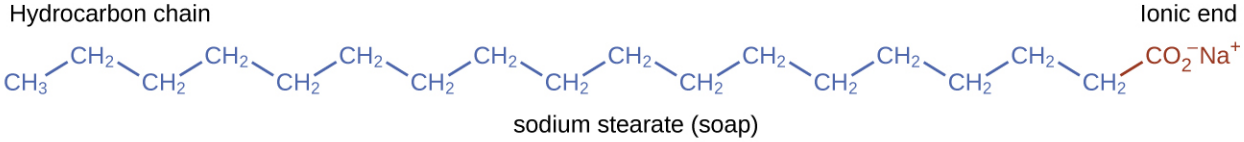


Figure 11.31 Soaps contain a nonpolar hydrocarbon end (blue) and an ionic end (red). The ionic end is a carboxylate group. The length of the hydrocarbon end can vary from soap to soap.

Detergents (soap substitutes) also contain nonpolar hydrocarbon chains, such as $C_{12}H_{25}$—, and an ionic group, such as a sulfate$—OSO_3^-$, or a sulfonate$—SO_3^-$ (**Figure 11.32**). Soaps form insoluble calcium and magnesium compounds in hard water; detergents form water-soluble products—a definite advantage for detergents.

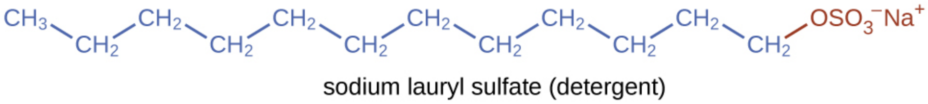


Figure 11.32 Detergents contain a nonpolar hydrocarbon end (blue) and an ionic end (red). The ionic end can be either a sulfate or a sulfonate. The length of the hydrocarbon end can vary from detergent to detergent.

The cleaning action of soaps and detergents can be explained in terms of the structures of the molecules involved. The hydrocarbon (nonpolar) end of a soap or detergent molecule dissolves in, or is attracted to, nonpolar substances such as oil, grease, or dirt particles. The ionic end is attracted by water (polar), illustrated in **Figure 11.33**. As a result, the soap or detergent molecules become oriented at the interface between the dirt particles and the water so they act as a kind of bridge between two different kinds of matter, nonpolar and polar. Molecules such as this are termed **amphiphilic** since they have both a hydrophobic ("water-fearing") part and a hydrophilic ("water-loving") part. As a consequence, dirt particles become suspended as colloidal particles and are readily washed away.

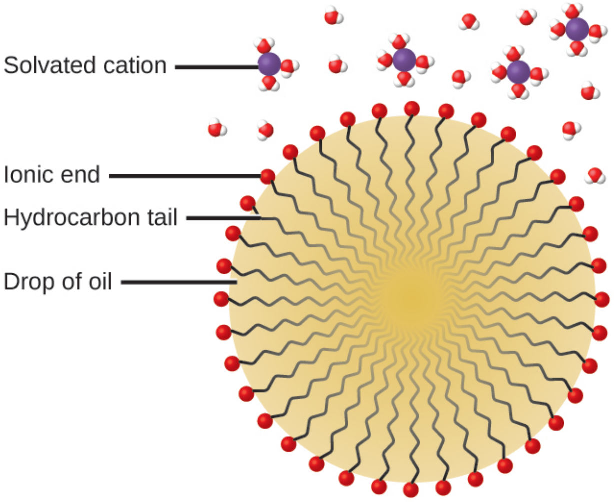


Figure 11.33 This diagrammatic cross section of an emulsified drop of oil in water shows how soap or detergent acts as an emulsifier.

Chemistry in Everyday Life

Deepwater Horizon Oil Spill

The blowout of the Deepwater Horizon oil drilling rig on April 20, 2010, in the Gulf of Mexico near Mississippi began the largest marine oil spill in the history of the petroleum industry. In the 87 days following the blowout, an estimated 4.9 million barrels (210 million gallons) of oil flowed from the ruptured well 5000 feet below the water's surface. The well was finally declared sealed on September 19, 2010.

Crude oil is immiscible with and less dense than water, so the spilled oil rose to the surface of the water. Floating booms, skimmer ships, and controlled burns were used to remove oil from the water's surface in an attempt to protect beaches and wetlands along the Gulf coast. In addition to removal of the oil, attempts were also made to lessen its environmental impact by rendering it "soluble" (in the loose sense of the term) and thus allowing it to be diluted to hopefully less harmful levels by the vast volume of ocean water. This approach used 1.84 million gallons of the oil dispersant Corexit 9527, most of which was injected underwater at the site of the leak, with small amounts being sprayed on top of the spill. Corexit 9527 contains 2-butoxyethanol ($C_6H_{14}O_2$), an amphiphilic molecule whose polar and nonpolar ends are useful for emulsifying oil into small droplets, increasing the surface area of the oil and making it more available to marine bacteria for digestion (**Figure 11.34**). While this approach avoids many of the immediate hazards that bulk oil poses to marine and coastal ecosystems, it introduces the possibility of long-term effects resulting from the introduction of the complex and potential toxic components of petroleum into the ocean's food chain. A number of organizations are involved in monitoring the extended impact of this oil spill, including the National Oceanic and Atmospheric Administration (visit this **website (http://openstaxcollege.org/l/16gulfspill)** for additional details).

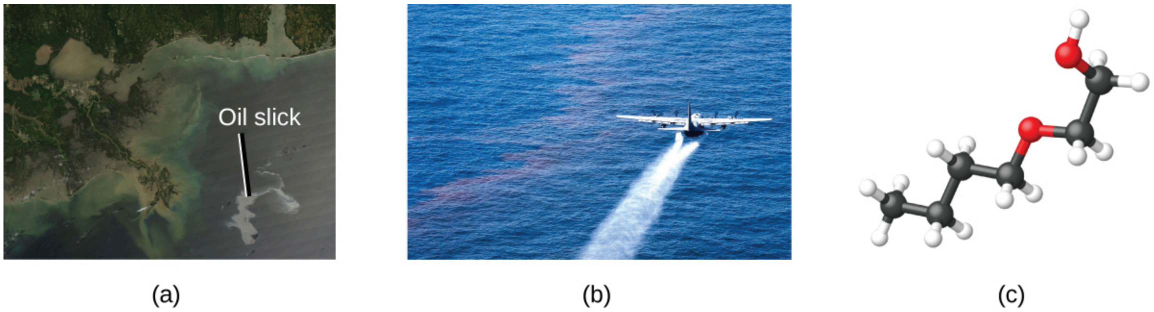


Figure 11.34 (a) This NASA satellite image shows the oil slick from the Deepwater Horizon spill. (b) A US Air Force plane sprays Corexit, a dispersant. (c) The molecular structure of 2-butoxyethanol is shown. (credit a: modification of work by "NASA, FT2, demis.nl"/Wikimedia Commons; credit b: modification of work by "NASA/MODIS Rapid Response Team"/Wikimedia Commons)

Electrical Properties of Colloidal Particles

Dispersed colloidal particles are often electrically charged. A colloidal particle of iron(III) hydroxide, for example, does not contain enough hydroxide ions to compensate exactly for the positive charges on the iron(III) ions. Thus, each individual colloidal particle bears a positive charge, and the colloidal dispersion consists of charged colloidal particles and some free hydroxide ions, which keep the dispersion electrically neutral. Most metal hydroxide colloids have positive charges, whereas most metals and metal sulfides form negatively charged dispersions. All colloidal particles in any one system have charges of the same sign. This helps keep them dispersed because particles containing like charges repel each other.

The charged nature of some colloidal particles may be exploited to remove them from a variety of mixtures. For example, the particles comprising smoke are often colloidally dispersed and electrically charged. Frederick Cottrell, an American chemist, developed a process to remove these particles. The charged particles are attracted to highly charged electrodes, where they are neutralized and deposited as dust (**Figure 11.36**). This is one of the important methods used to clean up the smoke from a variety of industrial processes. The process is also important in the recovery of valuable products from the smoke and flue dust of smelters, furnaces, and kilns. There are also similar electrostatic air filters designed for home use to improve indoor air quality.

Portrait of a Chemist

Frederick Gardner Cottrell

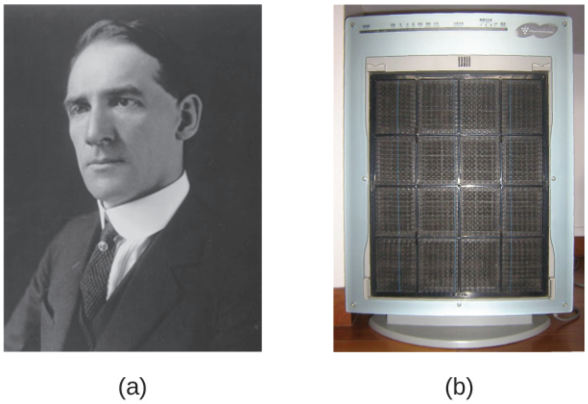


Figure 11.35 (a) Frederick Cottrell developed (b) the electrostatic precipitator, a device designed to curb air pollution by removing colloidal particles from air. (credit b: modification of work by “SpLot”/Wikimedia Commons)

Born in Oakland, CA, in 1877, Frederick Cottrell devoured textbooks as if they were novels and graduated from high school at the age of 16. He then entered the University of California (UC), Berkeley, completing a Bachelor’s degree in three years. He saved money from his $1200 annual salary as a chemistry teacher at Oakland High School to fund his studies in chemistry in Berlin with Nobel prize winner Jacobus Henricus van’t Hoff, and in Leipzig with Wilhelm Ostwald, another Nobel awardee. After earning his PhD in physical chemistry, he returned to the United States to teach at UC Berkeley. He also consulted for the DuPont Company, where he developed the electrostatic precipitator, a device designed to curb air pollution by removing colloidal particles from air. Cottrell used the proceeds from his invention to fund a nonprofit research corporation to finance scientific research.

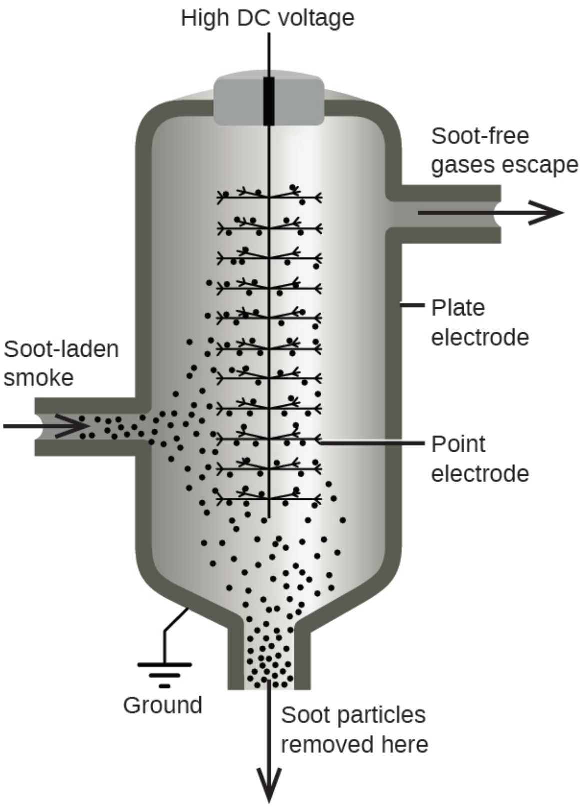


Figure 11.36 In a Cottrell precipitator, positively and negatively charged particles are attracted to highly charged electrodes, where they are neutralized and deposited as dust.

Gels

Gelatin desserts, such as Jell-O, are a type of colloid (Figure 11.37). Gelatin sets on cooling because the hot aqueous mixture of gelatin coagulates as it cools, yielding an extremely viscous body known as a **gel**. A gel is a colloidal dispersion of a liquid phase throughout a solid phase. It appears that the fibers of the dispersing medium form a complex three-dimensional network, the interstices being filled with the liquid medium or a dilute solution of the dispersing medium.

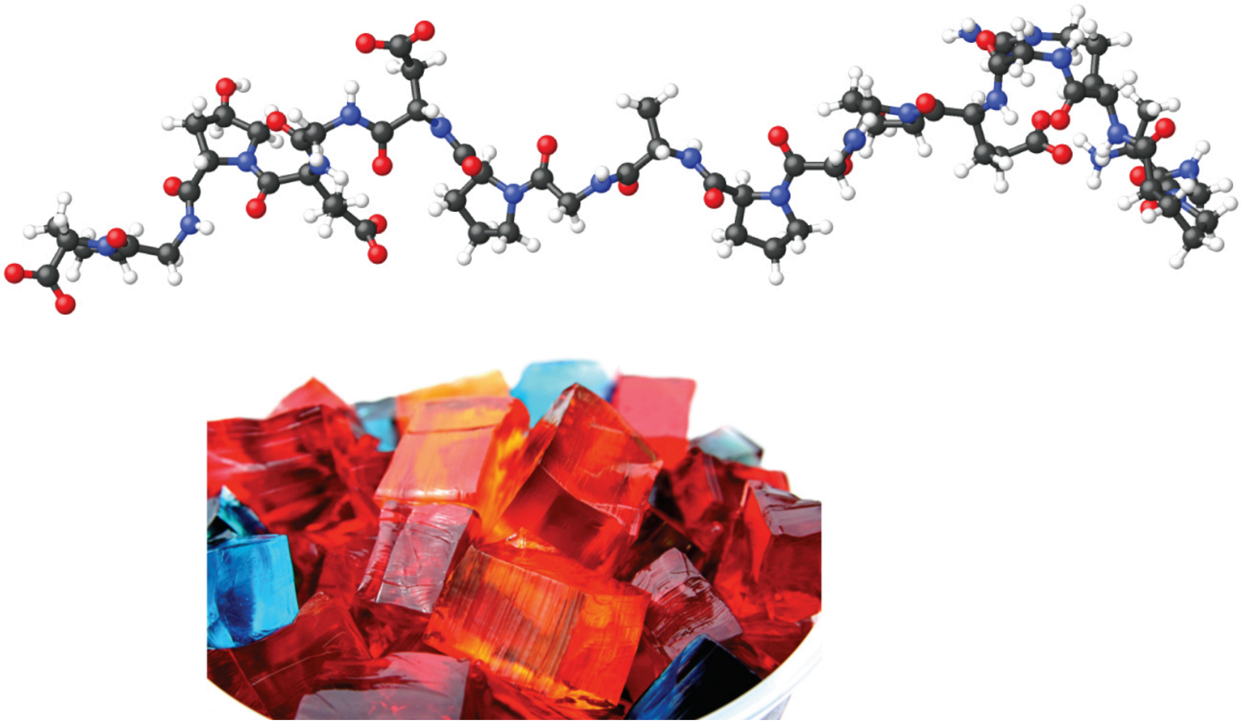


Figure 11.37 Gelatin desserts are colloids in which an aqueous solution of sweeteners and flavors is dispersed throughout a medium of solid proteins. (credit photo: modification of work by Steven Depolo)

Pectin, a carbohydrate from fruit juices, is a gel-forming substance important in jelly making. Silica gel, a colloidal dispersion of hydrated silicon dioxide, is formed when dilute hydrochloric acid is added to a dilute solution of sodium silicate. Canned Heat is a flammable gel made by mixing alcohol and a saturated aqueous solution of calcium acetate.

Key Terms

alloy solid mixture of a metallic element and one or more additional elements

amphiphilic molecules possessing both hydrophobic (nonpolar) and a hydrophilic (polar) parts

boiling point elevation elevation of the boiling point of a liquid by addition of a solute

boiling point elevation constant the proportionality constant in the equation relating boiling point elevation to solute molality; also known as the ebullioscopic constant

colligative property property of a solution that depends only on the concentration of a solute species

colloid (also, colloidal dispersion) mixture in which relatively large solid or liquid particles are dispersed uniformly throughout a gas, liquid, or solid

crenation process whereby biological cells become shriveled due to loss of water by osmosis

dispersed phase substance present as relatively large solid or liquid particles in a colloid

dispersion medium solid, liquid, or gas in which colloidal particles are dispersed

dissociation physical process accompanying the dissolution of an ionic compound in which the compound's constituent ions are solvated and dispersed throughout the solution

electrolyte substance that produces ions when dissolved in water

emulsifying agent amphiphilic substance used to stabilize the particles of some emulsions

emulsion colloid formed from immiscible liquids

freezing point depression lowering of the freezing point of a liquid by addition of a solute

freezing point depression constant (also, cryoscopic constant) proportionality constant in the equation relating freezing point depression to solute molality

gel colloidal dispersion of a liquid in a solid

hemolysis rupture of red blood cells due to the accumulation of excess water by osmosis

Henry's law the proportional relationship between the concentration of dissolved gas in a solution and the partial pressure of the gas in contact with the solution

hypertonic of greater osmotic pressure

hypotonic of less osmotic pressure

ideal solution solution that forms with no accompanying energy change

immiscible of negligible mutual solubility; typically refers to liquid substances

ion pair solvated anion/cation pair held together by moderate electrostatic attraction

ion-dipole attraction electrostatic attraction between an ion and a polar molecule

isotonic of equal osmotic pressure

miscible mutually soluble in all proportions; typically refers to liquid substances

molality (m) a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms

nonelectrolyte substance that does not produce ions when dissolved in water

osmosis diffusion of solvent molecules through a semipermeable membrane

osmotic pressure (Π) opposing pressure required to prevent bulk transfer of solvent molecules through a semipermeable membrane

partially miscible of moderate mutual solubility; typically refers to liquid substances

Raoult's law the relationship between a solution's vapor pressure and the vapor pressures and concentrations of its components

saturated of concentration equal to solubility; containing the maximum concentration of solute possible for a given temperature and pressure

semipermeable membrane a membrane that selectively permits passage of certain ions or molecules

solubility extent to which a solute may be dissolved in water, or any solvent

solvation exothermic process in which intermolecular attractive forces between the solute and solvent in a solution are established

spontaneous process physical or chemical change that occurs without the addition of energy from an external source

strong electrolyte substance that dissociates or ionizes completely when dissolved in water

supersaturated of concentration that exceeds solubility; a nonequilibrium state

suspension heterogeneous mixture in which relatively large component particles are temporarily dispersed but settle out over time

Tyndall effect scattering of visible light by a colloidal dispersion

unsaturated of concentration less than solubility

van't Hoff factor (i) the ratio of the number of moles of particles in a solution to the number of moles of formula units dissolved in the solution

weak electrolyte substance that ionizes only partially when dissolved in water

Key Equations

- $C_\text{g} = kP_\text{g}$
- $\left(P_\text{A} = X_\text{A} P_\text{A}^*\right)$
- $P_\text{solution} = \sum_i P_i = \sum_i X_i P_i^*$
- $P_\text{solution} = X_\text{solvent} P_\text{solvent}^*$
- $\Delta T_\text{b} = K_\text{b} m$
- $\Delta T_\text{f} = K_\text{f} m$
- $\mathit{\Pi} = MRT$

Summary

11.1 The Dissolution Process

A solution forms when two or more substances combine physically to yield a mixture that is homogeneous at the molecular level. The solvent is the most concentrated component and determines the physical state of the solution. The solutes are the other components typically present at concentrations less than that of the solvent. Solutions may form endothermically or exothermically, depending upon the relative magnitudes of solute and solvent intermolecular attractive forces. Ideal solutions form with no appreciable change in energy.

11.2 Electrolytes

Substances that dissolve in water to yield ions are called electrolytes. Electrolytes may be covalent compounds that chemically react with water to produce ions (for example, acids and bases), or they may be ionic compounds that dissociate to yield their constituent cations and anions, when dissolved. Dissolution of an ionic compound is facilitated by ion-dipole attractions between the ions of the compound and the polar water molecules. Soluble ionic substances and strong acids ionize completely and are strong electrolytes, while weak acids and bases ionize to only a small extent and are weak electrolytes. Nonelectrolytes are substances that do not produce ions when dissolved in water.

11.3 Solubility

The extent to which one substance will dissolve in another is determined by several factors, including the types and relative strengths of intermolecular attractive forces that may exist between the substances' atoms, ions, or molecules. This tendency to dissolve is quantified as a substance's solubility, its maximum concentration in a solution at equilibrium under specified conditions. A saturated solution contains solute at a concentration equal to its solubility. A supersaturated solution is one in which a solute's concentration exceeds its solubility—a nonequilibrium (unstable) condition that will result in solute precipitation when the solution is appropriately perturbed. Miscible liquids are soluble in all proportions, and immiscible liquids exhibit very low mutual solubility. Solubilities for gaseous solutes decrease with increasing temperature, while those for most, but not all, solid solutes increase with temperature. The concentration of a gaseous solute in a solution is proportional to the partial pressure of the gas to which the solution is exposed, a relation known as Henry's law.

11.4 Colligative Properties

Properties of a solution that depend only on the concentration of solute particles are called colligative properties. They include changes in the vapor pressure, boiling point, and freezing point of the solvent in the solution. The magnitudes of these properties depend only on the total concentration of solute particles in solution, not on the type of particles. The total concentration of solute particles in a solution also determines its osmotic pressure. This is the pressure that must be applied to the solution to prevent diffusion of molecules of pure solvent through a semipermeable membrane into the solution. Ionic compounds may not completely dissociate in solution due to activity effects, in which case observed colligative effects may be less than predicted.

11.5 Colloids

Colloids are mixtures in which one or more substances are dispersed as relatively large solid particles or liquid droplets throughout a solid, liquid, or gaseous medium. The particles of a colloid remain dispersed and do not settle due to gravity, and they are often electrically charged. Colloids are widespread in nature and are involved in many technological applications.

Exercises

11.1 The Dissolution Process

1. How do solutions differ from compounds? From other mixtures?

2. Which of the principal characteristics of solutions are evident in the solutions of $K_2Cr_2O_7$ shown in **Figure 11.2**?

3. When KNO_3 is dissolved in water, the resulting solution is significantly colder than the water was originally.

(a) Is the dissolution of KNO_3 an endothermic or an exothermic process?

(b) What conclusions can you draw about the intermolecular attractions involved in the process?

(c) Is the resulting solution an ideal solution?

4. Give an example of each of the following types of solutions:

(a) a gas in a liquid

(b) a gas in a gas

(c) a solid in a solid

5. Indicate the most important types of intermolecular attractions in each of the following solutions:

(a) The solution in **Figure 11.2**.

(b) $NO(l)$ in $CO(l)$

(c) $Cl_2(g)$ in $Br_2(l)$

(d) $HCl(g)$ in benzene $C_6H_6(l)$

(e) Methanol $CH_3OH(l)$ in $H_2O(l)$

6. Predict whether each of the following substances would be more soluble in water (polar solvent) or in a hydrocarbon such as heptane (C_7H_{16}, nonpolar solvent):

(a) vegetable oil (nonpolar)

(b) isopropyl alcohol (polar)

(c) potassium bromide (ionic)

7. Heat is released when some solutions form; heat is absorbed when other solutions form. Provide a molecular explanation for the difference between these two types of spontaneous processes.

8. Solutions of hydrogen in palladium may be formed by exposing Pd metal to H_2 gas. The concentration of hydrogen in the palladium depends on the pressure of H_2 gas applied, but in a more complex fashion than can be described by Henry’s law. Under certain conditions, 0.94 g of hydrogen gas is dissolved in 215 g of palladium metal (solution density = 10.8 g cm^3).

(a) Determine the molarity of this solution.

(b) Determine the molality of this solution.

(c) Determine the percent by mass of hydrogen atoms in this solution.

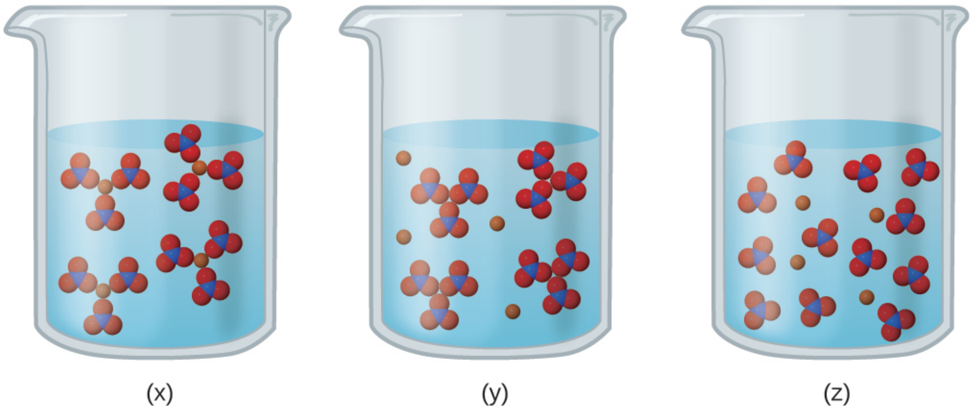
11.2 Electrolytes

9. Explain why the ions Na^+ and Cl^- are strongly solvated in water but not in hexane, a solvent composed of nonpolar molecules.

10. Explain why solutions of HBr in benzene (a nonpolar solvent) are nonconductive, while solutions in water (a polar solvent) are conductive.

11. Consider the solutions presented:

(a) Which of the following sketches best represents the ions in a solution of $Fe(NO_3)_3(aq)$?



(b) Write a balanced chemical equation showing the products of the dissolution of $Fe(NO_3)_3$.

12. Compare the processes that occur when methanol (CH_3OH), hydrogen chloride (HCl), and sodium hydroxide (NaOH) dissolve in water. Write equations and prepare sketches showing the form in which each of these compounds is present in its respective solution.

13. What is the expected electrical conductivity of the following solutions?

(a) $NaOH(aq)$

(b) $HCl(aq)$

(c) $C_6H_{12}O_6(aq)$ (glucose)

(d) $NH_3(aq)$

14. Why are most *solid* ionic compounds electrically nonconductive, whereas aqueous solutions of ionic compounds are good conductors? Would you expect a *liquid* (molten) ionic compound to be electrically conductive or nonconductive? Explain.

15. Indicate the most important type of intermolecular attraction responsible for solvation in each of the following solutions:

(a) the solutions in **Figure 11.7**

(b) methanol, CH_3OH, dissolved in ethanol, C_2H_5OH

(c) methane, CH_4, dissolved in benzene, C_6H_6

(d) the polar halocarbon CF_2Cl_2 dissolved in the polar halocarbon $CF_2ClCFCl_2$

(e) $O_2(l)$ in $N_2(l)$

11.3 Solubility

16. Suppose you are presented with a clear solution of sodium thiosulfate, $Na_2S_2O_3$. How could you determine whether the solution is unsaturated, saturated, or supersaturated?

17. Supersaturated solutions of most solids in water are prepared by cooling saturated solutions. Supersaturated solutions of most gases in water are prepared by heating saturated solutions. Explain the reasons for the difference in the two procedures.

18. Suggest an explanation for the observations that ethanol, C_2H_5OH, is completely miscible with water and that ethanethiol, C_2H_5SH, is soluble only to the extent of 1.5 g per 100 mL of water.

19. Calculate the percent by mass of KBr in a saturated solution of KBr in water at 10 °C. See **Figure 11.16** for useful data, and report the computed percentage to one significant digit.

20. Which of the following gases is expected to be most soluble in water? Explain your reasoning.

(a) CH_4

(b) CCl_4

(c) $CHCl_3$

21. At 0 °C and 1.00 atm, as much as 0.70 g of O_2 can dissolve in 1 L of water. At 0 °C and 4.00 atm, how many grams of O_2 dissolve in 1 L of water?

22. Refer to **Figure 11.10**.

(a) How did the concentration of dissolved CO_2 in the beverage change when the bottle was opened?

(b) What caused this change?

(c) Is the beverage unsaturated, saturated, or supersaturated with CO_2?

23. The Henry's law constant for CO_2 is 3.4×10^{-2} M/atm at 25 °C. Assuming ideal solution behavior, what pressure of carbon dioxide is needed to maintain a CO_2 concentration of 0.10 *M* in a can of lemon-lime soda?

24. The Henry's law constant for O_2 is 1.3×10^{-3} M/atm at 25 °C. Assuming ideal solution behavior, what mass of oxygen would be dissolved in a 40-L aquarium at 25 °C, assuming an atmospheric pressure of 1.00 atm, and that the partial pressure of O_2 is 0.21 atm?

25. Assuming ideal solution behavior, how many liters of HCl gas, measured at 30.0 °C and 745 torr, are required to prepare 1.25 L of a 3.20-*M* solution of hydrochloric acid?

11.4 Colligative Properties

26. Which is/are part of the macroscopic domain of solutions and which is/are part of the microscopic domain: boiling point elevation, Henry's law, hydrogen bond, ion-dipole attraction, molarity, nonelectrolyte, nonstoichiometric compound, osmosis, solvated ion?

27. What is the microscopic explanation for the macroscopic behavior illustrated in **Figure 11.14**?

28. Sketch a qualitative graph of the pressure versus time for water vapor above a sample of pure water and a sugar solution, as the liquids evaporate to half their original volume.

29. A solution of potassium nitrate, an electrolyte, and a solution of glycerin ($C_3H_5(OH)_3$), a nonelectrolyte, both boil at 100.3 °C. What other physical properties of the two solutions are identical?

30. What are the mole fractions of H_3PO_4 and water in a solution of 14.5 g of H_3PO_4 in 125 g of water?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

31. What are the mole fractions of HNO_3 and water in a concentrated solution of nitric acid (68.0% HNO_3 by mass)?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

32. Calculate the mole fraction of each solute and solvent:

(a) 583 g of H_2SO_4 in 1.50 kg of water—the acid solution used in an automobile battery

(b) 0.86 g of NaCl in 1.00×10^2 g of water—a solution of sodium chloride for intravenous injection

(c) 46.85 g of codeine, $C_{18}H_{21}NO_3$, in 125.5 g of ethanol, C_2H_5OH

(d) 25 g of I_2 in 125 g of ethanol, C_2H_5OH

33. Calculate the mole fraction of each solute and solvent:

(a) 0.710 kg of sodium carbonate (washing soda), Na_2CO_3, in 10.0 kg of water—a saturated solution at 0 °C

(b) 125 g of NH_4NO_3 in 275 g of water—a mixture used to make an instant ice pack

(c) 25 g of Cl_2 in 125 g of dichloromethane, CH_2Cl_2

(d) 0.372 g of tetrahydropyridine, C_5H_9N, in 125 g of chloroform, $CHCl_3$

34. Calculate the mole fractions of methanol, CH_3OH; ethanol, C_2H_5OH; and water in a solution that is 40% methanol, 40% ethanol, and 20% water by mass. (Assume the data are good to two significant figures.)

35. What is the difference between a 1 *M* solution and a 1 *m* solution?

36. What is the molality of phosphoric acid, H_3PO_4, in a solution of 14.5 g of H_3PO_4 in 125 g of water?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

37. What is the molality of nitric acid in a concentrated solution of nitric acid (68.0% HNO_3 by mass)?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

38. Calculate the molality of each of the following solutions:

(a) 583 g of H_2SO_4 in 1.50 kg of water—the acid solution used in an automobile battery

(b) 0.86 g of NaCl in 1.00×10^2 g of water—a solution of sodium chloride for intravenous injection

(c) 46.85 g of codeine, $C_{18}H_{21}NO_3$, in 125.5 g of ethanol, C_2H_5OH

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39. Calculate the molality of each of the following solutions:

(a) 0.710 kg of sodium carbonate (washing soda), Na_2CO_3, in 10.0 kg of water—a saturated solution at 0°C

(b) 125 g of NH_4NO_3 in 275 g of water—a mixture used to make an instant ice pack

(c) 25 g of Cl_2 in 125 g of dichloromethane, CH_2Cl_2

(d) 0.372 g of tetrahydropyridine, C_5H_9N, in 125 g of chloroform, $CHCl_3$

40. The concentration of glucose, $C_6H_{12}O_6$, in normal spinal fluid is $\frac{75\text{ mg}}{100\text{ g}}$. What is the molality of the solution?

41. A 13.0% solution of K_2CO_3 by mass has a density of 1.09 g/cm^3. Calculate the molality of the solution.

42. Why does 1 mol of sodium chloride depress the freezing point of 1 kg of water almost twice as much as 1 mol of glycerin?

43. Assuming ideal solution behavior, what is the boiling point of a solution of 115.0 g of nonvolatile sucrose, $C_{12}H_{22}O_{11}$, in 350.0 g of water?

(a) Outline the steps necessary to answer the question

(b) Answer the question

44. Assuming ideal solution behavior, what is the boiling point of a solution of 9.04 g of I_2 in 75.5 g of benzene, assuming the I_2 is nonvolatile?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

45. Assuming ideal solution behavior, what is the freezing temperature of a solution of 115.0 g of sucrose, $C_{12}H_{22}O_{11}$, in 350.0 g of water?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

46. Assuming ideal solution behavior, what is the freezing point of a solution of 9.04 g of I_2 in 75.5 g of benzene?

(a) Outline the steps necessary to answer the following question.

(b) Answer the question.

47. Assuming ideal solution behavior, what is the osmotic pressure of an aqueous solution of 1.64 g of $Ca(NO_3)_2$ in water at 25 °C? The volume of the solution is 275 mL.

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

48. Assuming ideal solution behavior, what is osmotic pressure of a solution of bovine insulin (molar mass, 5700 g mol^{-1}) at 18 °C if 100.0 mL of the solution contains 0.103 g of the insulin?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

49. Assuming ideal solution behavior, what is the molar mass of a solution of 5.00 g of a compound in 25.00 g of carbon tetrachloride (bp 76.8 °C; K_b = 5.02 °C/*m*) that boils at 81.5 °C at 1 atm?

(a) Outline the steps necessary to answer the question.

(b) Solve the problem.

50. A sample of an organic compound (a nonelectrolyte) weighing 1.35 g lowered the freezing point of 10.0 g of benzene by 3.66 °C. Assuming ideal solution behavior, calculate the molar mass of the compound.

51. A 1.0 *m* solution of HCl in benzene has a freezing point of 0.4 °C. Is HCl an electrolyte in benzene? Explain.

52. A solution contains 5.00 g of urea, $CO(NH_2)_2$, a nonvolatile compound, dissolved in 0.100 kg of water. If the vapor pressure of pure water at 25 °C is 23.7 torr, what is the vapor pressure of the solution (assuming ideal solution behavior)?

53. A 12.0-g sample of a nonelectrolyte is dissolved in 80.0 g of water. The solution freezes at −1.94 °C. Assuming ideal solution behavior, calculate the molar mass of the substance.

54. Arrange the following solutions in order by their decreasing freezing points: 0.1 *m* Na_3PO_4, 0.1 *m* C_2H_5OH, 0.01 *m* CO_2, 0.15 *m* NaCl, and 0.2 *m* $CaCl_2$.

55. Calculate the boiling point elevation of 0.100 kg of water containing 0.010 mol of NaCl, 0.020 mol of Na_2SO_4, and 0.030 mol of $MgCl_2$, assuming complete dissociation of these electrolytes and ideal solution behavior.

56. How could you prepare a 3.08 *m* aqueous solution of glycerin, $C_3H_8O_3$? Assuming ideal solution behavior, what is the freezing point of this solution?

57. A sample of sulfur weighing 0.210 g was dissolved in 17.8 g of carbon disulfide, CS_2 (K_b = 2.43 °C/*m*). If the boiling point elevation was 0.107 °C, what is the formula of a sulfur molecule in carbon disulfide (assuming ideal solution behavior)?

58. In a significant experiment performed many years ago, 5.6977 g of cadmium iodide in 44.69 g of water raised the boiling point 0.181 °C. What does this suggest about the nature of a solution of CdI_2?

59. Lysozyme is an enzyme that cleaves cell walls. A 0.100-L sample of a solution of lysozyme that contains 0.0750 g of the enzyme exhibits an osmotic pressure of 1.32×10^{-3} atm at 25 °C. Assuming ideal solution behavior, what is the molar mass of lysozyme?

60. The osmotic pressure of a solution containing 7.0 g of insulin per liter is 23 torr at 25 °C. Assuming ideal solution behavior, what is the molar mass of insulin?

61. The osmotic pressure of human blood is 7.6 atm at 37 °C. What mass of glucose, $C_6H_{12}O_6$, is required to make 1.00 L of aqueous solution for intravenous feeding if the solution must have the same osmotic pressure as blood at body temperature, 37 °C (assuming ideal solution behavior)?

62. Assuming ideal solution behavior, what is the freezing point of a solution of dibromobenzene, $C_6H_4Br_2$, in 0.250 kg of benzene, if the solution boils at 83.5 °C?

63. Assuming ideal solution behavior, what is the boiling point of a solution of NaCl in water if the solution freezes at −0.93 °C?

64. The sugar fructose contains 40.0% C, 6.7% H, and 53.3% O by mass. A solution of 11.7 g of fructose in 325 g of ethanol has a boiling point of 78.59 °C. The boiling point of ethanol is 78.35 °C, and K_b for ethanol is 1.20 °C/*m*. Assuming ideal solution behavior, what is the molecular formula of fructose?

65. The vapor pressure of methanol, CH_3OH, is 94 torr at 20 °C. The vapor pressure of ethanol, C_2H_5OH, is 44 torr at the same temperature.

(a) Calculate the mole fraction of methanol and of ethanol in a solution of 50.0 g of methanol and 50.0 g of ethanol.

(b) Ethanol and methanol form a solution that behaves like an ideal solution. Calculate the vapor pressure of methanol and of ethanol above the solution at 20 °C.

(c) Calculate the mole fraction of methanol and of ethanol in the vapor above the solution.

66. The triple point of air-free water is defined as 273.16 K. Why is it important that the water be free of air?

67. Meat can be classified as fresh (not frozen) even though it is stored at −1 °C. Why wouldn't meat freeze at this temperature?

68. An organic compound has a composition of 93.46% C and 6.54% H by mass. A solution of 0.090 g of this compound in 1.10 g of camphor melts at 158.4 °C. The melting point of pure camphor is 178.4 °C. K_f for camphor is 37.7 °C/*m*. Assuming ideal solution behavior, what is the molecular formula of the solute? Show your calculations.

69. A sample of $HgCl_2$ weighing 9.41 g is dissolved in 32.75 g of ethanol, C_2H_5OH (K_b = 1.20 °C/*m*). The boiling point elevation of the solution is 1.27 °C. Is $HgCl_2$ an electrolyte in ethanol? Show your calculations.

70. A salt is known to be an alkali metal fluoride. A quick approximate determination of freezing point indicates that 4 g of the salt dissolved in 100 g of water produces a solution that freezes at about −1.4 °C. Assuming ideal solution behavior, what is the formula of the salt? Show your calculations.

11.5 Colloids

71. Identify the dispersed phase and the dispersion medium in each of the following colloidal systems: starch dispersion, smoke, fog, pearl, whipped cream, floating soap, jelly, milk, and ruby.

72. Distinguish between dispersion methods and condensation methods for preparing colloidal systems.

73. How do colloids differ from solutions with regard to dispersed particle size and homogeneity?

74. Explain the cleansing action of soap.

75. How can it be demonstrated that colloidal particles are electrically charged?

Chapter 12

Thermodynamics

Figure 12.1 Geysers are a dramatic display of thermodynamic principles in nature. Water deep within the underground channels of the geyser is under high pressure and heated to high temperature by magma. When a pocket of water near the surface reaches boiling point and is expelled, the resulting drop in pressure causes larger volumes of water to flash boil, forcefully ejecting steam and water in an impressive eruption. (credit: modification of work by Yellowstone National Park)

Chapter Outline

Introduction

Among the many capabilities of chemistry is its ability to predict if a process will occur under specified conditions. Thermodynamics, the study of relationships between the energy and work associated with chemical and physical processes, provides this predictive ability. Previous chapters in this text have described various applications of thermochemistry, an important aspect of thermodynamics concerned with the heat flow accompanying chemical reactions and phase transitions. This chapter will introduce additional thermodynamic concepts, including those that enable the prediction of any chemical or physical changes under a given set of conditions.

12.1 Spontaneity

By the end of this section, you will be able to:

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. Iron exposed to the earth's atmosphere will corrode, but rust is not converted to iron without intentional chemical treatment. A **spontaneous process** is one that occurs naturally under certain conditions. A **nonspontaneous process**, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (**Figure 12.2**).

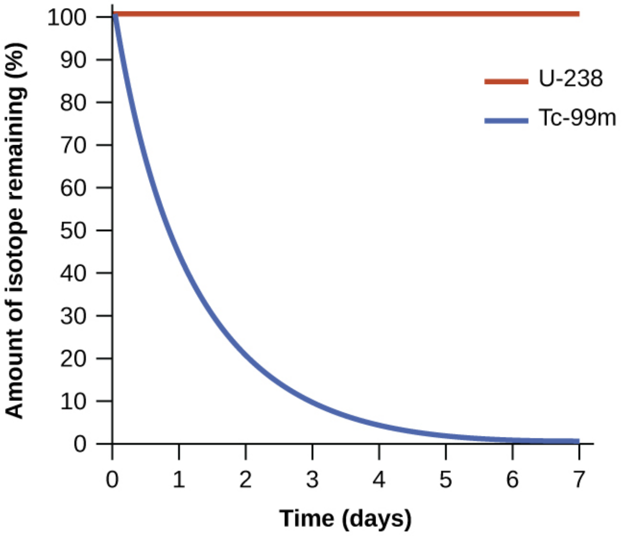


Figure 12.2 Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed.

As another example, consider the conversion of diamond into graphite (**Figure 12.3**).

$$\text{C}(s,\ \text{diamond}) \longrightarrow \text{C}(s,\ \text{graphite})$$

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow; so, for all practical purposes diamonds are indeed "forever." Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

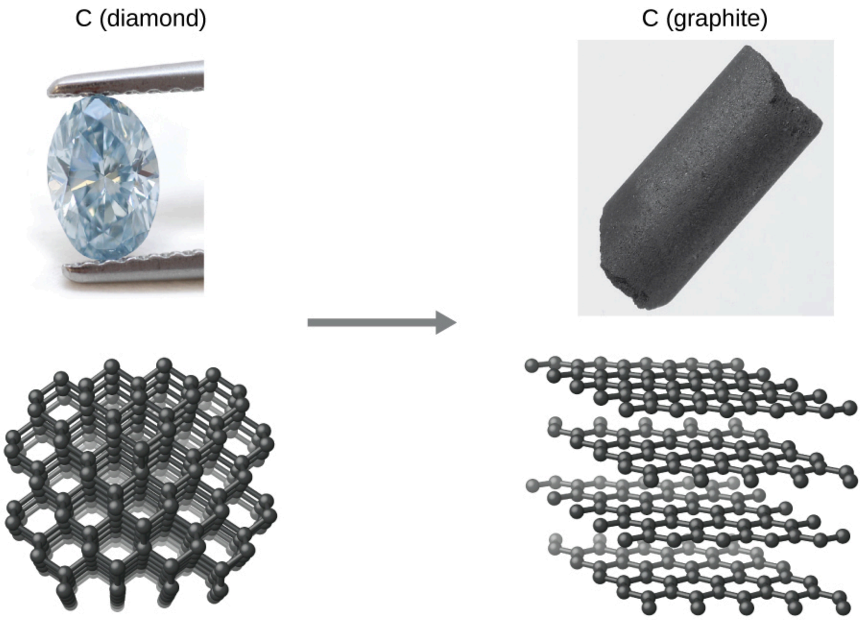


Figure 12.3 The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as *graphitization*, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modificaton of work by images-of-elements.com/carbon.php)

Dispersal of Matter and Energy

Extending the discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas in one flask and the other flask is empty ($P = 0$). (**Figure 12.4**). When the valve is opened, the gas spontaneously expands to fill both flasks equally. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

$$w = -P\Delta V = 0 \qquad\qquad (P = 0 \text{ in a vaccum})$$

Note as well that since the system is isolated, no heat has been exchanged with the surroundings ($q = 0$). The *first law of thermodynamics* confirms that there has been no change in the system's internal energy as a result of this process.

$$\Delta U = q + w = 0 + 0 = 0$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the driving force appears to be related to the *greater, more uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous expansion took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

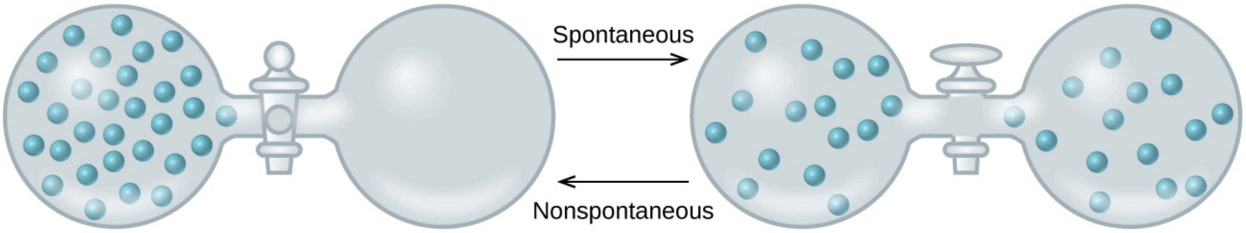


Figure 12.4 An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (**Figure 12.5**). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

$$q_X < 0 \qquad \text{and} \qquad q_Y = -q_X > 0$$

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.

Figure 12.5 When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

Example 12.1

Redistribution of Matter during a Spontaneous Process

Describe how matter is redistributed when the following spontaneous processes take place:

(a) A solid sublimes.

(b) A gas condenses.

(c) A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution

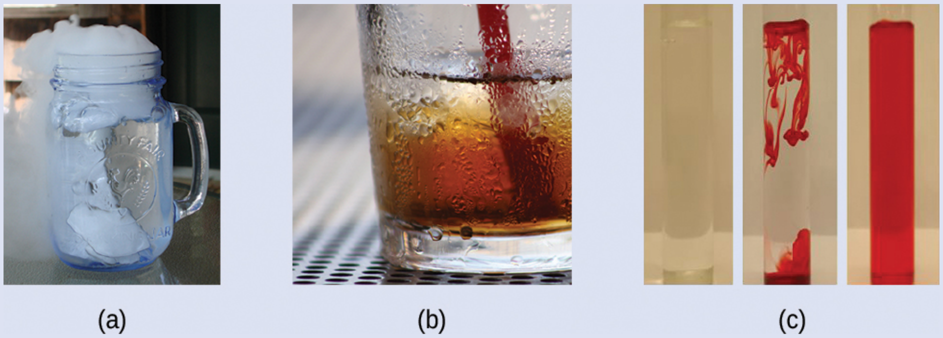


Figure 12.6 (credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Paul A. Flowers)

(a) Sublimation is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition.

(b) Condensation is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition.

(c) The process in question is diffusion. This process yields a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop of dye, zero in the water), and the final state of the system contains a single dye concentration throughout.

Check Your Learning

Describe how energy is redistributed when a spoon at room temperature is placed in a cup of hot coffee.

Answer: Heat will spontaneously flow from the hotter object (coffee) to the colder object (spoon), resulting in a more uniform distribution of thermal energy as the spoon warms and the coffee cools.

12.2 Entropy

By the end of this section, you will be able to:

- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (**Figure 12.7**) published the results of an extensive study regarding the efficiency of steam heat engines. A later review of Carnot’s findings by Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (T). In thermodynamics, a **reversible process** is one that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be “reversed”) by an infinitesimally small change in some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.

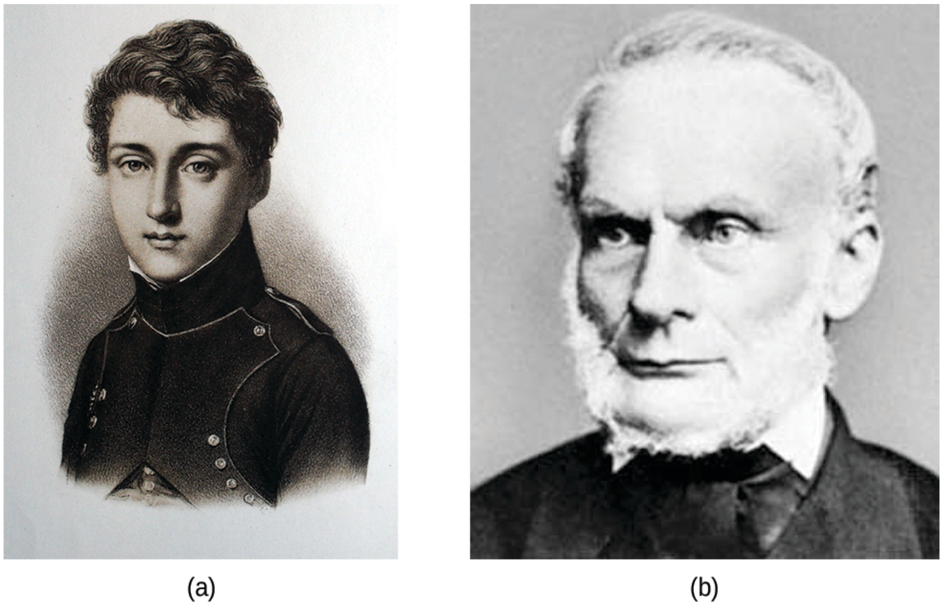


Figure 12.7 (a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property **entropy (S)** and defined its change for any process as the following:

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the *number of microstates* (W) possible for the system. A **microstate** is a specific configuration of all the locations and energies of the atoms or molecules that make up a system. The relation between a system's entropy and the number of possible microstates is

$$S = k \ln W$$

where k is the Boltzmann constant, 1.38×10^{-23} J/K.

As for other state functions, the change in entropy for a process is the difference between its final (S_{f}) and initial (S_{i}) values:

$$\Delta S = S_{\text{f}} - S_{\text{i}} = k \ln W_{\text{f}} - k \ln W_{\text{i}} = k \ln \frac{W_{\text{f}}}{W_{\text{i}}}$$

For processes involving an increase in the number of microstates, $W_{\text{f}} > W_{\text{i}}$, the entropy of the system increases and $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $W_{\text{f}} < W_{\text{i}}$, yield a decrease in system entropy, $\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

Consider the general case of a system comprised of N particles distributed among n boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in 2^4

= 16 different microstates as illustrated in **Figure 12.8**. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

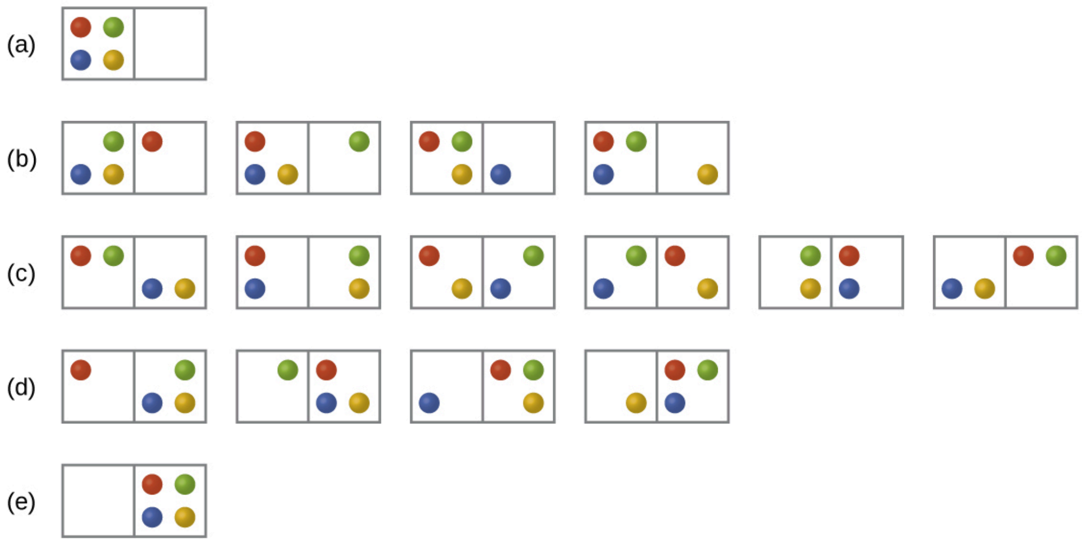


Figure 12.8 The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is $\frac{6}{16}$ or $\frac{3}{8}$. The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of $\frac{1}{16}$. The probability of finding all particles in only one box (either the left box or right box) is then $\left(\frac{1}{16} + \frac{1}{16}\right) = \frac{2}{16}$ or $\frac{1}{8}$.

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

This matter dispersal model of entropy is often described qualitatively in terms of the *disorder* of the system. By this description, microstates in which all the particles are in a single box are the most ordered, thus possessing the least entropy. Microstates in which the particles are more evenly distributed among the boxes are more disordered, possessing greater entropy.

The previous description of an ideal gas expanding into a vacuum (**Figure 12.4**) is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. Initially, the gas molecules are confined to just one of the two flasks. Opening the valve between the flasks increases the volume available to the gas molecules and, correspondingly, the number of microstates possible for the system. Since $W_f > W_i$, the expansion process involves an increase in entropy ($\Delta S > 0$) and is spontaneous.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of thermal energy (represented as "*") in **Figure 12.9**. The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. Thus, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects' temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

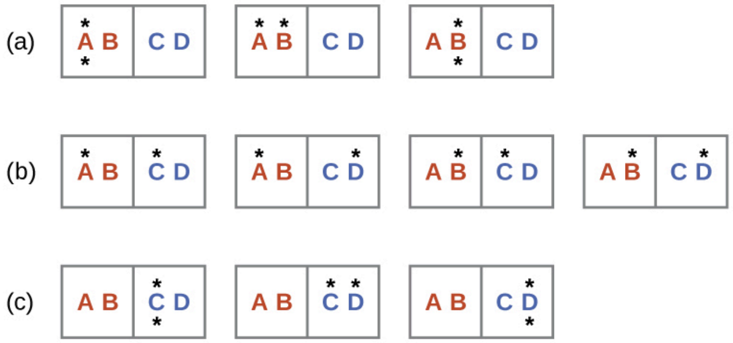
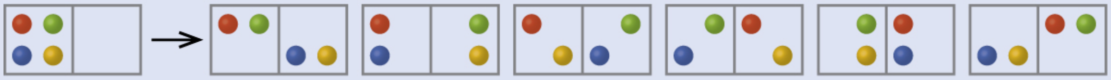


Figure 12.9 This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

Example 12.2

Determination of ΔS

Calculate the change in entropy for the process depicted below.



Solution

The initial number of microstates is one, the final six:

$$\Delta S = k \ln \frac{W_c}{W_a} = 1.38 \times 10^{-23}\ \text{J/K} \times \ln \frac{6}{1} = 2.47 \times 10^{-23}\ \text{J/K}$$

The sign of this result is consistent with expectation; since there are more microstates possible for the final state than for the initial state, the change in entropy should be positive.

Check Your Learning

Consider the system shown in **Figure 12.9**. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Answer: 0 J/K

Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in **Figure 12.10**. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{\text{liquid}} > S_{\text{solid}}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

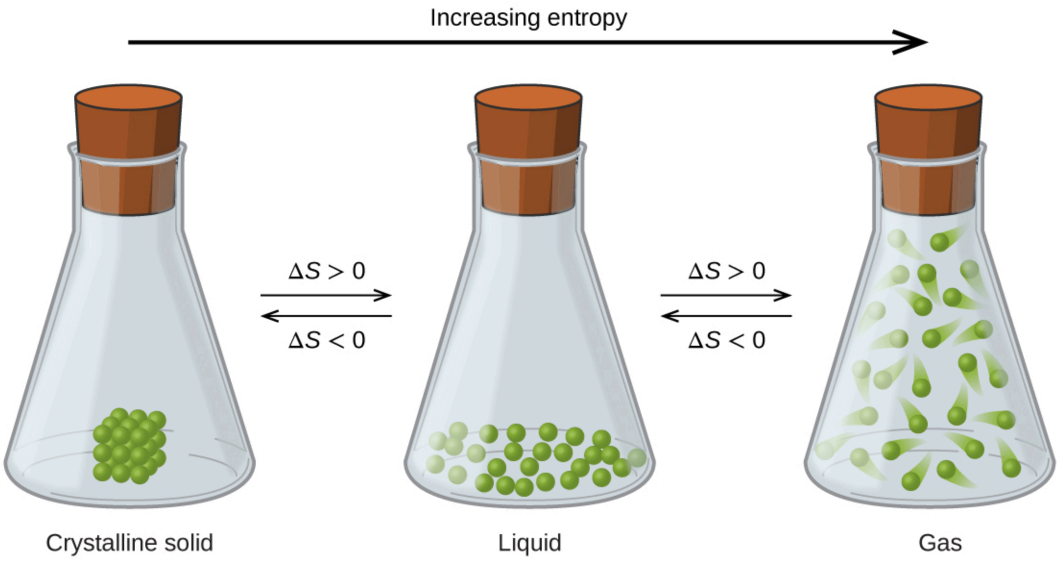


Figure 12.10 The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the gaseous phase, in which a given number of atoms or molecules occupy a *much* greater volume than in the liquid phase. Each atom or molecule can be found in many more locations, corresponding to a much greater number of microstates. Consequently, for any substance, $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (**Figure 12.11**).

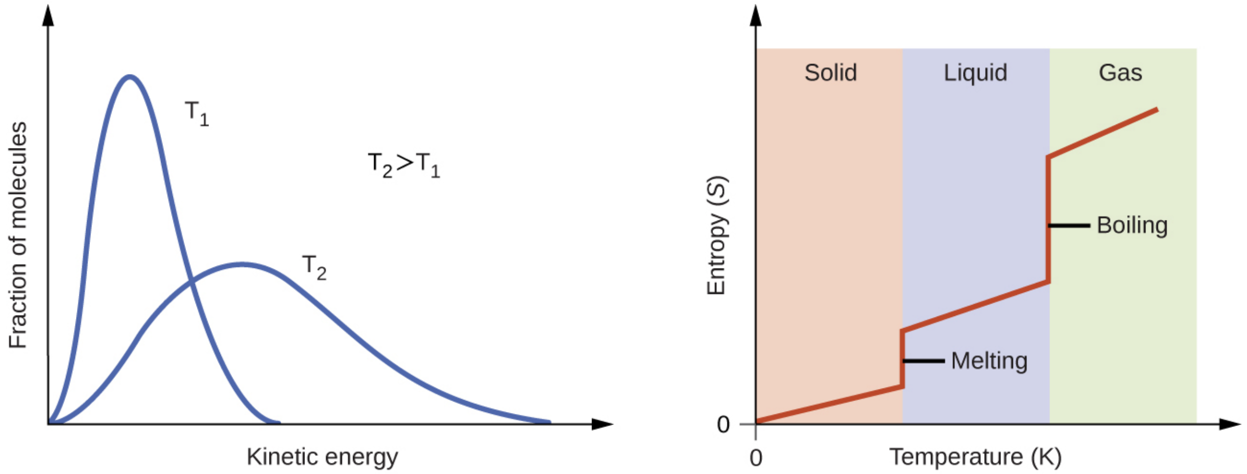


Figure 12.11 Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance undergoes a phase transition, its entropy changes significantly.

Link to Learning

Try this **simulator (http://openstaxcollege.org/l/16freemotion)** with interactive visualization of the dependence of particle location and freedom of motion on physical state and temperature.

The entropy of a substance is influenced by the structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle's mass and the spacing of quantized translational energy levels (a topic beyond the scope of this text). For molecules, greater numbers of atoms increase the number of ways in which the molecules can vibrate and thus the number of possible microstates and the entropy of the system.

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in **Example 12.3**.

Example 12.3

Predicting the Sign of Δ*S*

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

(a) One mole liquid water at room temperature $\longrightarrow$ one mole liquid water at 50 °C

(b) $\text{Ag}^+(aq) + \text{Cl}^-(aq) \longrightarrow \text{AgCl}(s)$

(c) $C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$

(d) $NH_3(s) \longrightarrow NH_3(l)$

Solution

(a) positive, temperature increases

(b) negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter

(c) negative, net decrease in the amount of gaseous species

(d) positive, phase transition from solid to liquid, net increase in dispersal of matter

Check Your Learning

Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

(a) $NaNO_3(s) \longrightarrow Na^+(aq) + NO_3{}^-(aq)$

(b) the freezing of liquid water

(c) $CO_2(s) \longrightarrow CO_2(g)$

(d) $CaCO(s) \longrightarrow CaO(s) + CO_2(g)$

Answer: (a) Positive; The solid dissolves to give an increase of mobile ions in solution. (b) Negative; The liquid becomes a more ordered solid. (c) Positive; The relatively ordered solid becomes a gas. (d) Positive; There is a net increase in the amount of gaseous species.

12.3 The Second and Third Laws of Thermodynamics

By the end of this section, you will be able to:

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

The Second Law of Thermodynamics

In the quest to identify a property that may reliably predict the spontaneity of a process, a promising candidate has been identified: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}}$$

The magnitudes of $-q_{\text{rev}}$ and q_{rev} are equal, their opposite arithmetic signs denoting loss of heat by the system and gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the entropy *decrease* of the system will be less than the entropy *increase* of the surroundings, and so *the entropy of the universe will increase*:

$$|\Delta S_{\text{sys}}| < |\Delta S_{\text{surr}}|$$
$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}}$$

   The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes (that is, *the direction of the heat flow*) will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*

3. The objects are at essentially the same temperature, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the magnitudes of the entropy changes are essentially the same for both the system and the surroundings. In this case, the entropy change of the universe is zero, and the system is *at equilibrium*.

$$|\Delta S_{\text{sys}}| \approx |\Delta S_{\text{surr}}|$$
$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the **second law of thermodynamics**: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in **Table 12.1**.

The Second Law of Thermodynamics

$\Delta S_{\text{univ}} > 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{\text{univ}} = 0$	at equilibrium

Table 12.1

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev}, and the second law may be stated as the following:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$$

We may use this equation to predict the spontaneity of a process as illustrated in **Example 12.4**.

Example 12.4

Will Ice Spontaneously Melt?

The entropy change for the process

$$H_2O(s) \longrightarrow H_2O(l)$$

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at −10.00 °C? Is it spontaneous at +10.00 °C?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, ΔS_{sys} = 22.1 J/K and q_{surr} = −6.00 kJ.

At −10.00 °C (263.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\text{ J/K} + \frac{-6.00 \times 10^3\text{ J}}{263.15\text{ K}} = -0.7\text{ J/K}\end{aligned}$$

$S_{\text{univ}} < 0$, so melting is nonspontaneous (*not* spontaneous) at −10.0 °C.

At 10.00 °C (283.15 K), the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$$

$$= 22.1\text{ J/K} + \frac{-6.00 \times 10^3\text{ J}}{283.15\text{ K}} = +0.9\text{ J/K}$$

$S_{\text{univ}} > 0$, so melting *is* spontaneous at 10.00 °C.

Check Your Learning

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of S_{univ}?

Answer: Entropy is a state function, so $\Delta S_{\text{freezing}} = -\Delta S_{\text{melting}}$ = −22.1 J/K and q_{surr} = +6.00 kJ. At −10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, −0.9 J/K.

The Third Law of Thermodynamics

The previous section described the various contributions of matter and energy dispersal that contribute to the entropy of a system. With these contributions in mind, consider the entropy of a pure, perfectly crystalline solid possessing no kinetic energy (that is, at a temperature of absolute zero, 0 K). This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion means there is but one possible location for each identical atom or molecule comprising the crystal ($W = 1$). According to the Boltzmann equation, the entropy of this system is zero.

$$S = k \ln W = k \ln(1) = 0$$

This limiting condition for a system's entropy represents the **third law of thermodynamics**: *the entropy of a pure, perfect crystalline substance at 0 K is zero.*

Careful calorimetric measurements can be made to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. **Standard entropies ($S°$)** are for one mole of substance under standard conditions (a pressure of 1 bar and a temperature of 298.15 K; see details regarding standard conditions in the thermochemistry chapter of this text). The **standard entropy change ($\Delta S°$)** for a reaction may be computed using standard entropies as shown below:

$$\Delta S° = \sum \nu S°(\text{products}) - \sum \nu S°(\text{reactants})$$

where ν represents stoichiometric coefficients in the balanced equation representing the process. For example, $\Delta S°$ for the following reaction at room temperature

$$m\text{A} + n\text{B} \longrightarrow x\text{C} + y\text{D},$$

is computed as:

$$= [xS^\circ(\text{C}) + yS^\circ(\text{D})] - [mS^\circ(\text{A}) + nS^\circ(\text{B})]$$

A partial listing of standard entropies is provided in **Table 12.2**, and additional values are provided in **Appendix G**. The example exercises that follow demonstrate the use of $S°$ values in calculating standard entropy changes for physical and chemical processes.

Substance	**$S°$ (J mol^{-1} K^{-1})**
carbon	
C(*s*, graphite)	5.740
C(*s*, diamond)	2.38
$CO(g)$	197.7
$CO_2(g)$	213.8
$CH_4(g)$	186.3
$C_2H_4(g)$	219.5
$C_2H_6(g)$	229.5
$CH_3OH(l)$	126.8
$C_2H_5OH(l)$	160.7
hydrogen	
$H_2(g)$	130.57
$H(g)$	114.6
$H_2O(g)$	188.71
$H_2O(l)$	69.91
$HCl(g)$	186.8
$H_2S(g)$	205.7
oxygen	
$O_2(g)$	205.03

Table 12.2 Standard entropies for selected substances measured at 1 atm and 298.15 K. (Values are approximately equal to those measured at 1 bar, the currently accepted standard state pressure.)

Example 12.5

Determination of Δ*S*°

Calculate the standard entropy change for the following process:

$$H_2O(g) \longrightarrow H_2O(l)$$

Solution

Calculate the entropy change using standard entropies as shown above:

$$\Delta S^\circ = (1\ \text{mol})(70.0\ \text{J mol}^{-1}\ \text{K}^{-1}) - (1\ \text{mol})(188.8\ \text{J mol}^{-1}\ \text{K}^{-1}) = -118.8\ \text{J/K}$$

The value for $\Delta S°$ is negative, as expected for this phase transition (condensation), which the previous section discussed.

Check Your Learning

Calculate the standard entropy change for the following process:

$$H_2(g) + C_2H_4(g) \longrightarrow C_2H_6(g)$$

Answer: −120.6 J/K

Example 12.6

Determination of ΔS°

Calculate the standard entropy change for the combustion of methanol, CH_3OH:

$$2CH_3OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(l)$$

Solution

Calculate the entropy change using standard entropies as shown above:

$$\Delta S° = \sum \nu S°(\text{products}) - \sum \nu S°(\text{reactants})$$
$$[2\ \text{mol} \times S°(CO_2(g)) + 4\ \text{mol} \times S°(H_2O(l))] - [2\ \text{mol} \times S°(CH_3OH(l)) + 3\ \text{mol} \times S°(O_2(g))]$$
$$= \{[2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.03)]\} = -161.1\ \text{J/K}$$

Check Your Learning

Calculate the standard entropy change for the following reaction:

$$Ca(OH)_2(s) \longrightarrow CaO(s) + H_2O(l)$$

Answer: 24.7 J/K

12.4 Free Energy

One of the challenges of using the second law of thermodynamics to determine if a process is spontaneous is that it requires measurements of the entropy change for the system *and* the entropy change for the surroundings. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the **Gibbs free energy (*G*)** (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS$$

Free energy is a state function, and at constant temperature and pressure, the **free energy change (Δ*G*)** may be expressed as the following:

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

(For simplicity's sake, the subscript "sys" will be omitted henceforth.)

The relationship between this system property and the spontaneity of a process may be understood by recalling the previously derived second law expression:

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T}$$

The first law requires that $q_{\text{surr}} = -q_{\text{sys}}$, and at constant pressure $q_{\text{sys}} = \Delta H$, so this expression may be rewritten as:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T}$$

Multiplying both sides of this equation by $-T$, and rearranging yields the following:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$$

Comparing this equation to the previous one for free energy change shows the following relation:

$$\Delta G = -T\Delta S_{\text{univ}}$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ}. **Table 12.3** summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Relation between Process Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{\text{univ}} > 0$	$\Delta G < 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	$\Delta G > 0$	nonspontaneous
$\Delta S_{\text{univ}} = 0$	$\Delta G = 0$	at equilibrium

Table 12.3

What's "Free" about Δ*G*?

In addition to indicating spontaneity, the free energy change also provides information regarding the amount of useful work (w) that may be accomplished by a spontaneous process. Although a rigorous treatment of this subject is beyond the scope of an introductory chemistry text, a brief discussion is helpful for gaining a better perspective on this important thermodynamic property.

For this purpose, consider a spontaneous, exothermic process that involves a decrease in entropy. The free energy, as defined by

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

may be interpreted as representing the difference between the energy produced by the process, ΔH, and the energy lost to the surroundings, $T\Delta S$. The difference between the energy produced and the energy lost is the energy available (or "free") to do useful work by the process, ΔG. If the process somehow could be made to take place under conditions of thermodynamic reversibility, the amount of work that could be done would be maximal:

$$\Delta G = w_{\text{max}}$$

However, as noted previously in this chapter, such conditions are not realistic. In addition, the technologies used to extract work from a spontaneous process (e.g., automobile engine, steam turbine) are never 100% efficient, and so the work done by these processes is always less than the theoretical maximum. Similar reasoning may be applied to a nonspontaneous process, for which the free energy change represents the *minimum* amount of work that must be done on the system to carry out the process.

Calculating Free Energy Change

Free energy is a state function, so its value depends only on the conditions of the initial and final states of the system. A convenient and common approach to the calculation of free energy changes for physical and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute **standard free energy changes, Δ*G*°**, according to the following relation:

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

Example 12.7

Using Standard Enthalpy and Entropy Changes to Calculate ΔG°

Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for $\Delta G°$ say about the spontaneity of this process?

Solution

The process of interest is the following:

$$H_2O(l) \longrightarrow H_2O(g)$$

The standard change in free energy may be calculated using the following equation:

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

From Appendix G:

Substance	ΔH_f° (kJ/mol)	$S°$(J/K·mol)
$H_2O(l)$	−286.83	70.0
$H_2O(g)$	−241.82	188.8

Using the appendix data to calculate the standard enthalpy and entropy changes yields:

$$\Delta H° = \Delta H_f^\circ\ (H_2O(g)) - \Delta H_f^\circ\ (H_2O(l))$$
$$= [-241.82\text{ kJ/mol} - (-286.83)]\text{kJ/mol} = 45.01\text{ kJ}$$

$$\Delta S° = 1\text{ mol} \times S°(H_2O(g)) - 1\text{ mol} \times S°(H_2O(l))$$
$$= (1\text{ mol})188.8\text{ J/mol·K} - (1\text{ mol})70.0\text{ J/mol K} = 118.8\text{ J/mol·K}$$

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

Substitution into the standard free energy equation yields:

$$\Delta G° = \Delta H° - T\Delta S°$$
$$= 45.01\text{ kJ} - (298\text{ K} \times 118.8\text{ J/K}) \times \frac{1\text{ kJ}}{1000\text{ J}}$$

$$45.01\text{ kJ} - 35.4\text{ kJ} = 9.6\text{ kJ}$$

At 298 K (25 °C) $\Delta G° > 0,$ so boiling is nonspontaneous (*not* spontaneous).

Check Your Learning

Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for $\Delta G°$ say about the spontaneity of this process?

$$C_2H_6(g) \longrightarrow H_2(g) + C_2H_4(g)$$

Answer: $\Delta G° = 102.0\text{ kJ/mol};$ the reaction is nonspontaneous (*not* spontaneous) at 25 °C.

The standard free energy change for a reaction may also be calculated from **standard free energy of formation $\Delta G°_f$** values of the reactants and products involved in the reaction. The standard free energy of formation is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpy of formation, ΔG_f° is by definition zero for elemental substances under standard state conditions. The approach used to calculate $\Delta G°$ for a reaction from ΔG_f° values is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction

$$m\text{A} + n\text{B} \longrightarrow x\text{C} + y\text{D},$$

the standard free energy change at room temperature may be calculated as

$$\begin{aligned}\Delta G^\circ &= \sum \nu\,\Delta G^\circ(\text{products}) - \sum \nu\,\Delta G^\circ(\text{reactants})\\ &= \left[x\Delta G_\text{f}^\circ\ (\text{C}) + y\Delta G_\text{f}^\circ\ (\text{D})\right] - \left[m\Delta G_\text{f}^\circ\ (\text{A}) + n\Delta G_\text{f}^\circ\ (\text{B})\right].\end{aligned}$$

Example 12.8

Using Standard Free Energies of Formation to Calculate ΔG°

Consider the decomposition of yellow mercury(II) oxide.

$$\text{HgO}(s,\ \text{yellow}) \longrightarrow \text{Hg}(l) + \frac{1}{2}\text{O}_2(g)$$

Calculate the standard free energy change at room temperature, ΔG°, using (a) standard free energies of formation and (b) standard enthalpies of formation and standard entropies. Do the results indicate the reaction to be spontaneous or nonspontaneous under standard conditions?

Solution

The required data are available in **Appendix G** and are shown here.

Compound	ΔG_f° (kJ/mol)	ΔH_f° (kJ/mol)	S° (J/K·mol)
HgO (*s*, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
$O_2(g)$	0	0	205.2

(a) Using free energies of formation:

$$\begin{aligned}\Delta G^\circ &= \sum \nu GS_\text{f}^\circ\ (\text{products}) - \sum \nu\Delta G_\text{f}^\circ\ (\text{reactants})\\ &= \left[1\Delta G_\text{f}^\circ\ \text{Hg}(l) + \frac{1}{2}\Delta G_\text{f}^\circ\ \text{O}_2(g)\right] - 1\Delta G_\text{f}^\circ\ \text{HgO}(s,\ \text{yellow})\\ &= \left[1\ \text{mol}(0\ \text{kJ/mol}) + \frac{1}{2}\text{mol}(0\ \text{kJ/mol})\right] - 1\ \text{mol}(-58.43\ \text{kJ/mol}) = 58.43\ \text{kJ/mol}\end{aligned}$$

(b) Using enthalpies and entropies of formation:

$$\Delta H° = \sum \nu \Delta H_\text{f}^\circ \;\; \text{(products)} - \sum \nu \Delta H_\text{f}^\circ \;\; \text{(reactants)}$$
$$= \left[1\Delta H_\text{f}^\circ \;\; \text{Hg}(l) + \tfrac{1}{2}\Delta H_\text{f}^\circ \;\; \text{O}_2(g)\right] - 1\Delta H_\text{f}^\circ \;\; \text{HgO}(s,\ \text{yellow})$$
$$= \left[1\ \text{mol}(0\ \text{kJ/mol}) + \tfrac{1}{2}\text{mol}(0\ \text{kJ/mol})\right] - 1\ \text{mol}(-90.46\ \text{kJ/mol}) = 90.46\ \text{kJ/mol}$$
$$\Delta S° = \sum \nu \Delta S°\text{(products)} - \sum \nu \Delta S°\text{(reactants)}$$
$$= \left[1\Delta S°\text{Hg}(l) + \tfrac{1}{2}\Delta S°\text{O}_2(g)\right] - 1\Delta S°\text{HgO}(s,\ \text{yellow})$$
$$= \left[1\ \text{mol}\ (75.9\ \text{J/mol K}) + \tfrac{1}{2}\text{mol}(205.2\ \text{J/mol K})\right] - 1\ \text{mol}(71.13\ \text{J/mol K}) = 107.4\ \text{J/mol K}$$
$$\Delta G° = \Delta H° - T\Delta S° = 90.46\ \text{kJ} - 298.15\ \text{K} \times 107.4\ \text{J/K·mol} \times \frac{1\ \text{kJ}}{1000\ \text{J}}$$
$$\Delta G° = (90.46 - 32.01)\ \text{kJ/mol} = 58.45\ \text{kJ/mol}$$

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is nonspontaneous (*not* spontaneous) at room temperature.

Check Your Learning

Calculate Δ*G*° using (a) free energies of formation and (b) enthalpies of formation and entropies (**Appendix G**). Do the results indicate the reaction to be spontaneous or nonspontaneous at 25 °C?

$$\text{C}_2\text{H}_4(g) \longrightarrow \text{H}_2(g) + \text{C}_2\text{H}_2(g)$$

Answer: 141.5 kJ/mol, nonspontaneous

Free Energy Changes for Coupled Reactions

The use of free energies of formation to compute free energy changes for reactions as described above is possible because ΔG is a state function, and the approach is analogous to the use of Hess' Law in computing enthalpy changes (see the chapter on thermochemistry). Consider the vaporization of water as an example:

$$\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$$

An equation representing this process may be derived by adding the formation reactions for the two phases of water (necessarily reversing the reaction for the liquid phase). The free energy change for the sum reaction is the sum of free energy changes for the two added reactions:

$$\begin{array}{ll}
\text{H}_2(g) + \tfrac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(g) & \Delta G_\text{f, gas}^\circ \\
\text{H}_2\text{O}(l) \rightarrow \text{H}_2(g) + \tfrac{1}{2}\text{O}_2(g) & -\Delta G_\text{f, liquid}^\circ \\
\hline
\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) & \Delta G = \Delta G_\text{f, gas}^\circ - \Delta G_\text{f, liquid}^\circ
\end{array}$$

This approach may also be used in cases where a nonspontaneous reaction is enabled by coupling it to a spontaneous reaction. For example, the production of elemental zinc from zinc sulfide is thermodynamically unfavorable, as indicated by a positive value for ΔG°:

$$\text{ZnS}(s) \rightarrow \text{Zn}(s) + \text{S}(s) \qquad \Delta G_1^\circ = 201.3\ \text{kJ}$$

The industrial process for production of zinc from sulfidic ores involves coupling this decomposition reaction to the thermodynamically favorable oxidation of sulfur:

$$\text{S}(s) + \text{O}_2(g) \rightarrow \text{SO}_2(g) \qquad \Delta G_2^\circ = -300.1\ \text{kJ}$$

The coupled reaction exhibits a negative free energy change and is spontaneous:

$$\text{ZnS}(s) + \text{O}_2(g) \rightarrow \text{Zn}(s) + \text{SO}(g) \qquad \Delta G° = 201.3\ \text{kJ} + -300.1\ \text{kJ} = -98.8\ \text{kJ}$$

This process is typically carried out at elevated temperatures, so this result obtained using standard free energy values is just an estimate. The gist of the calculation, however, holds true.

Example 12.9

Calculating Free Energy Change for a Coupled Reaction

Is a reaction coupling the decomposition of ZnS to the formation of H_2S expected to be spontaneous under standard conditions?

Solution

Following the approach outlined above and using free energy values from Appendix G:

$$\begin{array}{lll} \text{Decomposition of zinc sulfide:} & \mathrm{Zn}(s) \rightarrow \mathrm{Zn}(s) + \mathrm{S}(s) & \Delta G_1^\circ = 201.3\text{ kJ} \\ \text{Formation of hydrogen sulfide:} & \mathrm{S}(s) + \mathrm{H}_2(g) \rightarrow \mathrm{H}_2\mathrm{S}(g) & \Delta G_2^\circ = -33.4\text{ kJ} \\ \text{Coupled reaction:} & \mathrm{ZnS}(s) + \mathrm{H}_2(g) \rightarrow \mathrm{Zn}(s) + \mathrm{H}_2\mathrm{S}(g) & \Delta G^\circ = 201.3\text{ kJ} + -33.4\text{ kJ} = 167.9\text{ kJ} \end{array}$$

The coupled reaction exhibits a positive free energy change and is thus nonspontaneous.

Check Your Learning

What is the standard free energy change for the reaction below? Is the reaction expected to be spontaneous under standard conditions?

$$\mathrm{FeS}(s) + \mathrm{O}_2(g) \rightarrow \mathrm{Fe}(s) + \mathrm{SO}_2(g)$$

Answer: –199.7 kJ; spontaneous

Key Terms

entropy (S) state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates; often described as a measure of the disorder of the system

Gibbs free energy change (G) thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in G

microstate possible configuration or arrangement of matter and energy within a system

nonspontaneous process process that requires continual input of energy from an external source

reversible process process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes

second law of thermodynamics all spontaneous processes involve an increase in the entropy of the universe

spontaneous change process that takes place without a continuous input of energy from an external source

standard entropy ($S°$) entropy for one mole of a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K

standard entropy change ($\Delta S°$) change in entropy for a reaction calculated using the standard entropies

standard free energy change ($\Delta G°$) change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

standard free energy of formation (ΔG_f°) change in free energy accompanying the formation of one mole of substance from its elements in their standard states

third law of thermodynamics entropy of a perfect crystal at absolute zero (0 K) is zero

Key Equations

- $\Delta S = \frac{q_\text{rev}}{T}$
- $S = k \ln W$
- $\Delta S = k \ln \frac{W_\text{f}}{W_\text{i}}$
- $\Delta S° = \sum \nu S°(\text{products}) - \sum \nu S°(\text{reactants})$
- $\Delta S = \frac{q_\text{rev}}{T}$
- $\Delta S_\text{univ} = \Delta S_\text{sys} + \Delta S_\text{surr}$
- $\Delta S_\text{univ} = \Delta S_\text{sys} + \Delta S_\text{surr} = \Delta S_\text{sys} + \frac{q_\text{surr}}{T}$
- $\Delta G = \Delta H - T\Delta S$
- $\Delta G = \Delta G° + RT \ln Q$
- $\Delta G° = -RT \ln K$

Summary

12.1 Spontaneity

Chemical and physical processes have a natural tendency to occur in one direction under certain conditions. A spontaneous process occurs without the need for a continual input of energy from some external source, while a nonspontaneous process requires such. Systems undergoing a spontaneous process may or may not experience a gain or loss of energy, but they will experience a change in the way matter and/or energy is distributed within the system.

12.2 Entropy

Entropy (S) is a state function that can be related to the number of microstates for a system (the number of ways the system can be arranged) and to the ratio of reversible heat to kelvin temperature. It may be interpreted as a measure of the dispersal or distribution of matter and/or energy in a system, and it is often described as representing the “disorder” of the system.

For a given substance, entropy depends on phase with $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$. For different substances in the same physical state at a given temperature, entropy is typically greater for heavier atoms or more complex molecules. Entropy increases when a system is heated and when solutions form. Using these guidelines, the sign of entropy changes for some chemical reactions and physical changes may be reliably predicted.

12.3 The Second and Third Laws of Thermodynamics

The second law of thermodynamics states that a spontaneous process increases the entropy of the universe, $S_{\text{univ}} > 0$. If $\Delta S_{\text{univ}} < 0$, the process is nonspontaneous, and if $\Delta S_{\text{univ}} = 0$, the system is at equilibrium. The third law of thermodynamics establishes the zero for entropy as that of a perfect, pure crystalline solid at 0 K. With only one possible microstate, the entropy is zero. We may compute the standard entropy change for a process by using standard entropy values for the reactants and products involved in the process.

12.4 Free Energy

Gibbs free energy (G) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A number of approaches to the computation of free energy changes are possible.

Exercises

12.1 Spontaneity

1. What is a spontaneous reaction?

2. What is a nonspontaneous reaction?

3. Indicate whether the following processes are spontaneous or nonspontaneous.

(a) Liquid water freezing at a temperature below its freezing point

(b) Liquid water freezing at a temperature above its freezing point

(c) The combustion of gasoline

(d) A ball thrown into the air

(e) A raindrop falling to the ground

(f) Iron rusting in a moist atmosphere

4. A helium-filled balloon spontaneously deflates overnight as He atoms diffuse through the wall of the balloon. Describe the redistribution of matter and/or energy that accompanies this process.

5. Many plastic materials are organic polymers that contain carbon and hydrogen. The oxidation of these plastics in air to form carbon dioxide and water is a spontaneous process; however, plastic materials tend to persist in the environment. Explain.

12.2 Entropy

6. In **Figure 12.8** all possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS, if the particles are initially evenly distributed between the two boxes, but upon redistribution all end up in Box (b).

7. In **Figure 12.8** all of the possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS, for the system when it is converted from distribution (b) to distribution (d).

8. How does the process described in the previous item relate to the system shown in **Figure 12.4**?

9. Consider a system similar to the one in **Figure 12.8**, except that it contains six particles instead of four. What is the probability of having all the particles in only one of the two boxes in the case? Compare this with the similar probability for the system of four particles that we have derived to be equal to $\frac{1}{8}$. What does this comparison tell us about even larger systems?

10. Consider the system shown in **Figure 12.9**. What is the change in entropy for the process where the energy is initially associated only with particle A, but in the final state the energy is distributed between two different particles?

11. Consider the system shown in **Figure 12.9**. What is the change in entropy for the process where the energy is initially associated with particles A and B, and the energy is distributed between two particles in different boxes (one in A-B, the other in C-D)?

12. Arrange the following sets of systems in order of increasing entropy. Assume one mole of each substance and the same temperature for each member of a set.

(a) $H_2(g)$, $HBrO_4(g)$, $HBr(g)$

(b) $H_2O(l)$, $H_2O(g)$, $H_2O(s)$

(c) $He(g)$, $Cl_2(g)$, $P_4(g)$

13. At room temperature, the entropy of the halogens increases from I_2 to Br_2 to Cl_2. Explain.

14. Consider two processes: sublimation of $I_2(s)$ and melting of $I_2(s)$ (Note: the latter process can occur at the same temperature but somewhat higher pressure).

$$I_2(s) \longrightarrow I_2(g)$$

$$I_2(s) \longrightarrow I_2(l)$$

Is ΔS positive or negative in these processes? In which of the processes will the magnitude of the entropy change be greater?

15. Indicate which substance in the given pairs has the higher entropy value. Explain your choices.

(a) $C_2H_5OH(l)$ or $C_3H_7OH(l)$

(b) $C_2H_5OH(l)$ or $C_2H_5OH(g)$

(c) $2H(g)$ or $H(g)$

16. Predict the sign of the entropy change for the following processes.

(a) An ice cube is warmed to near its melting point.

(b) Exhaled breath forms fog on a cold morning.

(c) Snow melts.

17. Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

(a) $\mathrm{Pb}^{2+}(aq) + \mathrm{S}^{2-}(aq) \longrightarrow \mathrm{PbS}(s)$

(b) $2\mathrm{Fe}(s) + \frac{3}{2}\mathrm{O}_2(g) \longrightarrow \mathrm{Fe}_2\mathrm{O}_2(s)$

(c) $2\mathrm{C}_6\mathrm{H}_{14}(l) + 19\mathrm{O}_2(g) \longrightarrow 14\mathrm{H}_2\mathrm{O}(g) + 12\mathrm{CO}_2(g)$

18. Write the balanced chemical equation for the combustion of methane, $\mathrm{CH}_4(g)$, to give carbon dioxide and water vapor. Explain why it is difficult to predict whether ΔS is positive or negative for this chemical reaction.

19. Write the balanced chemical equation for the combustion of benzene, $\mathrm{C}_6\mathrm{H}_6(l)$, to give carbon dioxide and water vapor. Would you expect ΔS to be positive or negative in this process?

12.3 The Second and Third Laws of Thermodynamics

20. What is the difference between ΔS and $\Delta S°$ for a chemical change?

21. Calculate $\Delta S°$ for the following changes.

(a) $\mathrm{SnCl}_4(l) \longrightarrow \mathrm{SnCl}_4(g)$

(b) $\mathrm{CS}_2(g) \longrightarrow \mathrm{CS}_2(l)$

(c) $\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}(g)$

(d) $\mathrm{H}_2\mathrm{O}(l) \longrightarrow \mathrm{H}_2\mathrm{O}(g)$

(e) $2\mathrm{H}_2(g) + \mathrm{O}_2(g) \longrightarrow 2\mathrm{H}_2\mathrm{O}(l)$

(f) $2\mathrm{HCl}(g) + \mathrm{Pb}(s) \longrightarrow \mathrm{PbCl}_2(s) + \mathrm{H}_2(g)$

(g) $\mathrm{Zn}(s) + \mathrm{CuSO}_4(s) \longrightarrow \mathrm{Cu}(s) + \mathrm{ZnSO}_4(s)$

22. Determine the entropy change for the combustion of liquid ethanol, $\mathrm{C}_2\mathrm{H}_5\mathrm{OH}$, under the standard conditions to give gaseous carbon dioxide and liquid water.

23. Determine the entropy change for the combustion of gaseous propane, $\mathrm{C}_3\mathrm{H}_8$, under the standard conditions to give gaseous carbon dioxide and water.

24. "Thermite" reactions have been used for welding metal parts such as railway rails and in metal refining. One such thermite reaction is $\mathrm{Fe}_2\mathrm{O}_3(s) + 2\mathrm{Al}(s) \longrightarrow \mathrm{Al}_2\mathrm{O}_3(s) + 2\mathrm{Fe}(s).$ Is the reaction spontaneous at room temperature under standard conditions? During the reaction, the surroundings absorb 851.8 kJ/mol of heat.

25. Using the relevant $S°$ values listed in **Appendix G**, calculate $\Delta S°$ for the following changes:

(a) $\mathrm{N}_2(g) + 3\mathrm{H}_2(g) \longrightarrow 2\mathrm{NH}_3(g)$

(b) $\mathrm{N}_2(g) + \frac{5}{2}\mathrm{O}_2(g) \longrightarrow \mathrm{N}_2\mathrm{O}_5(g)$

26. From the following information, determine $\Delta S°$ for the following:

$\mathrm{N}(g) + \mathrm{O}(g) \longrightarrow \mathrm{NO}(g) \qquad \Delta S° = ?$

$\mathrm{N}_2(g) + \mathrm{O}_2(g) \longrightarrow 2\mathrm{NO}(g) \qquad \Delta S° = 24.8\ \mathrm{J/K}$

$\mathrm{N}_2(g) \longrightarrow 2\mathrm{N}(g) \qquad \Delta S° = 115.0\ \mathrm{J/K}$

$\mathrm{O}_2(g) \longrightarrow 2\mathrm{O}(g) \qquad \Delta S° = 117.0\ \mathrm{J/K}$

27. By calculating ΔS_{univ} at each temperature, determine if the melting of 1 mole of NaCl(*s*) is spontaneous at 500 °C and at 700 °C.

$$S°_{\mathrm{NaCl}(s)} = 72.11\frac{\mathrm{J}}{\mathrm{mol{\cdot}K}} \qquad S°_{\mathrm{NaCl}(l)} = 95.06\frac{\mathrm{J}}{\mathrm{mol{\cdot}K}} \qquad \Delta H°_{\text{fusion}} = 27.95\ \mathrm{kJ/mol}$$

What assumptions are made about the thermodynamic information (entropy and enthalpy values) used to solve this problem?

28. Use the standard entropy data in **Appendix G** to determine the change in entropy for each of the following reactions. All the processes occur at the standard conditions and 25 °C.

(a) $MnO_2(s) \longrightarrow Mn(s) + O_2(g)$

(b) $H_2(g) + Br_2(l) \longrightarrow 2HBr(g)$

(c) $Cu(s) + S(g) \longrightarrow CuS(s)$

(d) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$

(e) $CH_4(g) + O_2(g) \longrightarrow C(s,\ \text{graphite}) + 2H_2O(g)$

(f) $CS_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g)$

29. Use the standard entropy data in **Appendix G** to determine the change in entropy for each of the reactions listed in **Exercise 12.28**. All the processes occur at the standard conditions and 25 °C.

12.4 Free Energy

30. What is the difference between ΔG and $\Delta G°$ for a chemical change?

31. A reaction has $\Delta H°$ = 100 kJ/mol and $\Delta S° = 250$ J/mol·K. Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

32. Explain what happens as a reaction starts with $\Delta G < 0$ (negative) and reaches the point where $\Delta G = 0$.

33. Use the standard free energy of formation data in **Appendix G** to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

(a) $MnO_2(s) \longrightarrow Mn(s) + O_2(g)$

(b) $H_2(g) + Br_2(l) \longrightarrow 2HBr(g)$

(c) $Cu(s) + S(g) \longrightarrow CuS(s)$

(d) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$

(e) $CH_4(g) + O_2(g) \longrightarrow C(s,\ \text{graphite}) + 2H_2O(g)$

(f) $CS_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g)$

34. Use the standard free energy data in **Appendix G** to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

(a) $C(s,\ \text{graphite}) + O_2(g) \longrightarrow CO_2(g)$

(b) $O_2(g) + N_2(g) \longrightarrow 2NO(g)$

(c) $2Cu(s) + S(g) \longrightarrow Cu_2S(s)$

(d) $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$

(e) $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$

(f) $CaSO_4{\cdot}2H_2O(s) \longrightarrow CaSO_4(s) + 2H_2O(g)$

35. Given:

$$\begin{array}{ll} P_4(s) + 5O_2(g) \longrightarrow P_4O_{10}(s) & \Delta G° = -2697.0\ \text{kJ/mol} \\ 2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) & \Delta G° = -457.18\ \text{kJ/mol} \\ 6H_2O(g) + P_4O_{10}(s) \longrightarrow 4H_3PO_4(l) & \Delta G° = -428.66\ \text{kJ/mol} \end{array}$$

(a) Determine the standard free energy of formation, $\Delta G_f°$, for phosphoric acid.

(b) How does your calculated result compare to the value in **Appendix G**? Explain.

36. Is the formation of ozone ($O_3(g)$) from oxygen ($O_2(g)$) spontaneous at room temperature under standard state conditions?

37. Consider the decomposition of red mercury(II) oxide under standard state conditions.

$2HgO(s,\ \text{red}) \longrightarrow 2Hg(l) + O_2(g)$

(a) Is the decomposition spontaneous under standard state conditions?

(b) Above what temperature does the reaction become spontaneous?

38. Among other things, an ideal fuel for the control thrusters of a space vehicle should decompose in a spontaneous exothermic reaction when exposed to the appropriate catalyst. Evaluate the following substances under standard state conditions as suitable candidates for fuels.

(a) Ammonia: $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$

(b) Diborane: $B_2H_6(g) \longrightarrow 2B(g) + 3H_2(g)$

(c) Hydrazine: $N_2H_4(g) \longrightarrow N_2(g) + 2H_2(g)$

(d) Hydrogen peroxide: $H_2O_2(l) \longrightarrow H_2O(g) + \frac{1}{2}O_2(g)$

39. Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

(a) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$	T = 2000 °C	$K_p = 4.1 \times 10^{-4}$
(b) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$	T = 400 °C	$K_p = 50.0$
(c) $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$	T = 980 °C	$K_p = 1.67$
(d) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$	T = 900 °C	$K_p = 1.04$
(e) $HF(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + F^-(aq)$	T = 25 °C	$K_p = 7.2 \times 10^{-4}$
(f) $AgBr(s) \longrightarrow Ag^+(aq) + Br^-(aq)$	T = 25 °C	$K_p = 3.3 \times 10^{-13}$

40. Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

(a) $Cl_2(g) + Br_2(g) \longrightarrow 2BrCl(g)$	T = 25 °C	$K_p = 4.7 \times 10^{-2}$
(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	T = 500 °C	$K_p = 48.2$
(c) $H_2O(l) \rightleftharpoons H_2O(g)$	T = 60 °C	$K_p = 0.196$ atm
(d) $CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)$	T = 550 °C	$K_p = 4.90 \times 10^2$
(e) $CH_3NH_2(aq) + H_2O(l) \longrightarrow CH_3NH_3{}^+(aq) + OH^-(aq)$	T = 25 °C	$K_p = 4.4 \times 10^{-4}$
(f) $PbI_2(s) \longrightarrow Pb^{2+}(aq) + 2I^-(aq)$	T = 25 °C	$K_p = 8.7 \times 10^{-9}$

41. Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

(a) $O_2(g) + 2F_2(g) \longrightarrow 2OF_2(g)$	$\Delta G° = -9.2$ kJ
(b) $I_2(s) + Br_2(l) \longrightarrow 2IBr(g)$	$\Delta G° = 7.3$ kJ
(c) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$	$\Delta G° = -79$ kJ
(d) $N_2O_3(g) \longrightarrow NO(g) + NO_2(g)$	$\Delta G° = -1.6$ kJ
(e) $SnCl_4(l) \longrightarrow SnCl_4(l)$	$\Delta G° = 8.0$ kJ

42. Determine $\Delta G°$ for the following reactions.

(a) Antimony pentachloride decomposes at 448 °C. The reaction is:

$SbCl_5(g) \longrightarrow SbCl_3(g) + Cl_2(g)$

An equilibrium mixture in a 5.00 L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2.

(b) Chlorine molecules dissociate according to this reaction:

$Cl_2(g) \longrightarrow 2Cl(g)$

1.00% of Cl_2 molecules dissociate at 975 K and a pressure of 1.00 atm.

43. Given that the ΔG_f° for $Pb^{2+}(aq)$ and $Cl^{-}(aq)$ is −24.3 kJ/mole and −131.2 kJ/mole respectively, determine the solubility product, K_{sp}, for $PbCl_2(s)$.

44. Determine the standard free energy change, ΔG_f° , for the formation of $S^{2-}(aq)$ given that the ΔG_f° for $Ag^{+}(aq)$ and $Ag_2S(s)$ are 77.1 k/mole and −39.5 kJ/mole respectively, and the solubility product for $Ag_2S(s)$ is 8×10^{-51}.

45. Determine the standard enthalpy change, entropy change, and free energy change for the conversion of diamond to graphite. Discuss the spontaneity of the conversion with respect to the enthalpy and entropy changes. Explain why diamond spontaneously changing into graphite is not observed.

46. The evaporation of one mole of water at 298 K has a standard free energy change of 8.58 kJ.

$H_2O(l) \rightleftharpoons H_2O(g) \qquad \Delta G° = 8.58\ \text{kJ}$

(a) Is the evaporation of water under standard thermodynamic conditions spontaneous?

(b) Determine the equilibrium constant, K_P, for this physical process.

(c) By calculating ΔG, determine if the evaporation of water at 298 K is spontaneous when the partial pressure of water, P_{H_2O}, is 0.011 atm.

(d) If the evaporation of water were always nonspontaneous at room temperature, wet laundry would never dry when placed outside. In order for laundry to dry, what must be the value of P_{H_2O} in the air?

47. In glycolysis, the reaction of glucose (Glu) to form glucose-6-phosphate (G6P) requires ATP to be present as described by the following equation:

$\text{Glu} + \text{ATP} \longrightarrow \text{G6P} + \text{ADP} \qquad \Delta G° = -17\ \text{kJ}$

In this process, ATP becomes ADP summarized by the following equation:

$\text{ATP} \longrightarrow \text{ADP} \qquad \Delta G° = -30\ \text{kJ}$

Determine the standard free energy change for the following reaction, and explain why ATP is necessary to drive this process:

$\text{Glu} \longrightarrow \text{G6P} \qquad \Delta G° = \ ?$

48. One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):

$\text{G6P} \rightleftharpoons \text{F6P} \qquad \Delta G° = 1.7\ \text{kJ}$

(a) Is the reaction spontaneous or nonspontaneous under standard thermodynamic conditions?

(b) Standard thermodynamic conditions imply the concentrations of G6P and F6P to be 1 *M*, however, in a typical cell, they are not even close to these values. Calculate ΔG when the concentrations of G6P and F6P are 120 μ*M* and 28 μ*M* respectively, and discuss the spontaneity of the forward reaction under these conditions. Assume the temperature is 37 °C.

49. Without doing a numerical calculation, determine which of the following will reduce the free energy change for the reaction, that is, make it less positive or more negative, when the temperature is increased. Explain.

(a) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

(b) $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$

(c) $(NH_4)_2Cr_2O_7(s) \longrightarrow Cr_2O_3(s) + 4H_2O(g) + N_2(g)$

(d) $2Fe(s) + 3O_2(g) \longrightarrow Fe_2O_3(s)$

50. When ammonium chloride is added to water and stirred, it dissolves spontaneously and the resulting solution feels cold. Without doing any calculations, deduce the signs of ΔG, ΔH, and ΔS for this process, and justify your choices.

51. An important source of copper is from the copper ore, chalcocite, a form of copper(I) sulfide. When heated, the Cu_2S decomposes to form copper and sulfur described by the following equation:
$Cu_2S(s) \longrightarrow Cu(s) + S(s)$

(a) Determine $\Delta G°$ for the decomposition of $Cu_2S(s)$.

(b) The reaction of sulfur with oxygen yields sulfur dioxide as the only product. Write an equation that describes this reaction, and determine $\Delta G°$ for the process.

(c) The production of copper from chalcocite is performed by roasting the Cu_2S in air to produce the Cu. By combining the equations from Parts (a) and (b), write the equation that describes the roasting of the chalcocite, and explain why coupling these reactions together makes for a more efficient process for the production of the copper.

52. What happens to $\Delta G°$ (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?

(a) $S(s) + O_2(g) \longrightarrow SO_2(g)$

(b) $2SO_2(g) + O_2(g) \longrightarrow SO_3(g)$

(c) $HgO(s) \longrightarrow Hg(l) + O_2(g)$

Chapter 13

Fundamental Equilibrium Concepts

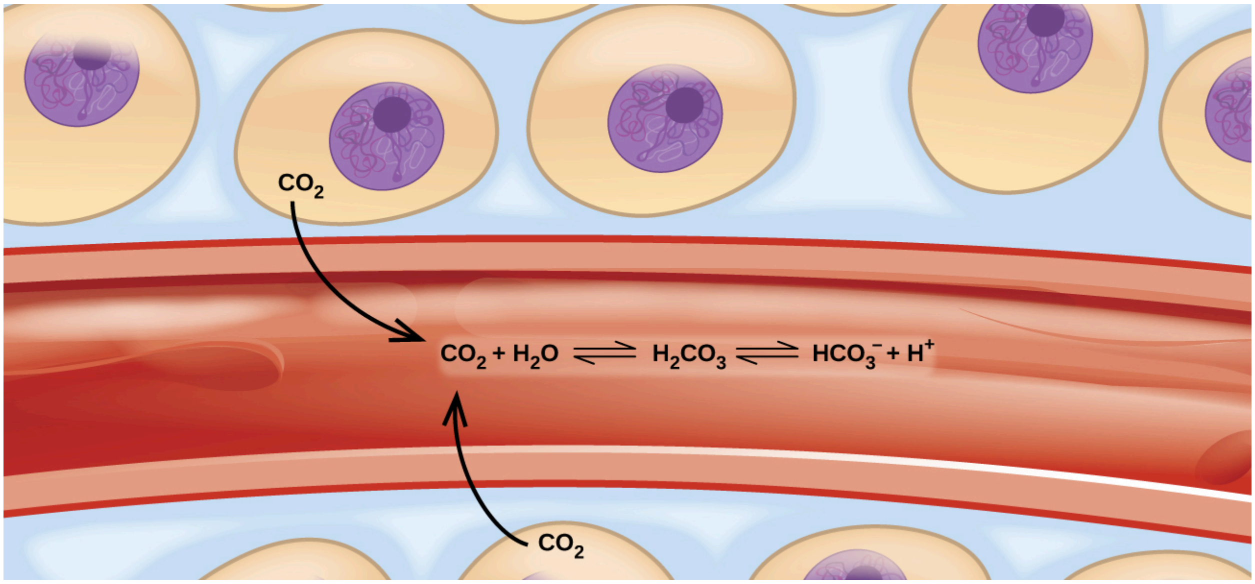


Figure 13.1 Transport of carbon dioxide in the body involves several reversible chemical reactions, including hydrolysis and acid ionization (among others).

Chapter Outline

Introduction

Imagine a beach populated with sunbathers and swimmers. As those basking in the sun get too hot, they enter the surf to swim and cool off. As the swimmers tire, they return to the beach to rest. If the rate at which sunbathers enter the surf were to equal the rate at which swimmers return to the sand, then the numbers (though not the identities) of sunbathers and swimmers would remain constant. This scenario illustrates a dynamic phenomenon known as *equilibrium*, in which opposing processes occur at equal rates. Chemical and physical processes are subject to this phenomenon; these processes are at equilibrium when the forward and reverse reaction rates are equal. Equilibrium systems are pervasive in nature; the various reactions involving carbon dioxide dissolved in blood are examples (see **Figure 13.1**). This chapter provides a thorough introduction to the essential aspects of chemical equilibria.

We now have a good understanding of chemical and physical change that allow us to determine, for any given process:

1. Whether the process is endothermic or exothermic
2. Whether the process is accompanied by an increase of decrease in entropy
3. Whether a process will be spontaneous, non-spontaneous, or what we have called an equilibrium process

Recall that when the value ΔG for a reaction is zero, we consider there to be no free energy change—that is, no free energy available to do useful work. Does this mean a reaction where $\Delta G = 0$ comes to a complete halt? No, it does not. Just as a liquid exists in equilibrium with its vapor in a closed container, where the rates of evaporation and condensation are equal, there is a connection to the state of equilibrium for a phase change or a chemical reaction. That is, at equilibrium, the forward and reverse rates of reaction are equal. We will develop that concept and extend it to a relationship between equilibrium and free energy later in this chapter.

In the explanation that follows, we will use the term Q to refer to any reactant or product concentration or pressure. When the concentrations or pressure of reactants and products are at equilibrium, the term K will be used. This will be more clearly explained as we go along in this chapter.

Now we will consider the connection between the free energy change and the equilibrium constant. The fundamental relationship is:
$\Delta G° = -\text{R}T\ln K$—this can be for K_c or K_p (and we will see later, any equilibrium constant we encounter).

We also know that the form of K can be used in non-equilibrium conditions as the reaction quotient, Q. The defining relationship here is

$$\Delta G = \Delta G° + RT\ln Q$$

Without the superscript, the value of ΔG can be calculated for any set of concentrations.

Note that since Q is a mass-action reaction of productions/reactants, as a reaction proceeds from left to right, product concentrations increase as reactant concentrations decrease, until $Q = K$, and at which time ΔG becomes zero:
$0 = \Delta G° + RT\ln K$, a relationship that reduces to our defining connection between Q and K.

Thus, we can see clearly that as a reaction moves toward equilibrium, the value of ΔG goes to zero.

Now, think back to the connection between the signs of $\Delta G°$ and $\Delta H°$

$\Delta H°$	$\Delta S°$	Result
Negative	Positive	Always spontaneous
Positive	Negative	Never spontaneous
Positive	Positive	Spontaneous at high temperatures
Negative	Negative	Spontaneous at low temperatures

Only in the last two cases is there a point at which the process swings from spontaneous to non-spontaneous (or the reverse); in these cases, the process must pass through equilibrium when the change occurs. The concept of the connection between the free energy change and the equilibrium constant is an important one that we will expand upon in future sections. The fact that the change in free energy for an equilibrium process is zero, and that displacement of a process from that zero point results in a drive to re-establish equilibrium is fundamental to understanding the behavior of chemical reactions and phase changes.

13.1 Chemical Equilibria

By the end of this section, you will be able to:

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium

The convention for writing chemical equations involves placing reactant formulas on the left side of a reaction arrow and product formulas on the right side. By this convention, and the definitions of “reactant” and “product,” a chemical equation represents the reaction in question as proceeding from left to right. **Reversible reactions**, however, may proceed in both forward (left to right) and reverse (right to left) directions. When the rates of the forward and reverse reactions are equal, the concentrations of the reactant and product species remain constant over time and the system is at **equilibrium**. The relative concentrations of reactants and products in equilibrium systems vary greatly;

some systems contain mostly products at equilibrium, some contain mostly reactants, and some contain appreciable amounts of both.

Figure 13.2 illustrates fundamental equilibrium concepts using the reversible decomposition of colorless dinitrogen tetroxide to yield brown nitrogen dioxide, an elementary reaction described by the equation:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Note that a special double arrow is used to emphasize the reversible nature of the reaction.

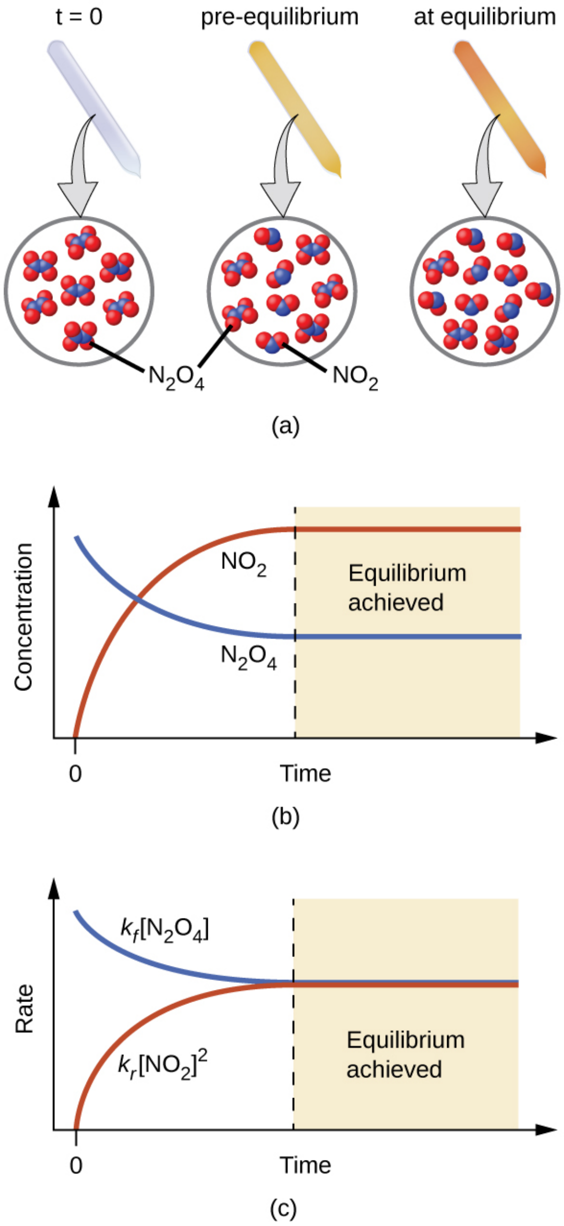


Figure 13.2 (a) A sealed tube containing colorless N_2O_4 darkens as it decomposes to yield brown NO_2. (b) Changes in concentration over time as the decomposition reaction achieves equilibrium. (c) At equilibrium, the forward and reverse reaction rates are equal.

For this elementary process, rate laws for the forward and reverse reactions may be derived directly from the reaction stoichiometry:

$$\text{rate}_f = k_f[\text{N}_{-2}\text{O}_4]$$
$$\text{rate}_r = k_r[\text{NO}_2]^2$$

As the reaction begins ($t = 0$), the concentration of the N_2O_4 reactant is finite and that of the NO_2 product is zero, so the forward reaction proceeds at a finite rate while the reverse reaction rate is zero. As time passes, N_2O_4 is consumed and its concentration falls, while NO_2 is produced and its concentration increases (**Figure 13.2b**). The decreasing concentration of the reactant slows the forward reaction rate, and the increasing product concentration speeds the reverse reaction rate (**Figure 13.2c**). This process continues until *the forward and reverse reaction rates become equal*, at which time the reaction has reached equilibrium, as characterized by constant concentrations of its reactants and products (shaded areas of **Figure 13.2b** and **Figure 13.2c**). It's important to emphasize that chemical equilibria are dynamic; a reaction at equilibrium has not "stopped," but is proceeding in the forward and reverse directions at the same rate. This dynamic nature is essential to understanding equilibrium behavior as discussed in this and subsequent chapters of the text.

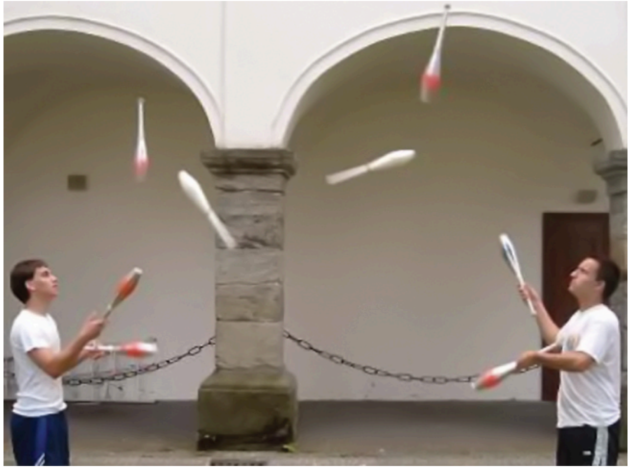


Figure 13.3 A two-person juggling act illustrates the dynamic aspect of chemical equilibria. Each person is throwing and catching clubs at the same rate, and each holds a (approximately) constant number of clubs.

Physical changes, such as phase transitions, are also reversible and may establish equilibria. This concept was introduced in another chapter of this text through discussion of the vapor pressure of a condensed phase (liquid or solid). As one example, consider the vaporization of bromine:

$$\text{Br}_2(l) \rightleftharpoons \text{Br}_2(g)$$

When liquid bromine is added to an otherwise empty container and the container is sealed, the forward process depicted above (vaporization) will commence and continue at a roughly constant rate as long as the exposed surface area of the liquid and its temperature remain constant. As increasing amounts of gaseous bromine are produced, the rate of the reverse process (condensation) will increase until it equals the rate of vaporization and equilibrium is established. A photograph showing this phase transition equilibrium is provided in **Figure 13.4**.

Figure 13.4 A sealed tube containing an equilibrium mixture of liquid and gaseous bromine. (credit: http://images-of-elements.com/bromine.php)

13.2 Equilibrium Constants

The status of a reversible reaction is conveniently assessed by evaluating its **reaction quotient (*Q*)**. For a reversible reaction described by

$$mA + nB \rightleftharpoons xC + yD,$$

the reaction quotient is derived directly from the stoichiometry of the balanced equation as

$$Q_c = \frac{[C]^x[D]^y}{[A]^m[B]^n},$$

where the subscript *c* denotes the use of molar concentrations in the expression. If the reactants and products are gaseous, a reaction quotient may be similarly derived using partial pressures:

$$Q_p = \frac{P_{Cx}\,P_{Dy}}{P_{Am}\,P_{Bn}}$$

Note that the reaction quotient equations above are a simplification of more rigorous expressions that use *relative* values for concentrations and pressures rather than *absolute* values. These relative concentration and pressure values are dimensionless (they have no units); consequently, so are the reaction quotients. For purposes of this introductory text, it will suffice to use the simplified equations and to disregard units when computing Q. In most cases, this will introduce only modest errors in calculations involving reaction quotients.

Example 13.1

Writing Reaction Quotient Expressions

Write the concentration-based reaction quotient expression for each of the following reactions:

(a) $3O_2(g) \rightleftharpoons 2O_3(g)$

(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(c) $4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g)$

Solution

(a) $Q_c = \frac{[O_3]^2}{[O_2]^3}$

(b) $Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

(c) $Q_c = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$

Check Your Learning

Write the concentration-based reaction quotient expression for each of the following reactions:

(a) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(b) $C_4H_8(g) \rightleftharpoons 2C_2H_4(g)$

(c) $2C_4H_{10}(g) + 13O_2(g) \rightleftharpoons 8CO_2(g) + 10H_2O(g)$

Answer: (a) $Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$; (b) $Q_c = \frac{[C_2H_4]^2}{[C_4H_8]}$; (c) $Q_c = \frac{[CO_2]^8[H_2O]^{10}}{[C_4H_{10}]^2[O_2]^{13}}$

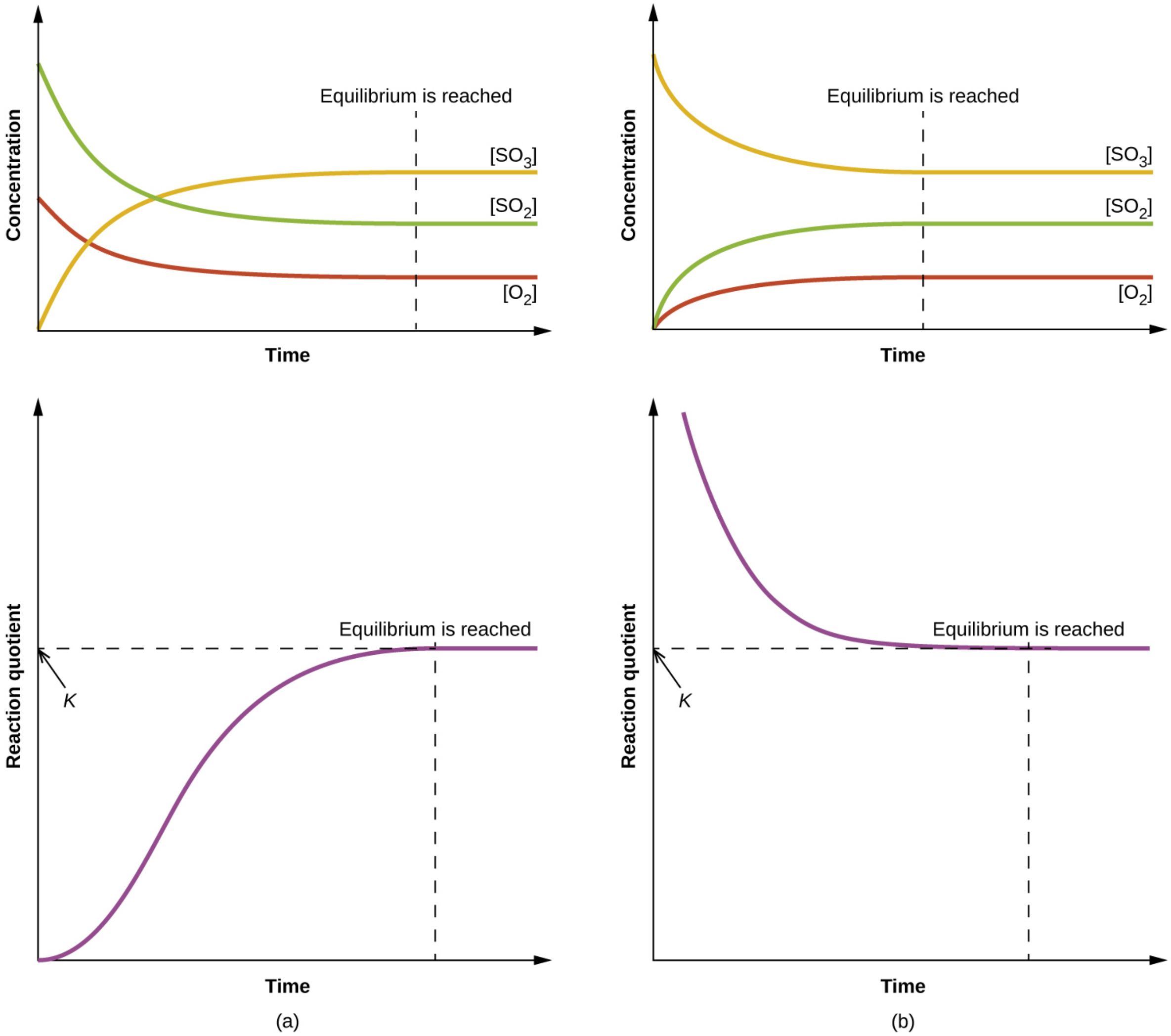


Figure 13.5 Changes in concentrations and Q_c for a chemical equilibrium achieved beginning with (a) a mixture of reactants only and (b) products only.

The numerical value of Q varies as a reaction proceeds towards equilibrium; therefore, it can serve as a useful indicator of the reaction's status. To illustrate this point, consider the oxidation of sulfur dioxide:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Two different experimental scenarios are depicted in **Figure 13.5**, one in which this reaction is initiated with a mixture of reactants only, SO_2 and O_2, and another that begins with only product, SO_3. For the reaction that begins with a mixture of reactants only, Q is initially equal to zero:

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2\ [O_2]} = \frac{0^2}{[SO_2]^2\ [O_2]} = 0$$

As the reaction proceeds toward equilibrium in the forward direction, reactant concentrations decrease (as does the denominator of Q_c), product concentration increases (as does the numerator of Q_c), and the reaction quotient consequently increases. When equilibrium is achieved, the concentrations of reactants and product remain constant, as does the value of Q_c.

If the reaction begins with only product present, the value of Q_c is initially undefined (immeasurably large, or infinite):

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} = \frac{[SO_3]^2}{0} \rightarrow \infty$$

In this case, the reaction proceeds toward equilibrium in the reverse direction. The product concentration and the numerator of Q_c decrease with time, the reactant concentrations and the denominator of Q_c increase, and the reaction quotient consequently decreases until it becomes constant at equilibrium.

The constant value of Q exhibited by a system at equilibrium is called the **equilibrium constant, *K***:

$$K \equiv Q \text{ at equilibrium}$$

Comparison of the data plots in **Figure 13.5** shows that both experimental scenarios resulted in the same value for the equilibrium constant. This is a general observation for all equilibrium systems, known as the **law of mass action**: At a given temperature, the reaction quotient for a system at equilibrium is constant.

Example 13.2

Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

When 0.10 mol NO_2 is added to a 1.0-L flask at 25 °C, the concentration changes so that at equilibrium, $[NO_2] = 0.016\ M$ and $[N_2O_4] = 0.042\ M$.

(a) What is the value of the reaction quotient before any reaction occurs?

(b) What is the value of the equilibrium constant for the reaction?

Solution

As for all equilibrium calculations in this text, use the simplified equations for Q and K and disregard any concentration or pressure units, as noted previously in this section.

(a) Before any product is formed, $[NO_2] = \frac{0.10\text{ mol}}{1.0\text{ L}} = 0.10\ M$, and $[N_2O_4] = 0\ M$. Thus,

$$Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0}{0.10^2} = 0$$

(b) At equilibrium, $K_c = Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2.$ The equilibrium constant is 1.6×10^2.

Check Your Learning

For the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, the concentrations at equilibrium are $[SO_2] = 0.90\ M$, $[O_2] = 0.35\ M$, and $[SO_3] = 1.1\ M$. What is the value of the equilibrium constant, K_c?

Answer: $K_c = 4.3$

By its definition, the magnitude of an equilibrium constant explicitly reflects the composition of a reaction mixture at equilibrium, and it may be interpreted with regard to the extent of the forward reaction. A reaction exhibiting a large K will reach equilibrium when most of the reactant has been converted to product, whereas a small K indicates the reaction achieves equilibrium after very little reactant has been converted. It's important to keep in mind that the magnitude of K does *not* indicate how rapidly or slowly equilibrium will be reached. Some equilibria are established so quickly as to be nearly instantaneous, and others so slowly that no perceptible change is observed over the course of days, years, or longer.

The equilibrium constant for a reaction can be used to predict the behavior of mixtures containing its reactants and/or products. As demonstrated by the sulfur dioxide oxidation process described above, a chemical reaction will proceed in whatever direction is necessary to achieve equilibrium. Comparing Q to K for an equilibrium system of interest allows prediction of what reaction (forward or reverse), if any, will occur.

To further illustrate this important point, consider the reversible reaction shown below:

$$\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \qquad K_c = 0.640 \qquad \text{T} = 800\ °\text{C}$$

The bar charts in **Figure 13.6** represent changes in reactant and product concentrations for three different reaction mixtures. The reaction quotients for mixtures 1 and 3 are initially lesser than the reaction's equilibrium constant, so each of these mixtures will experience a net forward reaction to achieve equilibrium. The reaction quotient for mixture 2 is initially greater than the equilibrium constant, so this mixture will proceed in the reverse direction until equilibrium is established.

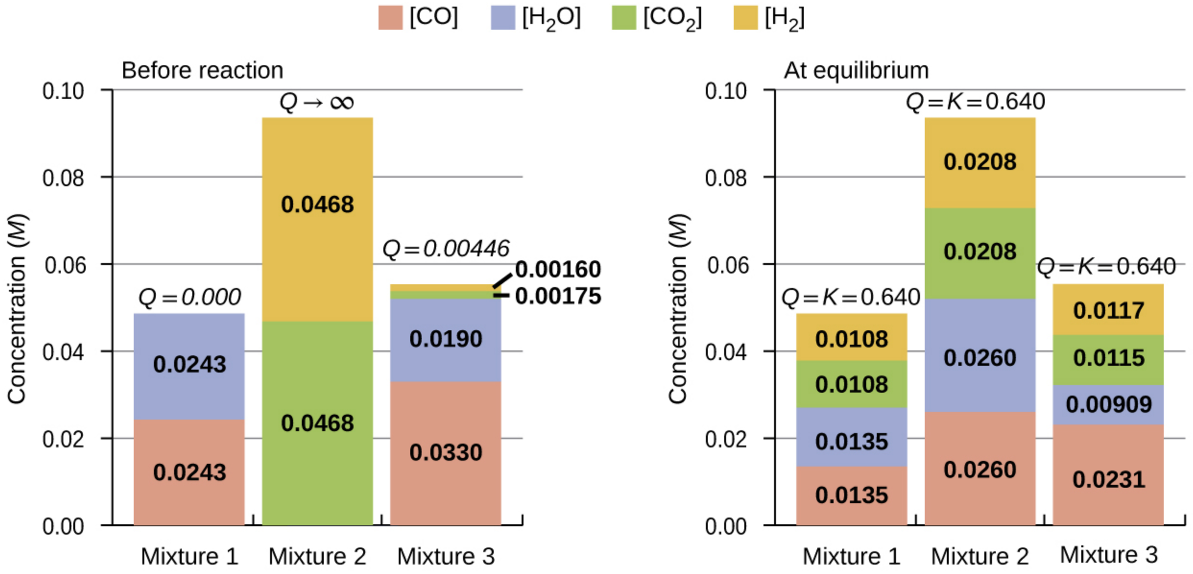


Figure 13.6 Compositions of three mixtures before ($Q_c \neq K_c$) and after ($Q_c = K_c$) equilibrium is established for the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$.

Example 13.3

Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$
$$K_c = 0.64$$

Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[CO]_i$	0.020 *M*	0.011 *M*	0.0094 *M*
$[H_2O]_i$	0.020 *M*	0.0011 *M*	0.0025 *M*
$[CO_2]_i$	0.0040 *M*	0.037 *M*	0.0015 *M*
$[H_2]_i$	0.0040 *M*	0.046 *M*	0.0076 *M*

Solution

Experiment 1:

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0040)(0.0040)}{(0.020)(0.020)} = 0.040.$$

$Q_c < K_c$ $(0.040 < 0.64)$

The reaction will proceed in the forward direction.

Experiment 2:

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will proceed in the reverse direction.

Experiment 3:

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will proceed in the forward direction.

Check Your Learning

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

(a) A 1.00-L flask containing 0.0500 mol of NO(g), 0.0155 mol of Cl2(g), and 0.500 mol of NOCl:

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) \qquad K_c = 4.6 \times 10^4$$

(b) A 5.0-L flask containing 17 g of NH_3, 14 g of N_2, and 12 g of H_2:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 0.060$$

(c) A 2.00-L flask containing 230 g of SO_3(g):

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \qquad K_c = 0.230$$

Answer: (a) $Q_c = 6.45 \times 10^3$, forward. (b) $Q_c = 0.23$, reverse. (c) $Q_c = 0$, forward.

Homogeneous Equilibria

A **homogeneous equilibrium** is one in which all reactants and products (and any catalysts, if applicable) are present in the same phase. By this definition, homogeneous equilibria take place in *solutions*. These solutions are most commonly either liquid or gaseous phases, as shown by the examples below:

$$C_2H_2(aq) + 2Br_2(aq) \rightleftharpoons C_2H_2Br_4(aq) \qquad K_c = \frac{[C_2H_2Br_4]}{[C_2H_2][Br_2]^2}$$

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3{}^-(aq) \qquad K_c = \frac{[I_3{}^-]}{[I_2][I^-]}$$

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \qquad K_c = \frac{[H_3O^+][F^-]}{[HF]}$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4{}^+(aq) + OH^-(aq) \qquad K_c = \frac{[NH_4{}^+][OH^-]}{[NH_3]}$$

These examples all involve aqueous solutions, those in which water functions as the solvent. In the last two examples, water also functions as a reactant, but its concentration is *not* included in the reaction quotient. The reason for this omission is related to the more rigorous form of the Q (or K) expression mentioned previously in this chapter, in which *relative concentrations for liquids and solids are equal to 1 and needn't be included*. Consequently, reaction quotients include concentration or pressure terms only for gaseous and solute species.

The equilibria below all involve gas-phase solutions:

$$\begin{aligned} C_2H_6(g) &\rightleftharpoons C_2H_4(g) + H_2(g) & K_c &= \frac{[C_2H_4][H_2]}{[C_2H_6]} \\ 3O_2(g) &\rightleftharpoons 2O_3(g) & K_c &= \frac{[O_3]^2}{[O_2]^3} \\ N_2(g) + 3H_2(g) &\rightleftharpoons 2NH_3(g) & K_c &= \frac{[NH_3]^2}{[N_2][H_2]^3} \\ C_3H_8(g) + 5O_2(g) &\rightleftharpoons 3CO_2(g) + 4H_2O(g) & K_c &= \frac{[CO_2]^3[H_2O]^4}{[C_3H_8][O_2]^5} \end{aligned}$$

For gas-phase solutions, the equilibrium constant may be expressed in terms of either the molar concentrations (K_c) or partial pressures (K_p) of the reactants and products. A relation between these two K values may be simply derived from the ideal gas equation and the definition of molarity:

$$\begin{aligned} PV &= nRT \\ P &= \left(\frac{n}{V}\right)RT \\ &= MRT \end{aligned}$$

where P is partial pressure, V is volume, n is molar amount, R is the gas constant, T is temperature, and M is molar concentration.

For the gas-phase reaction $m\text{A} + n\text{B} \rightleftharpoons x\text{C} + y\text{D}$:

$$\begin{aligned} K_P &= \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n} \\ &= \frac{([\text{C}] \times RT)^x ([\text{D}] \times RT)^y}{([\text{A}] \times RT)^m ([\text{B}] \times RT)^n} \\ &= \frac{[\text{C}]^x[\text{D}]^y}{[\text{A}]^m[\text{B}]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}} \\ &= K_c(RT)^{(x+y)-(m+n)} \\ &= K_c(RT)^{\Delta n} \end{aligned}$$

And so, the relationship between K_c and K_P is

$$K_P = K_c(RT)^{\Delta n}$$

where Δn is the difference in the molar amounts of product and reactant gases, in this case:

$$\Delta n = (x+y) - (m+n)$$

Example 13.4

Calculation of K_P

Write the equations relating K_c to K_P for each of the following reactions:

(a) $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$

(b) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(d) K_c is equal to 0.28 for the following reaction at 900 °C:

$$CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g)$$

What is K_P at this temperature?

Solution

(a) $\Delta n = (2) - (1) = 1$
$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^1 = K_c\,(RT)$

(b) $\Delta n = (2) - (2) = 0$
$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^0 = K_c$

(c) $\Delta n = (2) - (1 + 3) = -2$

$$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^{-2} = \frac{K_c}{(RT)^2}$$

(d) $K_P = K_c\,(\mathrm{RT})^{\Delta n} = (0.28)[(0.0821)(1173)]^{-2} = 3.0 \times 10^{-5}$

Check Your Learning

Write the equations relating K_c to K_P for each of the following reactions:

(a) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(b) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(c) $C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g)$

(d) At 227 °C, the following reaction has $K_c = 0.0952$:

$$CH_3OH(g) \rightleftharpoons CO(g) + 2H_2(g)$$

What would be the value of K_P at this temperature?

Answer: (a) $K_P = K_c\,(RT)^{-1}$; (b) $K_P = K_c\,(RT)$; (c) $K_P = K_c\,(RT)$; (d) 160 or 1.6×10^2

Heterogeneous Equilibria

A **heterogeneous equilibrium** involves reactants and products in two or more different phases, as illustrated by the following examples:

$$\begin{array}{rcl rcl}
PbCl_2(s) & \rightleftharpoons & Pb^{2+}(aq) + 2Cl^-(aq) & K_c & = & [Pb^{2+}][Cl^-]^2 \\
CaO(s) + CO_2(g) & \rightleftharpoons & CaCO_3(s) & K_c & = & \dfrac{1}{[CO_2]} \\
C(s) + 2S(g) & \rightleftharpoons & CS_2(g) & K_c & = & \dfrac{[CS_2]}{[S]^2} \\
Br_2(l) & \rightleftharpoons & Br_2(g) & K_c & = & [Br_2(g)]
\end{array}$$

Again, note that concentration terms are only included for gaseous and solute species, as discussed previously.

Two of the above examples include terms for gaseous species only in their equilibrium constants, and so K_p expressions may also be written:

$$\begin{array}{rcl rcl}
CaO(s) + CO_2(g) & \rightleftharpoons & CaCO_3(s) & K_P & = & \dfrac{1}{P_{CO_2}} \\
C(s) + 2S(g) & \rightleftharpoons & CS_2(g) & K_P & = & \dfrac{P_{CS_2}}{(P_S)^2}
\end{array}$$

13.3 Shifting Equilibria: Le Châtelier’s Principle

By the end of this section, you will be able to:

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Châtelier’s principle

A system at equilibrium is in a state of dynamic balance, with forward and reverse reactions taking place at equal rates. If an equilibrium system is subjected to a change in conditions that affects these reaction rates differently (a *stress*), then the rates are no longer equal and the system is not at equilibrium. The system will subsequently experience a net reaction in the direction of greater rate (a *shift*) that will re-establish the equilibrium. This phenomenon is summarized by **Le Châtelier’s principle**: *if an equilibrium system is stressed, the system will experience a shift in response to the stress that re-establishes equilibrium*.

Reaction rates are affected primarily by concentrations, as described by the reaction’s rate law, and temperature, as described by the Arrhenius equation. Consequently, changes in concentration and temperature are the two stresses that can shift an equilibrium.

Effect of a Change in Concentration

If an equilibrium system is subjected to a change in the concentration of a reactant or product species, the rate of either the forward or the reverse reaction will change. As an example, consider the equilibrium reaction

$$\mathrm{H_2}(g) + \mathrm{I_2}(g) \rightleftharpoons 2\mathrm{HI}(g) \qquad K_c = 50.0 \text{ at } 400\ ^\circ\mathrm{C}$$

The rate laws for the forward and reverse reactions are

$$\begin{array}{lll} \textit{forward} & \mathrm{H_2}(g) + \mathrm{I_2}(g) \rightarrow 2\mathrm{HI}(g) & \mathrm{rate}_f = k_f[\mathrm{H_2}]^m[\mathrm{I_2}]^n \\ \textit{reverse} & 2\mathrm{HI}(g) \rightarrow \mathrm{H_2}(g) + \mathrm{I_2}(g) & \mathrm{rate}_r = k_r[\mathrm{HI}]^x \end{array}$$

When this system is at equilibrium, the forward and reverse reaction rates are equal.

$$\mathrm{rate}_f = \mathrm{rate}_r$$

If the system is stressed by adding reactant, either H_2 or I_2, the resulting increase in concentration causes the rate of the forward reaction to increase, exceeding that of the reverse reaction:

$$\mathrm{rate}_f > \mathrm{rate}_r$$

The system will experience a temporary net reaction in the forward direction to re-establish equilibrium (*the equilibrium will shift right*). This same shift will result if some product HI is removed from the system, which decreases the rate of the reverse reaction, again resulting in the same imbalance in rates.

The same logic can be used to explain the left shift that results from either removing reactant or adding product to an equilibrium system. These stresses both result in an increased rate for the reverse reaction

$$\mathrm{rate}_f < \mathrm{rate}_r$$

and a temporary net reaction in the reverse direction to re-establish equilibrium.

As an alternative to this kinetic interpretation, the effect of changes in concentration on equilibria can be rationalized in terms of reaction quotients. When the system is at equilibrium,

$$Q_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]} = K_c$$

If reactant is added (increasing the denominator of the reaction quotient) or product is removed (decreasing the numerator), then $Q_c < K_c$ and the equilibrium will shift right. Note that the three different ways of inducing this stress result in three different changes in the composition of the equilibrium mixture. If H_2 is added, the right shift will consume I_2 and produce HI as equilibrium is re-established, yielding a mixture with a greater concentrations of H_2

and HI and a lesser concentration of I_2 than was present before. If I_2 is added, the new equilibrium mixture will have greater concentrations of I_2 and HI and a lesser concentration of H_2. Finally, if HI is removed, the new equilibrium mixture will have greater concentrations of H_2 and I_2 and a lesser concentration of HI. Despite these differences in composition, *the value of the equilibrium constant will be the same after the stress as it was before* (per the law of mass action). The same logic may be applied for stresses involving removing reactants or adding product, in which case $Q_c > K_c$ and the equilibrium will shift left.

For gas-phase equilibria such as this one, some additional perspectives on changing the concentrations of reactants and products are worthy of mention. The partial pressure P of an ideal gas is proportional to its molar concentration M,

$$M = \frac{n}{V} = \frac{P}{RT}$$

and so changes in the partial pressures of any reactant or product are essentially changes in concentrations and thus yield the same effects on equilibria. Aside from adding or removing reactant or product, the pressures (concentrations) of species in a gas-phase equilibrium can also be changed by *changing the volume occupied by the system*. Since all species of a gas-phase equilibrium occupy the same volume, a given change in volume will cause the same change in concentration for both reactants and products. In order to discern what shift, if any, this type of stress will induce the stoichiometry of the reaction must be considered.

At equilibrium, the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is described by the reaction quotient

$$Q_p = \frac{P_{HI}^2}{P_{H_2} P_{I_2}} = K_p$$

If the volume occupied by an equilibrium mixture of these species is decreased by a factor of 3, the partial pressures of all three species will be increased by a factor of 3:

$$Q_p{}' = \frac{(3P_{HI})^2}{3P_{H_2}\, 3P_{I_2}} = \frac{9P_{HI}^2}{9P_{H_2} P_{I_2}} = \frac{P_{HI}^2}{P_{H_2} P_{I_2}} = Q_p = K_p$$

$$Q_p{}' = Q_p = K_p$$

And so, changing the volume of this gas-phase equilibrium mixture does not result in a shift of the equilibrium.

A similar treatment of a different system, $2NO_2(g) \rightleftharpoons 2\,NO(g) + O_2(g)$, however, yields a different result:

$$Q_p = \frac{P_{NO}^2 P_{O_2}}{P_{(NO_2)}^2} = K_p$$

$$Q_p{}' = \frac{(3P_{NO})^2\, 3P_{O_2}}{(3P_{NO_2})^2} = \frac{9P_{NO}^2\, 3P_{O_2}}{9P_{(NO_2)}^2} = \frac{27P_{NO}^2\, P_{O_2}}{P_{(NO_2)}^2} = 3Q_p > K_p$$

$$Q_p{}' = 3Q_p > K_p$$

In this case, the change in volume results in a reaction quotient greater than the equilibrium constant, and so the equilibrium will shift left.

These results illustrate the relationship between the stoichiometry of a gas-phase equilibrium and the effect of a volume-induced pressure (concentration) change. If the total molar amounts of reactants and products are equal, as in the first example, a change in volume does not shift the equilibrium. If the molar amounts of reactants and products are different, a change in volume will shift the equilibrium in a direction that better "accommodates" the volume change. In the second example, two moles of reactant (NO_2) yield three moles of product ($2NO + O_2$), and so decreasing the system volume causes the equilibrium to shift left since the reverse reaction produces less gas (2 mol) than the forward reaction (3 mol). Conversely, increasing the volume of this equilibrium system would result in a shift towards products.

Link to Learning

Check out this **link (http://openstax.org/l/16equichange)** to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

Chemistry in Everyday Life

Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804) developed a method of infusing water with carbon dioxide to make carbonated water. Priestly's approach involved production of carbon dioxidey reacting oil of vitriol (sulfuric acid) with chalk (calcium carbonate).

The carbon dioxide was then dissolved in water, reacting to produce hydrogen carbonate, a weak acid that subsequently ionized to yield bicarbonate and hydrogen ions:

$$\begin{array}{ll} \text{dissolution} & CO_2(g) \rightleftharpoons CO_2(aq) \\ \text{hydrolysis} & CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \\ \text{ionization} & H_2CO_3(aq) \rightleftharpoons HCO_3{}^-(aq) + H^+(aq) \end{array}$$

These same equilibrium reactions are the basis of today's soft-drink carbonation process. Beverages are exposed to a high pressure of gaseous carbon dioxide during the process to shift the first equilibrium above to the right, resulting in desirably high concentrations of dissolved carbon dioxide and, per similar shifts in the other two equilibria, its hydrolysis and ionization products. A bottle or can is then nearly filled with the carbonated beverage, leaving a relatively small volume of air in the container above the beverage surface (the *headspace*) before it is sealed. The pressure of carbon dioxide in the container headspace is very low immediately after sealing, but it rises as the dissolution equilibrium is re-established by shifting to the left. Since the volume of the beverage is significantly greater than the volume of the headspace, only a relatively small amount of dissolved carbon dioxide is lost to the headspace.

When a carbonated beverage container is opened, a hissing sound is heard as pressurized CO_2 escapes from the headspace. This causes the dissolution equilibrium to shift left, resulting in a decrease in the concentration of dissolved CO_2 and subsequent left-shifts of the hydrolysis and ionization equilibria. Fortunately for the consumer, the dissolution equilibrium is usually re-established slowly, and so the beverage may be enjoyed while its dissolved carbon dioxide concentration remains palatably high. Once the equilibria are re-established, the $CO_2(aq)$ concentration will be significantly lowered, and the beverage acquires a characteristic taste referred to as "flat."

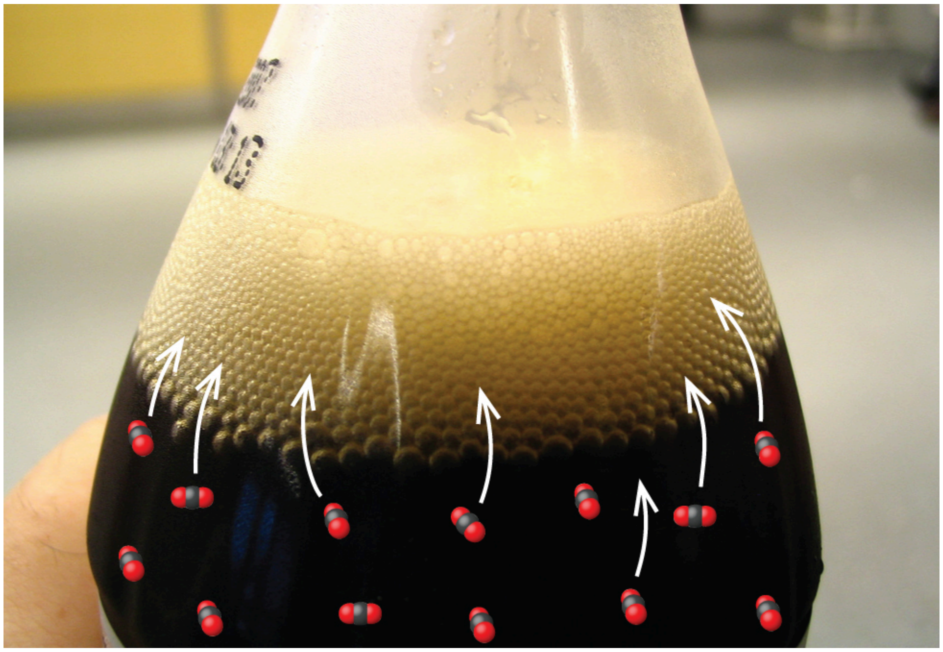


Figure 13.7 Opening a soft-drink bottle lowers the CO_2 pressure above the beverage, shifting the dissolution equilibrium and releasing dissolved CO_2 from the beverage. (credit: modification of work by “D Coetzee”/Flickr)

Effect of a Change in Temperature

Consistent with the law of mass action, an equilibrium stressed by a change in concentration will shift to re-establish equilibrium without any change in the value of the equilibrium constant, *K*. When an equilibrium shifts in response to a temperature change, however, it is re-established with a different relative composition that exhibits a different value for the equilibrium constant.

To understand this phenomenon, consider the elementary reaction

$$\text{A} \rightleftharpoons \text{B}$$

Since this is an elementary reaction, the rates laws for the forward and reverse may be derived directly from the balanced equation’s stoichiometry:

$$\text{rate}_f = k_f[\text{A}]$$
$$\text{rate}_r = k_r[\text{B}]$$

When the system is at equilibrium,

$$\text{rate}_r = \text{rate}_f$$

Substituting the rate laws into this equality and rearranging gives

$$\begin{aligned} k_f[\text{A}] &= k_r[\text{B}] \\ \frac{[\text{B}]}{[\text{A}]} &= \frac{k_f}{k_r} = K_c \end{aligned}$$

The equilibrium constant is seen to be a mathematical function of the rate constants for the forward and reverse reactions. Since the rate constants vary with temperature as described by the Arrhenius equation, is stands to reason that the equilibrium constant will likewise vary with temperature (assuming the rate constants are affected to different extents by the temperature change). For more complex reactions involving multistep reaction mechanisms, a similar but more complex mathematical relation exists between the equilibrium constant and the rate constants of the steps in the mechanism. Regardless of how complex the reaction may be, the temperature-dependence of its equilibrium constant persists.

Predicting the shift an equilibrium will experience in response to a change in temperature is most conveniently accomplished by considering the enthalpy change of the reaction. For example, the decomposition of dinitrogen tetroxide is an endothermic (heat-consuming) process:

$$\mathrm{N_2O_4}(g) \rightleftharpoons \mathrm{2NO_2}(g) \qquad \Delta H = 57.20\ \mathrm{kJ}$$

For purposes of applying Le Chatelier’s principle, heat (q) may be viewed as a reactant:

$$\text{heat} + \mathrm{N_2O_4}(g) \rightleftharpoons \mathrm{2NO_2}(g)$$

Raising the temperature of the system is akin to increasing the amount of a reactant, and so the equilibrium will shift to the right. Lowering the system temperature will likewise cause the equilibrium to shift left. For exothermic processes, heat is viewed as a product of the reaction and so the opposite temperature dependence is observed.

Link to Learning

This interactive **animation (http://openstax.org/l/16chatelier)** allows you to apply Le Châtelier’s principle to predict the effects of changes in concentration, pressure, and temperature on reactant and product concentrations.

13.4 Equilibrium Calculations

By the end of this section, you will be able to:

- Identify the changes in concentration or pressure that occur for chemical species in equilibrium systems
- Calculate equilibrium concentrations or pressures and equilibrium constants, using various algebraic approaches
- Explain how temperature affects the spontaneity of some proceses
- Relate standard free energy changes to equilibrium constants

Having covered the essential concepts of chemical equilibria in the preceding sections of this chapter, this final section will demonstrate the more practical aspect of using these concepts and appropriate mathematical strategies to perform various equilibrium calculations. These types of computations are essential to many areas of science and technology—for example, in the formulation and dosing of pharmaceutical products. After a drug is ingested or injected, it is typically involved in several chemical equilibria that affect its ultimate concentration in the body system of interest. Knowledge of the quantitative aspects of these equilibria is required to compute a dosage amount that will solicit the desired therapeutic effect.

Many of the useful equilibrium calculations that will be demonstrated here require terms representing changes in reactant and product concentrations. These terms are derived from the stoichiometry of the reaction, as illustrated by decomposition of ammonia:

$$\mathrm{2NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + \mathrm{3H_2}(g)$$

As shown earlier in this chapter, this equilibrium may be established within a sealed container that initially contains either $\mathrm{NH_3}$ only, or a mixture of any two of the three chemical species involved in the equilibrium. Regardless of its initial composition, a reaction mixture will show the same relationships between changes in the concentrations of the three species involved, as dictated by the reaction stoichiometry (see also the related content on expressing reaction rates in the chapter on kinetics). For example, if the nitrogen concentration increases by an amount x:

$$\Delta[\text{N}_2] = +x,$$

the corresponding changes in the other species concentrations are

$$\begin{aligned}
\Delta[\text{H}_2] &= \Delta[\text{N}_2]\left(\frac{3\text{ mol H}_2}{1\text{ mol N}_2}\right) = +3x \\
\Delta[\text{NH}_3] &= -\Delta[\text{N}_2]\left(\frac{2\text{ mol NH}_3}{1\text{ mol N}_2}\right) = -2x,
\end{aligned}$$

where the negative sign indicates a decrease in concentration.

Example 13.5

Determining Relative Changes in Concentration

Derive the missing terms representing concentration changes for each of the following reactions.

(a) $$\begin{array}{llll} \text{C}_2\text{H}_2(g)+ & 2\text{Br}_2(g) & \rightleftharpoons & \text{C}_2\text{H}_2\text{Br}_4(g) \\ x & \underline{\quad\quad} & & \underline{\quad\quad} \end{array}$$

(b) $$\begin{array}{llll} \text{I}_2(aq)+ & \text{I}^-(aq) & \rightleftharpoons & \text{I}_3{}^-(aq) \\ \underline{\quad\quad} & \underline{\quad\quad} & & x \end{array}$$

(c) $$\begin{array}{llllll} \text{C}_3\text{H}_8(g)+ & 5\text{O}_2(g) & \rightleftharpoons & 3\text{CO}_2(g)+ & 4\text{H}_2\text{O}(g) \\ x & \underline{\quad\quad} & & \underline{\quad\quad} & \underline{\quad\quad} \end{array}$$

Solution

(a) $$\begin{array}{llll} \text{C}_2\text{H}_2(g)+ & 2\text{Br}_2(g) & \rightleftharpoons & \text{C}_2\text{H}_2\text{Br}_4(g) \\ x & 2x & & -x \end{array}$$

(b) $$\begin{array}{llll} \text{I}_2(aq)+ & \text{I}^-(aq) & \rightleftharpoons & \text{I}_3{}^-(aq) \\ -x & -x & & x \end{array}$$

(c) $$\begin{array}{lllll} \text{C}_3\text{H}_8(g)+ & 5\text{O}_2(g) & \rightleftharpoons & 3\text{CO}_2(g)+ & 4\text{H}_2\text{O}(g) \\ x & 5x & & -3x & -4x \end{array}$$

Check Your Learning

Complete the changes in concentrations for each of the following reactions:

(a) $$\begin{array}{llll} 2\text{SO}_2(g)+ & \text{O}_2(g) & \rightleftharpoons & 2\text{SO}_3(g) \\ \underline{\quad\quad} & x & & \underline{\quad\quad} \end{array}$$

(b) $$\begin{array}{lll} \text{C}_4\text{H}_8(g) & \rightleftharpoons & 2\text{C}_2\text{H}_4(g) \\ \underline{\quad\quad} & & -2x \end{array}$$

(c) $$\begin{array}{lllll} 4\text{NH}_3(g)+ & 7\text{H}_2\text{O}(g) & \rightleftharpoons & 4\text{NO}_2(g)+ & 6\text{H}_2\text{O}(g) \\ \underline{\quad\quad} & \underline{\quad\quad} & & \underline{\quad\quad} & \underline{\quad\quad} \end{array}$$

Answer: (a) $2x$, x, $-2x$; (b) x, $-2x$; (c) $4x$, $7x$, $-4x$, $-6x$ or $-4x$, $-7x$, $4x$, $6x$

Calculation of an Equilibrium Constant

The equilibrium constant for a reaction is calculated from the equilibrium concentrations (or pressures) of its reactants and products. If these concentrations are known, the calculation simply involves their substitution into the K expression, as was illustrated by **Example 13.2**. A slightly more challenging example is provided next, in which the reaction stoichiometry is used to derive equilibrium concentrations from the information provided. The basic strategy of this computation is helpful for many types of equilibrium computations and relies on the use of terms for the reactant and product concentrations *initially* present, for how they *change* as the reaction proceeds, and for what they are when the system reaches *equilibrium*. The acronym ICE is commonly used to refer to this mathematical approach, and the concentrations terms are usually gathered in a tabular format called an ICE table.

Example 13.6

Calculation of an Equilibrium Constant

Iodine molecules react reversibly with iodide ions to produce triiodide ions.

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3{}^-(aq)$$

If a solution with the concentrations of I_2 and I^- both equal to 1.000×10^{-3} M before reaction gives an equilibrium concentration of I_2 of 6.61×10^{-4} M, what is the equilibrium constant for the reaction?

Solution

To calculate the equilibrium constants, equilibrium concentrations are needed for all the reactants and products:

$$K_C = \frac{[I_3{}^-]}{[I_2][I^-]}$$

Provided are the initial concentrations of the reactants and the equilibrium concentration of the product. Use this information to derive terms for the equilibrium concentrations of the reactants, presenting all the information in an ICE table.

	I_2 +	I^- $\rightleftharpoons$	$I_3{}^-$
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	$-x$	$-x$	$+x$
Equilibrium concentration (*M*)	$1.000 \times 10^{-3} - x$	$1.000 \times 10^{-3} - x$	x

At equilibrium the concentration of I_2 is 6.61×10^{-4} M so that

$$\begin{aligned} 1.000 \times 10^{-3} - x &= 6.61 \times 10^{-4} \\ x &= 1.000 \times 10^{-3} - 6.61 \times 10^{-4} \\ &= 3.39 \times 10^{-4}\ M \end{aligned}$$

The ICE table may now be updated with numerical values for all its concentrations:

	I_2 +	I^- $\rightleftharpoons$	$I_3{}^-$
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	-3.39×10^{-4}	-3.39×10^{-4}	$+3.39 \times 10^{-4}$
Equilibrium concentration (*M*)	6.61×10^{-4}	6.61×10^{-4}	3.39×10^{-4}

Finally, substitute the equilibrium concentrations into the *K* expression and solve:

$$\begin{aligned} K_c &= \frac{[I_3{}^-]}{[I_2][I^-]} \\ &= \frac{3.39 \times 10^{-4}\ M}{(6.61 \times 10^{-4}\ M)(6.61 \times 10^{-4}\ M)} = 776 \end{aligned}$$

Check Your Learning

Ethanol and acetic acid react and form water and ethyl acetate, the solvent responsible for the odor of some nail polish removers.

$$C_2H_5OH + CH_3CO_2H \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

When 1 mol each of C_2H_5OH and CH_3CO_2H are allowed to react in 1 L of the solvent dioxane, equilibrium is established when $\frac{1}{3}$ mol of each of the reactants remains. Calculate the equilibrium constant for the reaction. (Note: Water is a solute in this reaction.)

Answer: $K_c = 4$

Calculation of a Missing Equilibrium Concentration

When the equilibrium constant and all but one equilibrium concentration are provided, the other equilibrium concentration(s) may be calculated. A computation of this sort is illustrated in the next example exercise.

Example 13.7

Calculation of a Missing Equilibrium Concentration

Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 °C, the value of the K_c for the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, is 4.1×10^{-4}. Calculate the equilibrium concentration of NO(g) in air at 1 atm pressure and 2000 °C. The equilibrium concentrations of N_2 and O_2 at this pressure and temperature are 0.036 M and 0.0089 M, respectively.

Solution

Substitute the provided quantities into the equilibrium constant expression and solve for [NO]:

$$\begin{aligned} K_c &= \frac{[NO]^2}{[N_2][O_2]} \\ [NO]^2 &= K_c[N_2][O_2] \\ [NO] &= \sqrt{K_c[N_2][O_2]} \\ &= \sqrt{(4.1 \times 10^{-4})(0.036)(0.0089)} \\ &= \sqrt{1.31 \times 10^{-7}} \\ &= 3.6 \times 10^{-4} \end{aligned}$$

Thus [NO] is 3.6×10^{-4} mol/L at equilibrium under these conditions.

To confirm this result, it may be used along with the provided equilibrium concentrations to calculate a value for K:

$$\begin{aligned} K_c &= \frac{[NO]^2}{[N_2][O_2]} \\ &= \frac{(3.6 \times 10^{-4})^2}{(0.036)(0.0089)} \\ &= 4.0 \times 10^{-4} \end{aligned}$$

This result is consistent with the provided value for K within nominal uncertainty, differing by just 1 in the least significant digit's place.

Check Your Learning

The equilibrium constant K_c for the reaction of nitrogen and hydrogen to produce ammonia at a certain temperature is 6.00×10^{-2}. Calculate the equilibrium concentration of ammonia if the equilibrium concentrations of nitrogen and hydrogen are 4.26 *M* and 2.09 *M*, respectively.

Answer: 1.53 mol/L

Calculation of Equilibrium Concentrations from Initial Concentrations

Perhaps the most challenging type of equilibrium calculation can be one in which equilibrium concentrations are derived from initial concentrations and an equilibrium constant. For these calculations, a four-step approach is typically useful:

1. Identify the direction in which the reaction will proceed to reach equilibrium.
2. Develop an ICE table.
3. Calculate the concentration changes and, subsequently, the equilibrium concentrations.
4. Confirm the calculated equilibrium concentrations.

The last two example exercises of this chapter demonstrate the application of this strategy.

Example 13.8

Calculation of Equilibrium Concentrations

Under certain conditions, the equilibrium constant K_c for the decomposition of $PCl_5(g)$ into $PCl_3(g)$ and $Cl_2(g)$ is 0.0211. What are the equilibrium concentrations of PCl_5, PCl_3, and Cl_2 in a mixture that initially contained only PCl_5 at a concentration of 1.00 *M*?

Solution

Use the stepwise process described earlier.

Step 1. *Determine the direction the reaction proceeds.*
The balanced equation for the decomposition of PCl_5 is

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Because only the reactant is present initially $Q_c = 0$ and the reaction will proceed to the right.

Step 2. *Develop an ICE table.*

	PCl_5 $\rightleftharpoons$	PCl_3 +	Cl_2
Initial concentration (*M*)	1.00	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$1.00 - x$	x	x

Step 3. *Solve for the change and the equilibrium concentrations.*
Substituting the equilibrium concentrations into the equilibrium constant equation gives

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = 0.0211$$
$$= \frac{(x)(x)}{(1.00 - x)}$$
$$0.0211 = \frac{(x)(x)}{(1.00 - x)}$$
$$0.0211(1.00 - x) = x^2$$
$$x^2 + 0.0211x - 0.0211 = 0$$

Appendix B shows an equation of the form $ax^2 + bx + c = 0$ can be rearranged to solve for x:

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

In this case, $a = 1$, $b = 0.0211$, and $c = -0.0211$. Substituting the appropriate values for a, b, and c yields:

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(1)(-0.0211)}}{2(1)}$$
$$= \frac{-0.0211 \pm \sqrt{(4.45 \times 10^{-4}) + (8.44 \times 10^{-2})}}{2}$$
$$= \frac{-0.0211 \pm 0.291}{2}$$

The two roots of the quadratic are, therefore,

$$x = \frac{-0.0211 + 0.291}{2} = 0.135$$

and

$$x = \frac{-0.0211 - 0.291}{2} = -0.156$$

For this scenario, only the positive root is physically meaningful (concentrations are either zero or positive), and so $x = 0.135$ *M*.

The equilibrium concentrations are

$$[PCl_5] = 1.00 - 0.135 = 0.87\ M$$
$$[PCl_3] = x = 0.135\ M$$
$$[Cl_2] = x = 0.135\ M$$

Step 4. *Confirm the calculated equilibrium concentrations.*
Substitution into the expression for K_c (to check the calculation) gives

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

The equilibrium constant calculated from the equilibrium concentrations is equal to the value of K_c given in the problem (when rounded to the proper number of significant figures).

Check Your Learning

Acetic acid, CH_3CO_2H, reacts with ethanol, C_2H_5OH, to form water and ethyl acetate, $CH_3CO_2C_2H_5$.

$$CH_3CO_2H + C_2H_5OH \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

The equilibrium constant for this reaction with dioxane as a solvent is 4.0. What are the equilibrium concentrations for a mixture that is initially 0.15 *M* in CH_3CO_2H, 0.15 *M* in C_2H_5OH, 0.40 *M* in $CH_3CO_2C_2H_5$, and 0.40 *M* in H_2O?

Answer: $[CH_3CO_2H] = 0.36$ *M*, $[C_2H_5OH] = 0.36$ *M*, $[CH_3CO_2C_2H_5] = 0.17$ *M*, $[H_2O] = 0.17$ *M*

Check Your Learning

A 1.00-L flask is filled with 1.00 moles of H_2 and 2.00 moles of I_2. The value of the equilibrium constant for the reaction of hydrogen and iodine reacting to form hydrogen iodide is 50.5 under the given conditions. What are the equilibrium concentrations of H_2, I_2, and HI in moles/L?

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Answer: $[H_2] = 0.06\ M$, $[I_2] = 1.06\ M$, $[HI] = 1.88\ M$

Example 13.9

Calculation of Equilibrium Concentrations Using an Algebra-Simplifying Assumption

What are the concentrations at equilibrium of a 0.15 *M* solution of HCN?

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq) \qquad K_c = 4.9 \times 10^{-10}$$

Solution

Using "*x*" to represent the concentration of each product at equilibrium gives this ICE table.

	$HCN(aq) \rightleftharpoons$	$H^+(aq)$ +	$CN^-(aq)$
Initial concentration (*M*)	0.15	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$0.15 - x$	x	x

Substitute the equilibrium concentration terms into the K_c expression

$$K_c = \frac{(x)(x)}{0.15 - x}$$

Rearrange to the quadratic form and solve for *x*

$$x^2 + 4.9 \times 10^{-10} - 7.35 \times 10^{-11} = 0$$
$$x = 8.56 \times 10^{-6}\ M\ (3\text{ sig. figs.}) = 8.6 \times 10^{-6}\ M\ (2\text{ sig. figs.})$$

Thus $[H^+] = [CN^-] = x = 8.6 \times 10^{-6}\ M$ and $[HCN] = 0.15 - x = 0.15\ M$.

Note in this case that the change in concentration is significantly less than the initial concentration (a consequence of the small *K*), and so the initial concentration experiences a negligible change:

$$\text{if } x \ll 0.15\text{ M, then } (0.15 - x) \approx 0.15$$

This approximation allows for a more expedient mathematical approach to the calculation that avoids the need to solve for the roots of a quadratic equation:

$$K_c = \frac{(x)(x)}{0.15 - x} \approx \frac{x^2}{0.15}$$
$$4.9 \times 10^{-10} = \frac{x^2}{0.15}$$
$$x^2 = (0.15)(4.9 \times 10^{-10}) = 7.4 \times 10^{-11}$$
$$x = \sqrt{7.4 \times 10^{-11}} = 8.6 \times 10^{-6}\ M$$

The value of *x* calculated is, indeed, much less than the initial concentration

$$8.6 \times 10^{-6} \ll 0.15$$

and so the approximation was justified. If this simplified approach were to yield a value for *x* that did *not* justify the approximation, the calculation would need to be repeated without making the approximation.

Check Your Learning

What are the equilibrium concentrations in a 0.25 M NH_3 solution?

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4{}^+(aq) + OH^-(aq) \qquad K_c = 1.8 \times 10^{-5}$$

Answer: $[OH^-] = [NH_4{}^+] = 0.0021\ M$; $[NH_3] = 0.25\ M$

Temperature Dependence of Spontaneity

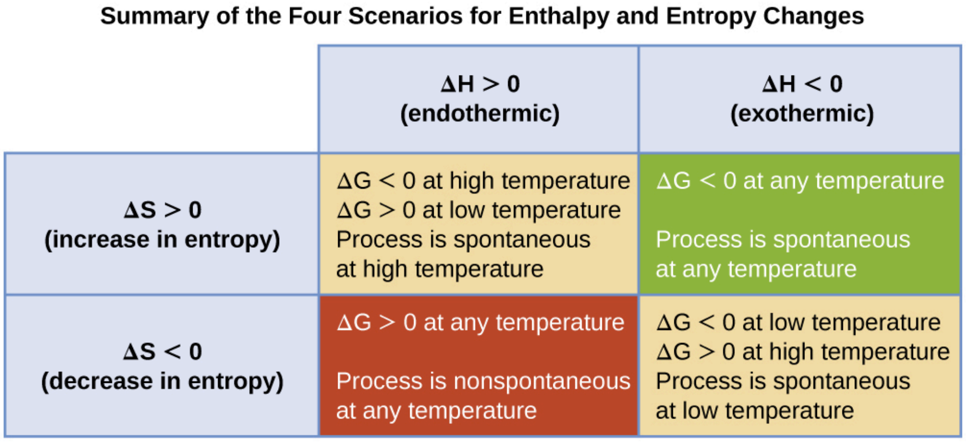
As was previously demonstrated in the section on entropy in an earlier chapter, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. Likewise, some chemical reactions can also exhibit temperature dependent spontaneities. To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

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

The spontaneity of a process, as reflected in the arithmetic sign of its free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both ΔH and ΔS are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, ΔG will be negative if the magnitude of the $T\Delta S$ term is greater than ΔH. If the $T\Delta S$ term is less than ΔH, the free energy change will be positive. Such a process is *spontaneous at high temperatures and nonspontaneous at low temperatures.*
2. **Both ΔH and ΔS are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, ΔG will be negative if the magnitude of the $T\Delta S$ term is less than ΔH. If the $T\Delta S$ term's magnitude is greater than ΔH, the free energy change will be positive. Such a process is *spontaneous at low temperatures and nonspontaneous at high temperatures.*
3. **ΔH is positive and ΔS is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, ΔG will be positive regardless of the temperature. Such a process is *nonspontaneous at all temperatures.*
4. **ΔH is negative and ΔS is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, ΔG will be negative regardless of the temperature. Such a process is *spontaneous at all temperatures.*

These four scenarios are summarized in **Figure 13.8**.



Summary of the Four Scenarios for Enthalpy and Entropy Changes

	ΔH > 0 (endothermic)	ΔH < 0 (exothermic)
ΔS > 0 (increase in entropy)	ΔG < 0 at high temperature ΔG > 0 at low temperature Process is spontaneous at high temperature	ΔG < 0 at any temperature Process is spontaneous at any temperature
ΔS < 0 (decrease in entropy)	ΔG > 0 at any temperature Process is nonspontaneous at any temperature	ΔG < 0 at low temperature ΔG > 0 at high temperature Process is spontaneous at low temperature

Figure 13.8 There are four possibilities regarding the signs of enthalpy and entropy changes.

Example 13.10

Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

$$2\text{C}(s) + \text{O}_2(g) \longrightarrow 2\text{CO}(g)$$

How does the spontaneity of this process depend upon temperature?

Solution

Combustion processes are exothermic ($\Delta H < 0$). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S > 0$). The reaction is therefore spontaneous ($\Delta G < 0$) at all temperatures.

Check Your Learning

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4\text{Fe}(s) + 3\text{O}_2(g) \longrightarrow 2\text{Fe}_2\text{O}_3(s)$$

How does the spontaneity of this process depend upon temperature?

Answer: ΔH and ΔS are negative; the reaction is spontaneous at low temperatures.

When considering the conclusions drawn regarding the temperature dependence of spontaneity, it is important to keep in mind what the terms "high" and "low" mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is nonspontaneous at one temperature but spontaneous at another will necessarily undergo a change in "spontaneity" (as reflected by its ΔG) as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which ΔG is plotted on the y axis versus T on the x axis:

$$\Delta G = \Delta H - T\Delta S$$
$$y = b + mx$$

Such a plot is shown in Figure 13.9. A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependent spontaneity as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative ΔG) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the x-intercept of the line, that is, the value of T for which ΔG is zero:

$$\Delta G = 0 = \Delta H - T\Delta S$$
$$T = \frac{\Delta H}{\Delta S}$$

So, saying a process is spontaneous at “high” or “low” temperatures means the temperature is above or below, respectively, that temperature at which Δ*G* for the process is zero. As noted earlier, the condition of ΔG = 0 describes a system at equilibrium.

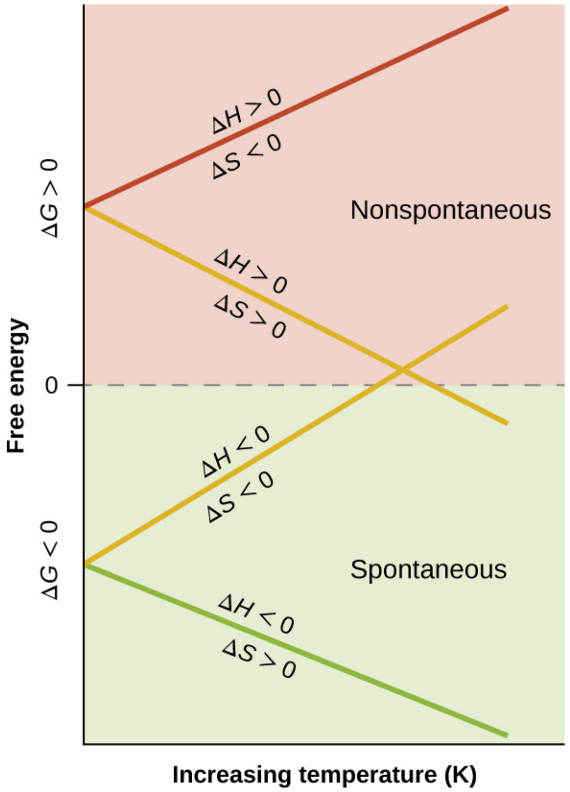


Figure 13.9 These plots show the variation in Δ*G* with temperature for the four possible combinations of arithmetic sign for Δ*H* and Δ*S*.

Example 13.11

Equilibrium Temperature for a Phase Transition

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its liquid and gaseous phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in **Appendix G** to estimate the boiling point of water.

Solution

The process of interest is the following phase change:

$$H_2O(l) \longrightarrow H_2O(g)$$

When this process is at equilibrium, Δ*G* = 0, so the following is true:

$$0 = \Delta H^\circ - T\Delta S^\circ \qquad \text{or} \qquad T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Using the standard thermodynamic data from **Appendix G**,

$$\begin{aligned}\Delta H^\circ &= 1\text{ mol} \times \Delta H^\circ_\text{f}\ (\text{H}_2\text{O}(g)) - 1\text{ mol} \times \Delta H^\circ_\text{f}\ (\text{H}_2\text{O}(l)) \\ &= (1\text{ mol}) - 241.82\text{ kJ/mol} - (1\text{ mol})(-241.82\text{ kJ/mol}) = 44.01\text{ kJ} \\ \Delta S^\circ &= 1\text{ mol} \times \Delta S^\circ\ (\text{H}_2\text{O}(g)) - 1\text{ mol} \times \Delta S^\circ\ (\text{H}_2\text{O}(l)) \\ &= (1\text{ mol})188.8\text{ J/K·mol} - (1\text{ mol})70.0\text{ J/K·mol} = 118.8\text{ J/K} \\ T &= \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01 \times 10^3\text{ J}}{118.8\text{ J/K}} = 370.5\text{ K} = 97.3\text{ °C}\end{aligned}$$

The accepted value for water's normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K (**Appendix G**). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

Check Your Learning

Use the information in **Appendix G** to estimate the boiling point of CS_2.

Answer: 313 K (accepted value 319 K)

Free Energy and Equilibrium

The free energy change for a process may be viewed as a measure of its driving force. A negative value for ΔG represents a driving force for the process in the forward direction, while a positive value represents a driving force for the process in the reverse direction. When ΔG is zero, the forward and reverse driving forces are equal, and the process occurs in both directions at the same rate (the system is at equilibrium).

In the section on equilibrium, the *reaction quotient*, Q, was introduced as a convenient measure of the status of an equilibrium system. Recall that Q is the numerical value of the mass action expression for the system, and that you may use its value to identify the direction in which a reaction will proceed in order to achieve equilibrium. When Q is lesser than the equilibrium constant, K, the reaction will proceed in the forward direction until equilibrium is reached and $Q = K$. Conversely, if $Q > K$, the process will proceed in the reverse direction until equilibrium is achieved.

The free energy change for a process taking place with reactants and products present under *nonstandard conditions* (pressures other than 1 bar; concentrations other than 1 M) is related to the standard free energy change, according to this equation:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

R is the gas constant (8.314 J/K mol), T is the kelvin or absolute temperature, and Q is the reaction quotient. This equation may be used to predict the spontaneity for a process under any given set of conditions as illustrated in **Example 13.12**.

Example 13.12

Calculating ΔG under Nonstandard Conditions

What is the free energy change for the process shown here under the specified conditions?

$T = 25\text{ °C},\ P_{\text{N}_2} = 0.870\text{ atm},\quad P_{\text{H}_2} = 0.250\text{ atm},\quad \text{and}\ P_{\text{NH}_3} = 12.9\text{ atm}$

$$2\text{NH}_3(g) \longrightarrow 3\text{H}_2(g) + \text{N}_2(g) \qquad \Delta G^\circ = 33.0\text{ kJ/mol}$$

Solution

The equation relating free energy change to standard free energy change and reaction quotient may be used directly:

$$\Delta G = \Delta G° + RT \ln Q = 33.0 \frac{\text{kJ}}{\text{mol}} + \left(8.314 \frac{\text{J}}{\text{mol K}} \times 298 \text{ K} \times \ln \frac{(0.250^3) \times 0.870}{12.9^2}\right) = 9680 \frac{\text{J}}{\text{mol}} \text{ or } 9.68 \text{ kJ/mol}$$

Since the computed value for ΔG is positive, the reaction is nonspontaneous under these conditions.

Check Your Learning

Calculate the free energy change for this same reaction at 875 °C in a 5.00 L mixture containing 0.100 mol of each gas. Is the reaction spontaneous under these conditions?

Answer: $\Delta G = -47$ kJ/mol; yes

For a system at equilibrium, $Q = K$ and $\Delta G = 0$, and the previous equation may be written as

$$0 = \Delta G° + RT \ln K \qquad \text{(at equilibrium)}$$

$$\Delta G° = -RT \ln K \qquad \text{or} \qquad K = e^{-\frac{\Delta G°}{RT}}$$

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized in **Table 13.1**.

Relations between Standard Free Energy Changes and Equilibrium Constants

K	$\Delta G°$	Composition of an Equilibrium Mixture
> 1	< 0	Products are more abundant
< 1	> 0	Reactants are more abundant
= 1	= 0	Reactants and products are comparably abundant

Table 13.1

Example 13.13

Calculating an Equilibrium Constant using Standard Free Energy Change

Given that the standard free energies of formation of $Ag^+(aq)$, $Cl^-(aq)$, and $AgCl(s)$ are 77.1 kJ/mol, −131.2 kJ/mol, and −109.8 kJ/mol, respectively, calculate the solubility product, K_{sp}, for AgCl.

Solution

The reaction of interest is the following:

$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \qquad K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

The standard free energy change for this reaction is first computed using standard free energies of formation for its reactants and products:

$$\begin{aligned}\Delta G° &= \left[\Delta G_f°\left(\text{Ag}^+(aq)\right) + \Delta G_f°\left(\text{Cl}^-(aq)\right)\right] - \left[\Delta G_f°\left(\text{AgCl}(s)\right)\right] \\ &= [77.1 \text{ kJ/mol} - 131.2 \text{ kJ/mol}] - [-109.8 \text{ kJ/mol}] = 55.7 \text{ kJ/mol}\end{aligned}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change:

$$K_{\text{sp}} = e^{-\frac{\Delta G^\circ}{RT}} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{55.7 \times 10^3\ \text{J/mol}}{8.314\ \text{J/mol·K} \times 298.15\ \text{K}}\right) = \exp(-22.470) = e^{-22.470} = 1.74 \times 10^{-10}$$

This result is in reasonable agreement with the value provided in **Appendix J**.

Check Your Learning

Use the thermodynamic data provided in **Appendix G** to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

$$2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$$

Answer: $K = 6.9$

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy change versus the extent of the reaction (for example, as reflected in the value of Q), equilibrium is established when the system's free energy is minimized (**Figure 13.10**). If a system consists of reactants and products in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.

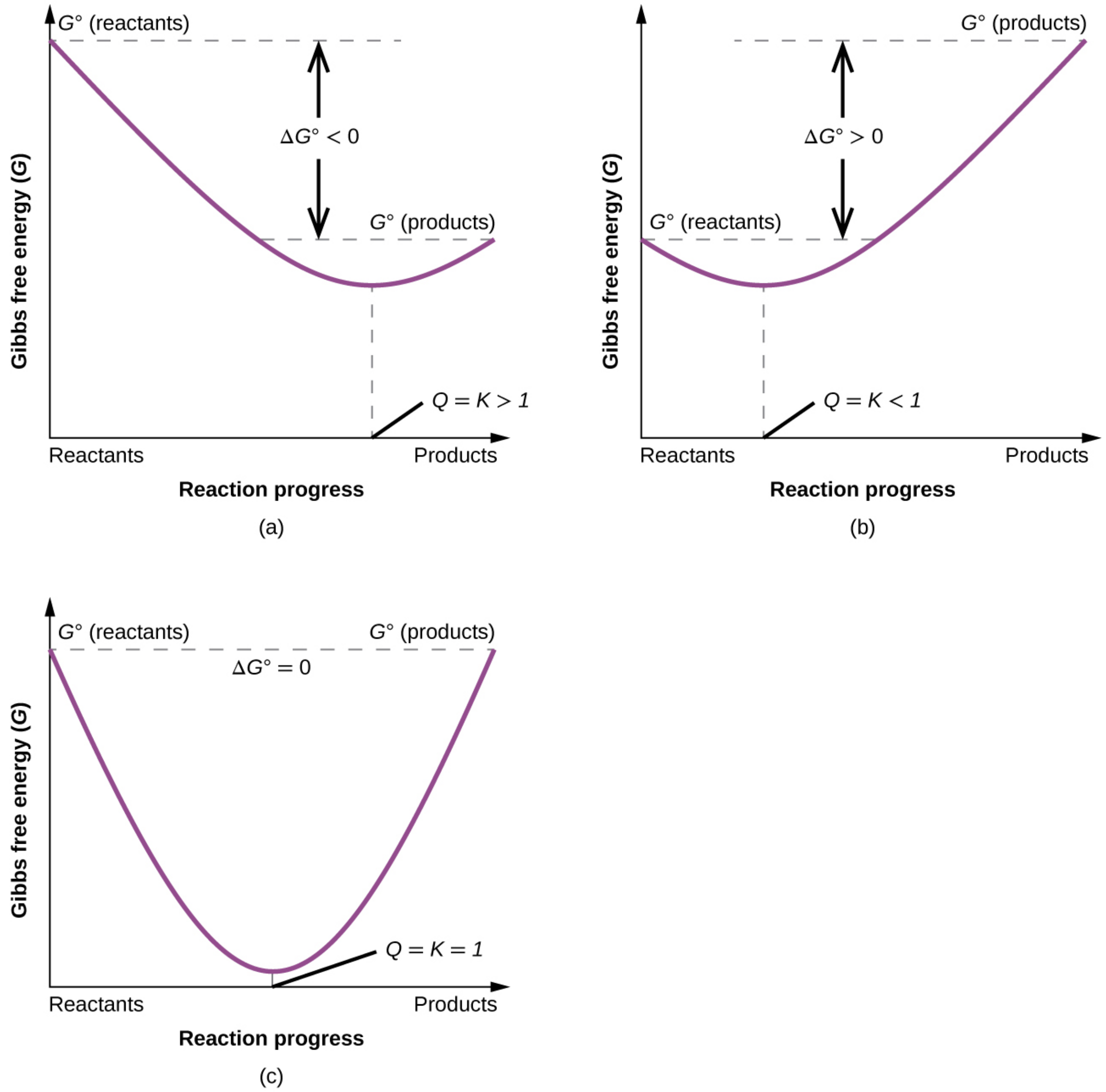


Figure 13.10 These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium.

Key Terms

equilibrium state of a reversible reaction in which the forward and reverse processes occur at equal rates

equilibrium constant (K) value of the reaction quotient for a system at equilibrium; may be expressed using concentrations (K_c) or partial pressures (K_p)

heterogeneous equilibria equilibria in which reactants and products occupy two or more different phases

homogeneous equilibria equilibria in which all reactants and products occupy the same phase

law of mass action when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

Le Châtelier's principle an equilibrium subjected to stress will shift in a way to counter the stress and re-establish equilibrium

reaction quotient (Q) mathematical function describing the relative amounts of reactants and products in a reaction mixture; may be expressed in terms of concentrations (Q_c) or pressures (Q_p)

reversible reaction chemical reaction that can proceed in both the forward and reverse directions under given conditions

Key Equations

- $Q_c = \frac{[\mathrm{C}]^x[\mathrm{D}]^y}{[\mathrm{A}]^m[\mathrm{B}]^n}$ for the reaction $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $Q_P = \frac{(P_C)^x(P_D)^y}{(P_A)^m(P_B)^n}$ for the reaction $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $P = MRT$
- $K_c = Q_c$ at equilibrium
- $K_p = Q_p$ at equilibrium
- $K_P = K_c\,(RT)^{\Delta n}$

Summary

13.1 Chemical Equilibria

A reversible reaction is at equilibrium when the forward and reverse processes occur at equal rates. Chemical equilibria are dynamic processes characterized by constant amounts of reactant and product species.

13.2 Equilibrium Constants

The composition of a reaction mixture may be represented by a mathematical function known as the reaction quotient, Q. For a reaction at equilibrium, the composition is constant, and Q is called the equilibrium constant, K.

A homogeneous equilibrium is an equilibrium in which all components are in the same phase. A heterogeneous equilibrium is an equilibrium in which components are in two or more phases.

13.3 Shifting Equilibria: Le Châtelier's Principle

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure. The system's response to these disturbances is described by Le Châtelier's principle: An equilibrium system subjected to a disturbance will shift in a way that counters the disturbance and re-establishes equilibrium. A catalyst will increase the rate of both the forward and reverse reactions of a reversible process, increasing the rate at which equilibrium is reached but not altering the equilibrium mixture's composition (K does not change).

13.4 Equilibrium Calculations

Calculating values for equilibrium constants and/or equilibrium concentrations is of practical benefit to many applications. A mathematical strategy that uses initial concentrations, changes in concentrations, and equilibrium concentrations (and goes by the acronym ICE) is useful for several types of equilibrium calculations. We also learned that a negative value for ΔG indicates a spontaneous process; a positive ΔG indicates a nonspontaneous process; and a ΔG of zero indicates that the system is at equilibrium. We also saw how free energy, spontaneity, and equilibrium relate.

Exercises

13.1 Chemical Equilibria

1. What does it mean to describe a reaction as "reversible"?

2. When writing an equation, how is a reversible reaction distinguished from a nonreversible reaction?

3. If a reaction is reversible, when can it be said to have reached equilibrium?

4. Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal?

5. If the concentrations of products and reactants are equal, is the system at equilibrium?

13.2 Equilibrium Constants

6. Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

7. Explain why an equilibrium between $Br_2(l)$ and $Br_2(g)$ would not be established if the container were not a closed vessel shown in **Figure 13.4**.

8. If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure NO_2 or with pure N_2O_4?
$2NO_2(g) \rightleftharpoons N_2O_4(g)$

9. Among the solubility rules previously discussed is the statement: All chlorides are soluble except Hg_2Cl_2, AgCl, $PbCl_2$, and CuCl.

(a) Write the expression for the equilibrium constant for the reaction represented by the equation $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by the equation $Pb^{2+}(aq) + 2Cl^-(aq) \rightleftharpoons PbCl_2(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

10. Among the solubility rules previously discussed is the statement: Carbonates, phosphates, borates, and arsenates—except those of the ammonium ion and the alkali metals—are insoluble.

(a) Write the expression for the equilibrium constant for the reaction represented by the equation $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3{}^{2-}(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by the equation $3Ba^{2+}(aq) + 2PO_4{}^{3-}(aq) \rightleftharpoons Ba_3(PO_4)_2(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

11. Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3C_2H_2(g) \rightleftharpoons C_6H_6(g)$. Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer.

12. Show that the complete chemical equation, the total ionic equation, and the net ionic equation for the reaction represented by the equation $KI(aq) + I_2(aq) \rightleftharpoons KI_3(aq)$ give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and $I_3{}^-$.

13. For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Is $K_c > 1$, < 1, or ≈ 1 for a titration reaction?

14. For a precipitation reaction to be useful in a gravimetric analysis, the product of the reaction must be insoluble. Is $K_c > 1$, < 1, or ≈ 1 for a useful precipitation reaction?

15. Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

(a) $CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g)$

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(c) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(d) $BaSO_3(s) \rightleftharpoons BaO(s) + SO_2(g)$

(e) $P_4(g) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$

(f) $Br_2(g) \rightleftharpoons 2Br(g)$

(g) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$

(h) $CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$

16. Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(b) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

(c) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(d) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$

(e) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

(f) $2Pb(NO_3)_2(s) \rightleftharpoons 2PbO(s) + 4NO_2(g) + O_2(g)$

(g) $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(l)$

(h) $S_8(g) \rightleftharpoons 8S(g)$

17. The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

(a) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_c = 17$; $[NH_3] = 0.20\,M$, $[N_2] = 1.00\,M$, $[H_2] = 1.00\,M$
(b) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_P = 6.8 \times 10^4$; $NH_3 = 3.0$ atm, $N_2 = 2.0$ atm, $H_2 = 1.0$ atm
(c) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_c = 0.230$; $[SO_3] = 0.00\,M$, $[SO_2] = 1.00\,M$, $[O_2] = 1.00\,M$
(d) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_P = 16.5$; $SO_3 = 1.00$ atm, $SO_2 = 1.00$ atm, $O_2 = 1.00$ atm
(e) $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K_c = 4.6 \times 10^4$; $[NO] = 1.00\,M$, $[Cl_2] = 1.00\,M$, $[NOCl] = 0\,M$
(f) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_P = 0.050$; $NO = 10.0$ atm, $N_2 = O_2 = 5$ atm

18. The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

(a) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_c = 17$; $[NH_3] = 0.50\,M$, $[N_2] = 0.15\,M$, $[H_2] = 0.12\,M$
(b) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_P = 6.8 \times 10^4$; $NH_3 = 2.00$ atm, $N_2 = 10.00$ atm, $H_2 = 10.00$ atm
(c) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_c = 0.230$; $[SO_3] = 2.00\,M$, $[SO_2] = 2.00\,M$, $[O_2] = 2.00\,M$
(d) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_P = 6.5$ atm; $SO_2 = 1.00$ atm, $O_2 = 1.130$ atm, $SO_3 = 0$ atm
(e) $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K_P = 2.5 \times 10^3$; $NO = 1.00$ atm, $Cl_2 = 1.00$ atm, $NOCl = 0$ atm
(f) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_c = 0.050$; $[N_2] = 0.100\,M$, $[O_2] = 0.200\,M$, $[NO] = 1.00\,M$

19. The following reaction has $K_P = 4.50 \times 10^{-5}$ at 720 K.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium? $P(NH_3) = 93$ atm, $P(N_2) = 48$ atm, and $P(H_2) = 52$ atm

20. Determine if the following system is at equilibrium. If not, in which direction will the system need to shift to reach equilibrium?

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

$[SO_2Cl_2] = 0.12\ M$, $[Cl_2] = 0.16\ M$ and $[SO_2] = 0.050\ M$. K_c for the reaction is 0.078.

21. Which of the systems described in Exercise 13.15 are homogeneous equilibria? Which are heterogeneous equilibria?

22. Which of the systems described in Exercise 13.16 are homogeneous equilibria? Which are heterogeneous equilibria?

23. For which of the reactions in Exercise 13.15 does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

24. For which of the reactions in Exercise 13.16 does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

25. Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	$K_c = 0.50$ at 400 °C
(b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	$K_c = 50.2$ at 448 °C
(c) $Na_2SO_4 \cdot 10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g)$	$K_P = 4.08 \times 10^{-25}$ at 25 °C
(d) $H_2O(l) \rightleftharpoons H_2O(g)$	$K_P = 0.122$ at 50 °C

26. Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

(a) $Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g)$	$K_c = 4.7 \times 10^{-2}$ at 25 °C
(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	$K_P = 48.2$ at 500 °C
(c) $CaCl_2 \cdot 6H_2O(s) \rightleftharpoons CaCl_2(s) + 6H_2O(g)$	$K_P = 5.09 \times 10^{-44}$ at 25 °C
(d) $H_2O(l) \rightleftharpoons H_2O(g)$	$K_P = 0.196$ at 60 °C

27. What is the value of the equilibrium constant expression for the change $H_2O(l) \rightleftharpoons H_2O(g)$ at 30 °C? (See Appendix E.)

28. Write the expression of the reaction quotient for the ionization of HOCN in water.

29. Write the reaction quotient expression for the ionization of NH_3 in water.

30. What is the approximate value of the equilibrium constant K_P for the change $C_2H_5OC_2H_5(l) \rightleftharpoons C_2H_5OC_2H_5(g)$ at 25 °C. (The equilibrium vapor pressure for this substance is 570 torr at 25 °C.)

13.3 Shifting Equilibria: Le Châtelier's Principle

31. The following equation represents a reversible decomposition:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Under what conditions will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains?

32. Explain how to recognize the conditions under which changes in volume will affect gas-phase systems at equilibrium.

33. What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant?

34. The following reaction occurs when a burner on a gas stove is lit:

$$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$$

Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer.

35. A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide, SO_3, from sulfur dioxide, SO_2, and oxygen, O_2, shown here. At high temperatures, the rate of formation of SO_3 is higher, but the equilibrium amount (concentration or partial pressure) of SO_3 is lower than it would be at lower temperatures.

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

(a) Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?

(b) Is the reaction endothermic or exothermic?

36. Suggest four ways in which the concentration of hydrazine, N_2H_4, could be increased in an equilibrium described by the following equation:

$$N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g) \qquad \Delta H = 95\text{ kJ}$$

37. Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:

$$P_4(g) + 6H_2(g) \rightleftharpoons 4PH_3(g) \qquad \Delta H = 110.5\text{ kJ}$$

38. How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

(a) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g) \qquad \Delta H = 92\text{ kJ}$

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = 181\text{ kJ}$

(c) $2O_3(g) \rightleftharpoons 3O_2(g) \qquad \Delta H = -285\text{ kJ}$

(d) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \qquad \Delta H = -176\text{ kJ}$

39. How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

(a) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g) \qquad \Delta H = 484\text{ kJ}$

(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.2\text{ kJ}$

(c) $2Br(g) \rightleftharpoons Br_2(g) \qquad \Delta H = -224\text{ kJ}$

(d) $H_2(g) + I_2(s) \rightleftharpoons 2HI(g) \qquad \Delta H = 53\text{ kJ}$

40. Methanol can be prepared from carbon monoxide and hydrogen at high temperature and pressure in the presence of a suitable catalyst.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -90.2\text{ kJ}$$

(b) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more H_2 is added?

(c) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CO is removed?

(d) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CH_3OH is added?

(e) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if the temperature of the system is increased?

41. Nitrogen and oxygen react at high temperatures.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = 181\ \text{kJ}$

(b) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if more O_2 is added?

(c) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if N_2 is removed?

(d) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if NO is added?

(e) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the volume of the reaction vessel is decreased?

(f) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the temperature of the system is increased?

42. Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.

(a) Write the expression for the equilibrium constant for the reversible reaction
$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad \Delta H = 131.30\ \text{kJ}$

(b) What will happen to the concentration of each reactant and product at equilibrium if more C is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if CO is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

43. Pure iron metal can be produced by the reduction of iron(III) oxide with hydrogen gas.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction
$Fe_2O_3(s) + 3H_2(g) \rightleftharpoons 2Fe(s) + 3H_2O(g) \qquad \Delta H = 98.7\ \text{kJ}$

(b) What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if H_2 is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the volume of the reaction vessel is decreased?

(f) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

44. Ammonia is a weak base that reacts with water according to this equation:
$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4{}^+(aq) + OH^-(aq)$

Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?

(a) Addition of NaOH

(b) Addition of HCl

(c) Addition of NH_4Cl

45. Acetic acid is a weak acid that reacts with water according to this equation:

$$CH_3CO_2H(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

Will any of the following increase the percent of acetic acid that reacts and produces $CH_3CO_2^-$ ion?

(a) Addition of HCl

(b) Addition of NaOH

(c) Addition of $NaCH_3CO_2$

46. Suggest two ways in which the equilibrium concentration of Ag^+ can be reduced in a solution of Na^+, Cl^-, Ag^+, and NO_3^-, in contact with solid AgCl.

$$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \rightleftharpoons AgCl(s) + Na^+(aq) + NO_3^-(aq)$$

$$\Delta H = -65.9\ \text{kJ}$$

47. How can the pressure of water vapor be increased in the following equilibrium?

$$H_2O(l) \rightleftharpoons H_2O(g) \qquad \Delta H = 41\ \text{kJ}$$

48. A solution is saturated with silver sulfate and contains excess solid silver sulfate:

$$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$$

A small amount of solid silver sulfate containing a radioactive isotope of silver is added to this solution. Within a few minutes, a portion of the solution phase is sampled and tests positive for radioactive Ag^+ ions. Explain this observation.

49. The amino acid alanine has two isomers, α-alanine and β-alanine. When equal masses of these two compounds are dissolved in equal amounts of a solvent, the solution of α-alanine freezes at the lowest temperature. Which form, α-alanine or β-alanine, has the larger equilibrium constant for ionization $(HX \rightleftharpoons H^+ + X^-)$?

13.4 Equilibrium Calculations

50. A reaction is represented by this equation: $A(aq) + 2B(aq) \rightleftharpoons 2C(aq) \qquad K_c = 1 \times 10^3$

(a) Write the mathematical expression for the equilibrium constant.

(b) Using concentrations ≤1 *M*, identify two sets of concentrations that describe a mixture of A, B, and C at equilibrium.

51. A reaction is represented by this equation: $2W(aq) \rightleftharpoons X(aq) + 2Y(aq) \qquad K_c = 5 \times 10^{-4}$

(a) Write the mathematical expression for the equilibrium constant.

(b) Using concentrations of ≤1 *M*, identify two sets of concentrations that describe a mixture of W, X, and Y at equilibrium.

52. What is the value of the equilibrium constant at 500 °C for the formation of NH_3 according to the following equation?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

An equilibrium mixture of $NH_3(g)$, $H_2(g)$, and $N_2(g)$ at 500 °C was found to contain 1.35 *M* H_2, 1.15 *M* N_2, and 4.12×10^{-1} *M* NH_3.

53. Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures.

$$CH_4(g) + H_2O(g) \rightleftharpoons 3H_2(g) + CO(g)$$

What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4, 0.126 *M*; H_2O, 0.242 *M*; CO, 0.126 *M*; H_2 1.15 *M*, at a temperature of 760 °C?

54. A 0.72-mol sample of PCl_5 is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of $PCl_3(g)$ and 0.40 mol of $Cl_2(g)$. Calculate the value of the equilibrium constant for the decomposition of PCl_5 to PCl_3 and Cl_2 at this temperature.

55. At 1 atm and 25 °C, NO_2 with an initial concentration of 1.00 *M* is 0.0033% decomposed into NO and O_2. Calculate the value of the equilibrium constant for the reaction.

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

56. Calculate the value of the equilibrium constant K_P for the reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ from these equilibrium pressures: NO, 0.050 atm; Cl_2, 0.30 atm; NOCl, 1.2 atm.

57. When heated, iodine vapor dissociates according to this equation:

$$I_2(g) \rightleftharpoons 2I(g)$$

At 1274 K, a sample exhibits a partial pressure of I_2 of 0.1122 atm and a partial pressure due to I atoms of 0.1378 atm. Determine the value of the equilibrium constant, K_P, for the decomposition at 1274 K.

58. A sample of ammonium chloride was heated in a closed container.

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

At equilibrium, the pressure of $NH_3(g)$ was found to be 1.75 atm. What is the value of the equilibrium constant K_P for the decomposition at this temperature?

59. At a temperature of 60 °C, the vapor pressure of water is 0.196 atm. What is the value of the equilibrium constant K_P for the vaporization equilibrium at 60 °C?

$$H_2O(l) \rightleftharpoons H_2O(g)$$

60. Complete the changes in concentrations (or pressure, if requested) for each of the following reactions.

(a)

$2SO_3(g)$	$\rightleftharpoons$	$2SO_2(g) +$	$O_2(g)$
___		___	$+x$
___		___	0.125 *M*

(b)

$4NH_3(g)$	$+ 3O_2(g)$	$\rightleftharpoons$	$2N_2(g) +$	$6H_2O(g)$
___	$3x$		___	___
___	0.24 *M*		___	___

(c) Change in pressure:

$2CH_4(g)$	$\rightleftharpoons$	$C_2H_2(g) +$	$3H_2(g)$
___		x	___
___		25 torr	___

(d) Change in pressure:

$CH_4(g) +$	$H_2O(g)$	$\rightleftharpoons$	$CO(g) +$	$3H_2(g)$
___	x		___	___
___	5 atm		___	___

(e)

$NH_4Cl(s)$	$\rightleftharpoons$	$NH_3(g) +$	$HCl(g)$
		x	___
		1.03×10^{-4} *M*	___

(f) change in pressure:

$Ni(s) +$	$4CO(g)$	$\rightleftharpoons$	$Ni(CO)_4(g)$
	$4x$		___
	0.40 atm		___

61. Complete the changes in concentrations (or pressure, if requested) for each of the following reactions.

(a)

$$\begin{array}{llll} 2H_2(g) + & O_2(g) & \rightleftharpoons & 2H_2O(g) \\ \_\_\_ & \_\_\_ & & +2x \\ \_\_\_ & \_\_\_ & & 1.50\ M \end{array}$$

(b)

$$\begin{array}{llllll} CS_2(g) + & 4H_2(g) & \rightleftharpoons & CH_4(g) + & 2H_2S(g) \\ x & \_\_\_ & & \_\_\_ & \_\_\_ \\ 0.020\ M & \_\_\_ & & \_\_\_ & \_\_\_ \end{array}$$

(c) Change in pressure:

$$\begin{array}{llll} H_2(g) + & Cl_2(g) & \rightleftharpoons & 2HCl(g) \\ x & \_\_\_ & & \_\_\_ \\ 1.50\text{ atm} & \_\_\_ & & \_\_\_ \end{array}$$

(d) Change in pressure:

$$\begin{array}{lllll} 2NH_3(g) & +\,2O_2(g) & \rightleftharpoons & N_2O(g) + & 3H_2O(g) \\ \_\_\_ & \_\_\_ & & \_\_\_ & x \\ \_\_\_ & \_\_\_ & & \_\_\_ & 60.6\text{ torr} \end{array}$$

(e)

$$\begin{array}{llll} NH_4HS(s) & \rightleftharpoons & NH_3(g) + & H_2S(g) \\ & & x & \_\_\_ \\ & & 9.8 \times 10^{-6}\ M & \_\_\_ \end{array}$$

(f) Change in pressure:

$$\begin{array}{llll} Fe(s) + & 5CO(g) & \rightleftharpoons & Fe(CO)_5(g) \\ & \_\_\_ & & x \\ & \_\_\_ & & 0.012\text{ atm} \end{array}$$

62. Why are there no changes specified for Ni in **Exercise 13.60**, part (f)? What property of Ni does change?

63. Why are there no changes specified for NH_4HS in **Exercise 13.61**, part (e)? What property of NH_4HS does change?

64. Analysis of the gases in a sealed reaction vessel containing NH_3, N_2, and H_2 at equilibrium at 400 °C established the concentration of N_2 to be 1.2 *M* and the concentration of H_2 to be 0.24 *M*.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 0.50 \text{ at } 400\ °C$$

Calculate the equilibrium molar concentration of NH_3.

65. Calculate the number of moles of HI that are at equilibrium with 1.25 mol of H_2 and 1.25 mol of I_2 in a 5.00−L flask at 448 °C.

$$H_2 + I_2 \rightleftharpoons 2HI \qquad K_c = 50.2 \text{ at } 448\ °C$$

66. What is the pressure of BrCl in an equilibrium mixture of Cl_2, Br_2, and BrCl if the pressure of Cl_2 in the mixture is 0.115 atm and the pressure of Br_2 in the mixture is 0.450 atm?

$$Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g) \qquad K_P = 4.7 \times 10^{-2}$$

67. What is the pressure of CO_2 in a mixture at equilibrium that contains 0.50 atm H_2, 2.0 atm of H_2O, and 1.0 atm of CO at 990 °C?

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \qquad K_P = 1.6 \text{ at } 990\ °C$$

68. Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.

$$\mathrm{CoO}(s) + \mathrm{CO}(g) \rightleftharpoons \mathrm{Co}(s) + \mathrm{CO_2}(g) \qquad K_c = 4.90 \times 10^2 \text{ at } 550\ °\mathrm{C}$$

What concentration of CO remains in an equilibrium mixture with $[CO_2] = 0.100\ M$?

69. Carbon reacts with water vapor at elevated temperatures.

$$\mathrm{C}(s) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{H_2}(g) \qquad K_c = 0.2 \text{ at } 1000\ °\mathrm{C}$$

Assuming a reaction mixture initially contains only reactants, what is the concentration of CO in an equilibrium mixture with $[H_2O] = 0.500\ M$ at 1000 °C?

70. Sodium sulfate 10−hydrate, $Na_2SO_4{\cdot}10H_2O$, dehydrates according to the equation

$$\mathrm{Na_2SO_4{\cdot}10H_2O}(s) \rightleftharpoons \mathrm{Na_2SO_4}(s) + \mathrm{10H_2O}(g) \qquad K_P = 4.08 \times 10^{-25} \text{ at } 25\ °\mathrm{C}$$

What is the pressure of water vapor at equilibrium with a mixture of $Na_2SO_4{\cdot}10H_2O$ and $NaSO_4$?

71. Calcium chloride 6−hydrate, $CaCl_2{\cdot}6H_2O$, dehydrates according to the equation

$$\mathrm{CaCl_2{\cdot}6H_2O}(s) \rightleftharpoons \mathrm{CaCl_2}(s) + \mathrm{6H_2O}(g) \qquad K_P = 5.09 \times 10^{-44} \text{ at } 25\ °\mathrm{C}$$

What is the pressure of water vapor at equilibrium with a mixture of $CaCl_2{\cdot}6H_2O$ and $CaCl_2$ at 25 °C?

72. A student solved the following problem and found the equilibrium concentrations to be $[SO_2] = 0.590\ M$, $[O_2] = 0.0450\ M$, and $[SO_3] = 0.260\ M$. How could this student check the work without reworking the problem? The problem was: For the following reaction at 600 °C:

$$\mathrm{2SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons \mathrm{2SO_3}(g) \qquad K_c = 4.32$$

What are the equilibrium concentrations of all species in a mixture that was prepared with $[SO_3] = 0.500\ M$, $[SO_2] = 0\ M$, and $[O_2] = 0.350\ M$?

73. A student solved the following problem and found $[N_2O_4] = 0.16\ M$ at equilibrium. How could this student recognize that the answer was wrong without reworking the problem? The problem was: What is the equilibrium concentration of N_2O_4 in a mixture formed from a sample of NO_2 with a concentration of 0.10 M?

$$\mathrm{2NO_2}(g) \rightleftharpoons \mathrm{N_2O_4}(g) \qquad K_c = 160$$

74. Assume that the change in concentration of N_2O_4 is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of both species in 1.00 L of a solution prepared from 0.129 mol of N_2O_4 with chloroform as the solvent.

$$\mathrm{N_2O_4}(g) \rightleftharpoons \mathrm{2NO_2}(g) \qquad K_c = 1.07 \times 10^{-5} \text{ in chloroform}$$

(b) Confirm that the change is small enough to be neglected.

75. Assume that the change in concentration of $COCl_2$ is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of all species in an equilibrium mixture that results from the decomposition of $COCl_2$ with an initial concentration of 0.3166 M.

$$\mathrm{COCl_2}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{Cl_2}(g) \qquad K_c = 2.2 \times 10^{-10}$$

(b) Confirm that the change is small enough to be neglected.

76. Assume that the change in pressure of H_2S is small enough to be neglected in the following problem.

(a) Calculate the equilibrium pressures of all species in an equilibrium mixture that results from the decomposition of H_2S with an initial pressure of 0.824 atm.

$$\mathrm{2H_2S}(g) \rightleftharpoons \mathrm{2H_2}(g) + \mathrm{S_2}(g) \qquad K_P = 2.2 \times 10^{-6}$$

(b) Confirm that the change is small enough to be neglected.

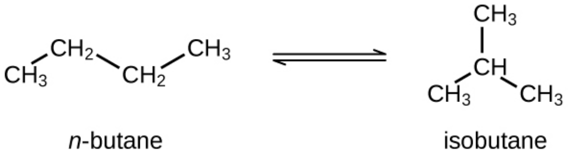
77. What are all concentrations after a mixture that contains $[H_2O] = 1.00\ M$ and $[Cl_2O] = 1.00\ M$ comes to equilibrium at 25 °C?

$$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g) \qquad K_c = 0.0900$$

78. Calculate the number of grams of HI that are at equilibrium with 1.25 mol of H_2 and 63.5 g of iodine at 448 °C.

$$H_2 + I_2 \rightleftharpoons 2HI \qquad K_c = 50.2 \text{ at } 448\ °C$$

79. Butane exists as two isomers, *n*−butane and isobutane.



$K_P = 2.5$ at 25 °C

What is the pressure of isobutane in a container of the two isomers at equilibrium with a total pressure of 1.22 atm?

80. What is the minimum mass of $CaCO_3$ required to establish equilibrium at a certain temperature in a 6.50-L container if the equilibrium constant (K_c) is 0.50 for the decomposition reaction of $CaCO_3$ at that temperature?

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

81. The equilibrium constant (K_c) for this reaction is 1.60 at 990 °C:

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

Calculate the number of moles of each component in the final equilibrium mixture obtained from adding 1.00 mol of H_2, 2.00 mol of CO_2, 0.750 mol of H_2O, and 1.00 mol of CO to a 5.00-L container at 990 °C.

82. In a 3.0-L vessel, the following equilibrium partial pressures are measured: N_2, 190 torr; H_2, 317 torr; NH_3, 1.00×10^3 torr.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(a) How will the partial pressures of H_2, N_2, and NH_3 change if H_2 is removed from the system? Will they increase, decrease, or remain the same?

(b) Hydrogen is removed from the vessel until the partial pressure of nitrogen, at equilibrium, is 250 torr. Calculate the partial pressures of the other substances under the new conditions.

83. The equilibrium constant (K_c) for this reaction is 5.0 at a given temperature.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

(a) On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of CO, 0.30 mol of water vapor, and 0.90 mol of H_2 in a liter. How many moles of CO_2 were there in the equilibrium mixture?

(b) Maintaining the same temperature, additional H_2 was added to the system, and some water vapor was removed by drying. A new equilibrium mixture was thereby established containing 0.40 mol of CO, 0.30 mol of water vapor, and 1.2 mol of H_2 in a liter. How many moles of CO_2 were in the new equilibrium mixture? Compare this with the quantity in part (a), and discuss whether the second value is reasonable. Explain how it is possible for the water vapor concentration to be the same in the two equilibrium solutions even though some vapor was removed before the second equilibrium was established.

84. Antimony pentachloride decomposes according to this equation:

$$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$$

An equilibrium mixture in a 5.00-L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2. How many grams of each will be found if the mixture is transferred into a 2.00-L flask at the same temperature?

85. Consider the equilibrium

$$4NO_2(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 7O_2(g)$$

(a) What is the expression for the equilibrium constant (K_c) of the reaction?

(b) How must the concentration of NH_3 change to reach equilibrium if the reaction quotient is less than the equilibrium constant?

(c) If the reaction were at equilibrium, how would an increase in the volume of the reaction vessel affect the pressure of NO_2?

(d) If the change in the pressure of NO_2 is 28 torr as a mixture of the four gases reaches equilibrium, how much will the pressure of O_2 change?

86. The binding of oxygen by hemoglobin (Hb), giving oxyhemoglobin (HbO_2), is partially regulated by the concentration of H_3O^+ and dissolved CO_2 in the blood. Although the equilibrium is complicated, it can be summarized as

$$HbO_2(aq) + H_3O^+(aq) + CO_2(g) \rightleftharpoons CO_2{-}Hb{-}H^+ + O_2(g) + H_2O(l)$$

(a) Write the equilibrium constant expression for this reaction.

(b) Explain why the production of lactic acid and CO_2 in a muscle during exertion stimulates release of O_2 from the oxyhemoglobin in the blood passing through the muscle.

87. Liquid N_2O_3 is dark blue at low temperatures, but the color fades and becomes greenish at higher temperatures as the compound decomposes to NO and NO_2. At 25 °C, a value of $K_P = 1.91$ has been established for this decomposition. If 0.236 moles of N_2O_3 are placed in a 1.52-L vessel at 25 °C, calculate the equilibrium partial pressures of $N_2O_3(g)$, $NO_2(g)$, and $NO(g)$.

88. A 1.00-L vessel at 400 °C contains the following equilibrium concentrations: N_2, 1.00 M; H_2, 0.50 M; and NH_3, 0.25 M. How many moles of hydrogen must be removed from the vessel to increase the concentration of nitrogen to 1.1 M? The equilibrium reaction is

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

89. Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

(a) $I_2(s) + Cl_2(g) \longrightarrow 2ICl(g) \qquad \Delta G° = -10.88\text{ kJ}$

(b) $H_2(g) + I_2(s) \longrightarrow 2HI(g) \qquad \Delta G° = 3.4\text{ kJ}$

(c) $CS_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g) \qquad \Delta G° = -39\text{ kJ}$

(d) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) \qquad \Delta G° = -141.82\text{ kJ}$

(e) $CS_2(g) \longrightarrow CS_2(l) \qquad \Delta G° = -1.88\text{ kJ}$

90. Calculate the equilibrium constant at the temperature given.

(a) $O_2(g) + 2F_2(g) \longrightarrow 2F_2O(g) \qquad (T = 100\text{ °C})$

(b) $I_2(s) + Br_2(l) \longrightarrow 2IBr(g) \qquad (T = 0.0\text{ °C})$

(c) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g) \qquad (T = 575\text{ °C})$

(d) $N_2O_3(g) \longrightarrow NO(g) + NO_2(g) \qquad (T = -10.0\text{ °C})$

(e) $SnCl_4(l) \longrightarrow SnCl_4(g) \qquad (T = 200\text{ °C})$

91. Calculate the equilibrium constant at the temperature given.

(a) $I_2(s) + Cl_2(g) \longrightarrow 2ICl(g)$ (T = 100 °C)

(b) $H_2(g) + I_2(s) \longrightarrow 2HI(g)$ (T = 0.0 °C)

(c) $CS_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g)$ (T = 125 °C)

(d) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$ (T = 675 °C)

(e) $CS_2(g) \longrightarrow CS_2(l)$ (T = 90 °C)

92. Consider the following reaction at 298 K:
$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_P = 0.142$

What is the standard free energy change at this temperature? Describe what happens to the initial system, where the reactants and products are in standard states, as it approaches equilibrium.

93. Determine the normal boiling point (in kelvin) of dichloroethane, CH_2Cl_2. Find the actual boiling point using the Internet or some other source, and calculate the percent error in the temperature. Explain the differences, if any, between the two values.

94. Under what conditions is $N_2O_3(g) \longrightarrow NO(g) + NO_2(g)$ spontaneous?

95. At room temperature, the equilibrium constant (K_w) for the self-ionization of water is 1.00×10^{-14}. Using this information, calculate the standard free energy change for the aqueous reaction of hydrogen ion with hydroxide ion to produce water. (Hint: The reaction is the reverse of the self-ionization reaction.)

96. Hydrogen sulfide is a pollutant found in natural gas. Following its removal, it is converted to sulfur by the reaction $2H_2S(g) + SO_2(g) \rightleftharpoons \frac{3}{8}S_8(s,\ \text{rhombic}) + 2H_2O(l)$. What is the equilibrium constant for this reaction? Is the reaction endothermic or exothermic?

97. Consider the decomposition of $CaCO_3(s)$ into $CaO(s)$ and $CO_2(g)$. What is the equilibrium partial pressure of CO_2 at room temperature?

98. In the laboratory, hydrogen chloride ($HCl(g)$) and ammonia ($NH_3(g)$) often escape from bottles of their solutions and react to form the ammonium chloride ($NH_4Cl(s)$), the white glaze often seen on glassware. Assuming that the number of moles of each gas that escapes into the room is the same, what is the maximum partial pressure of HCl and NH_3 in the laboratory at room temperature? (Hint: The partial pressures will be equal and are at their maximum value when at equilibrium.)

99. Benzene can be prepared from acetylene. $3C_2H_2(g) \rightleftharpoons C_6H_6(g)$. Determine the equilibrium constant at 25 °C and at 850 °C. Is the reaction spontaneous at either of these temperatures? Why is all acetylene not found as benzene?

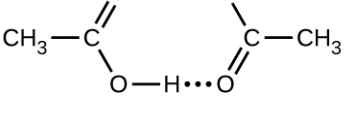
100. Carbon dioxide decomposes into CO and O_2 at elevated temperatures. What is the equilibrium partial pressure of oxygen in a sample at 1000 °C for which the initial pressure of CO_2 was 1.15 atm?

101. Carbon tetrachloride, an important industrial solvent, is prepared by the chlorination of methane at 850 K.
$CH_4(g) + 4Cl_2(g) \longrightarrow CCl_4(g) + 4HCl(g)$

What is the equilibrium constant for the reaction at 850 K? Would the reaction vessel need to be heated or cooled to keep the temperature of the reaction constant?

102. Acetic acid, CH_3CO_2H, can form a dimer, $(CH_3CO_2H)_2$, in the gas phase.
$2CH_3CO_2H(g) \longrightarrow (CH_3CO_2H)_2(g)$

The dimer is held together by two hydrogen bonds with a total strength of 66.5 kJ per mole of dimer.



At 25 °C, the equilibrium constant for the dimerization is 1.3×10^3 (pressure in atm). What is $\Delta S°$ for the reaction?

Chapter 14

Acid-Base Equilibria

Figure 14.1 Sinkholes such as this are the result of reactions between acidic groundwaters and basic rock formations, like limestone. (credit: modification of work by Emil Kehnel)

Chapter Outline

Introduction

Liquid water is essential to life on our planet, and chemistry involving the characteristic ions of water, H^+ and OH^-, is widely encountered in nature and society. As introduced in another chapter of this text, acid-base chemistry involves the transfer of hydrogen ions from donors (acids) to acceptors (bases). These H+ transfer reactions are reversible, and the equilibria established by acid-base systems are essential aspects of phenomena ranging from sinkhole formation (**Figure 14.1**) to oxygen transport in the human body. This chapter will further explore acid-base chemistry with an emphasis on the equilibrium aspects of this important reaction class.

14.1 Brønsted-Lowry Acids and Bases

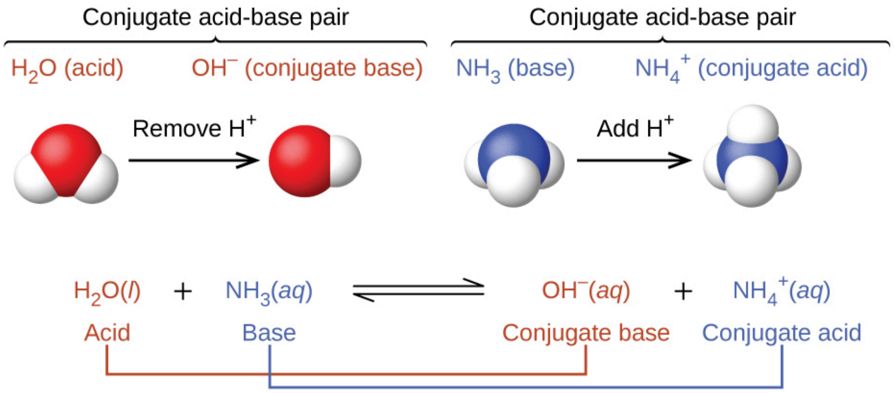
By the end of this section, you will be able to:

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

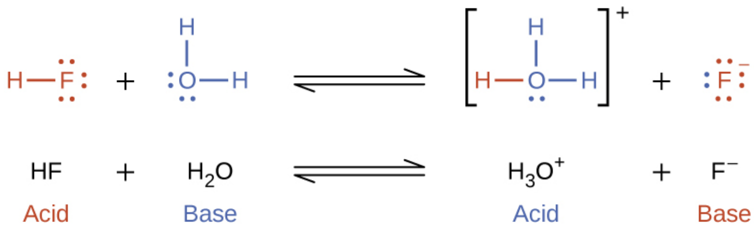
The acid-base reaction class has been studied for quite some time. In 1680, Robert Boyle reported traits of acid solutions that included their ability to dissolve many substances, to change the colors of certain natural dyes, and to lose these traits after coming in contact with alkali (base) solutions. In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Johannes Brønsted and Thomas Lowry proposed a more general description in 1923 in which acids and bases were defined in terms of the transfer of hydrogen ions, H^+. (Note that these hydrogen ions are often referred to simply as *protons*, since that subatomic particle is the only component of cations derived from the most abundant hydrogen isotope, ^1H.) A compound that donates a proton to another compound is called a **Brønsted-Lowry acid**, and a compound that accepts a proton is called a **Brønsted-Lowry base**. An acid-base reaction is, thus, the transfer of a proton from a donor (acid) to an acceptor (base).

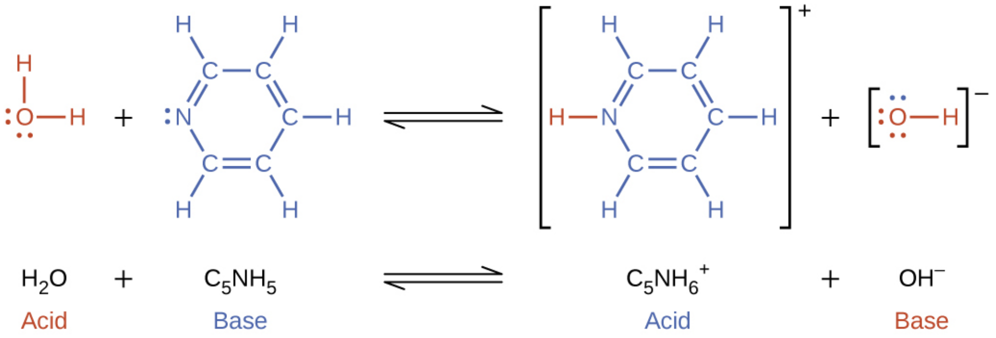
The concept of *conjugate pairs* is useful in describing Brønsted-Lowry acid-base reactions (and other reversible reactions, as well). When an acid donates H^+, the species that remains is called the **conjugate base** of the acid because it reacts as a proton acceptor in the reverse reaction. Likewise, when a base accepts H^+, it is converted to its **conjugate acid**. The reaction between water and ammonia illustrates this idea. In the forward direction, water acts as an acid by donating a proton to ammonia and subsequently becoming a hydroxide ion, OH^-, the conjugate base of water. The ammonia acts as a base in accepting this proton, becoming an ammonium ion, $NH_4{}^+$, the conjugate acid of ammonia. In the reverse direction, a hydroxide ion acts as a base in accepting a proton from ammonium ion, which acts as an acid.



The reaction between a Brønsted-Lowry acid and water is called **acid ionization**. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



Base ionization of a species occurs when it accepts protons from water molecules. In the example below, pyridine molecules, C_5NH_5, undergo base ionization when dissolved in water, yielding hydroxide and pyridinium ions:

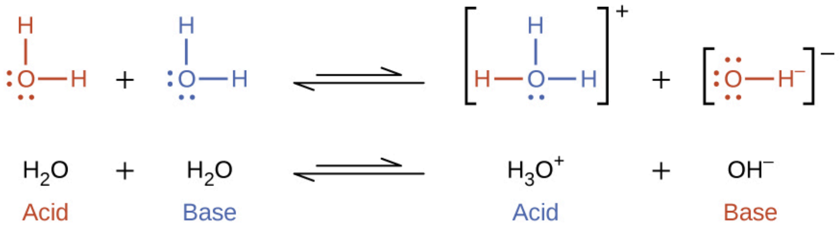


The preceding ionization reactions suggest that water may function as both a base (as in its reaction with hydrogen fluoride) and an acid (as in its reaction with ammonia). Species capable of either donating or accepting protons are called **amphiprotric**, or more generally, **amphoteric**, a term that may be used for acids and bases per definitions other than the Brønsted-Lowry one. The equations below show the two possible acid-base reactions for two amphiprotic species, bicarbonate ion and water:

$$HCO_3{}^-(aq) + H_2O(l) \qquad\qquad CO_3{}^{2-}(aq) + H_3O^+(aq)$$
$$HCO_3{}^-(aq) + H_2O(l) \qquad\qquad H_2CO_3(aq) + OH^-(aq)$$

The first equation represents the reaction of bicarbonate as an acid with water as a base, whereas the second represents reaction of bicarbonate as a base with water as an acid. When bicarbonate is added to water, both these equilibria are established simultaneously and the composition of the resulting solution may be determined through appropriate equilibrium calculations, as described later in this chapter.

In the liquid state, molecules of an amphiprotic substance can react with one another as illustrated for water in the equations below:



The process in which like molecules react to yield ions is called **autoionization**. Liquid water undergoes autoionization to a very slight extent; at 25 °C, approximately two out of every billion water molecules are ionized. The extent of the water autoionization process is reflected in the value of its equilibrium constant, the **ion-product constant for water, K_w**:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad\qquad K_w = [H_3O^+][OH^-]$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, K_w has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is about 5.6 ×

10^{-13}, roughly 50 times larger than the value at 25 °C.

Example 14.1

Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-] = x$. At 25 °C:

$$K_w = [H_3O^+][OH^-] = x = 1.0 \times 10^{-14}$$

So:

$$x = [H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, 1.0×10^{-7} M.

Check Your Learning

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer: $[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$

Example 14.2

The Inverse Relation between $[H_3O^+]$ and $[OH^-]$

A solution of an acid in water has a hydronium ion concentration of 2.0×10^{-6} M. What is the concentration of hydroxide ion at 25 °C?

Solution

Use the value of the ion-product constant for water at 25 °C

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

to calculate the missing equilibrium concentration.

Rearrangement of the K_w expression shows that $[OH^-]$ is inversely proportional to $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

Compared with pure water, a solution of acid exhibits a higher concentration of hydronium ions (due to ionization of the acid) and a proportionally lower concentration of hydroxide ions. This may be explained via Le Châtelier's principle as a left shift in the water autoionization equilibrium resulting from the stress of increased hydronium ion concentration.

Substituting the ion concentrations into the K_w expression confirms this calculation, resulting in the expected value:

$$K_w = [H_3O^+][OH^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Check Your Learning

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 *M* at 25 °C?

Answer: $[H_3O^+] = 1 \times 10^{-11}\ M$

Example 14.3

Representing the Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of $HSO_3{}^-$

(a) as an acid with OH^-

(b) as a base with HI

Solution

(a) $HSO_3{}^-(aq) + OH^-(aq) \rightleftharpoons SO_3{}^{2-}(aq) + H_2O(l)$

(b) $HSO_3{}^-(aq) + HI(aq) \rightleftharpoons H_2SO_3(aq) + I^-(aq)$

Check Your Learning

Write separate equations representing the reaction of $H_2PO_4{}^-$

(a) as a base with HBr

(b) as an acid with OH^-

Answer: (a) $H_2PO_4{}^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)$; (b) $H_2PO_4{}^-(aq) + OH^-(aq) \rightleftharpoons HPO_4{}^{2-}(aq) + H_2O(l)$

14.2 pH and pOH

By the end of this section, you will be able to:

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is **neutral** if it contains equal concentrations of hydronium and hydroxide ions; **acidic** if it contains a greater concentration of hydronium ions than hydroxide ions; and **basic** if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities that may span many orders of magnitude is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$\text{pX} = -\log \text{X}$$

The **pH** of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or **pOH**:

$$\text{pOH} = -\log[\text{OH}^-]$$

or

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$K_\text{w} = [\text{H}_3\text{O}^+][\text{OH}^-]$$
$$-\log K_\text{w} = -\log\left([\text{H}_3\text{O}^+][\text{OH}^-]\right) = -\log[\text{H}_3\text{O}^+] + -\log[\text{OH}^-]$$
$$\text{p}K_\text{w} = \text{pH} + \text{pOH}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = \text{pH} + \text{pOH}$$

As was shown in **Example 14.1**, the hydronium ion molarity in pure water (or any neutral solution) is 1.0×10^{-7} *M* at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.0 \times 10^{-7}) = 7.00$$
$$\text{pOH} = -\log[\text{OH}^-] = -\log(1.0 \times 10^{-7}) = 7.00$$

And so, *at this temperature*, acidic solutions are those with hydronium ion molarities greater than 1.0×10^{-7} *M* and hydroxide ion molarities less than 1.0×10^{-7} *M* (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than 1.0×10^{-7} *M* and hydroxide ion molarities greater than 1.0×10^{-7} *M* (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the “Check Your Learning” exercise accompanying **Example 14.1** showed the hydronium molarity of pure water at 80 °C is 4.9×10^{-7} *M*, which corresponds to pH and pOH values of:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(4.9 \times 10^{-7}) = 6.31$$
$$\text{pOH} = -\log[\text{OH}^-] = -\log(4.9 \times 10^{-7}) = 6.31$$

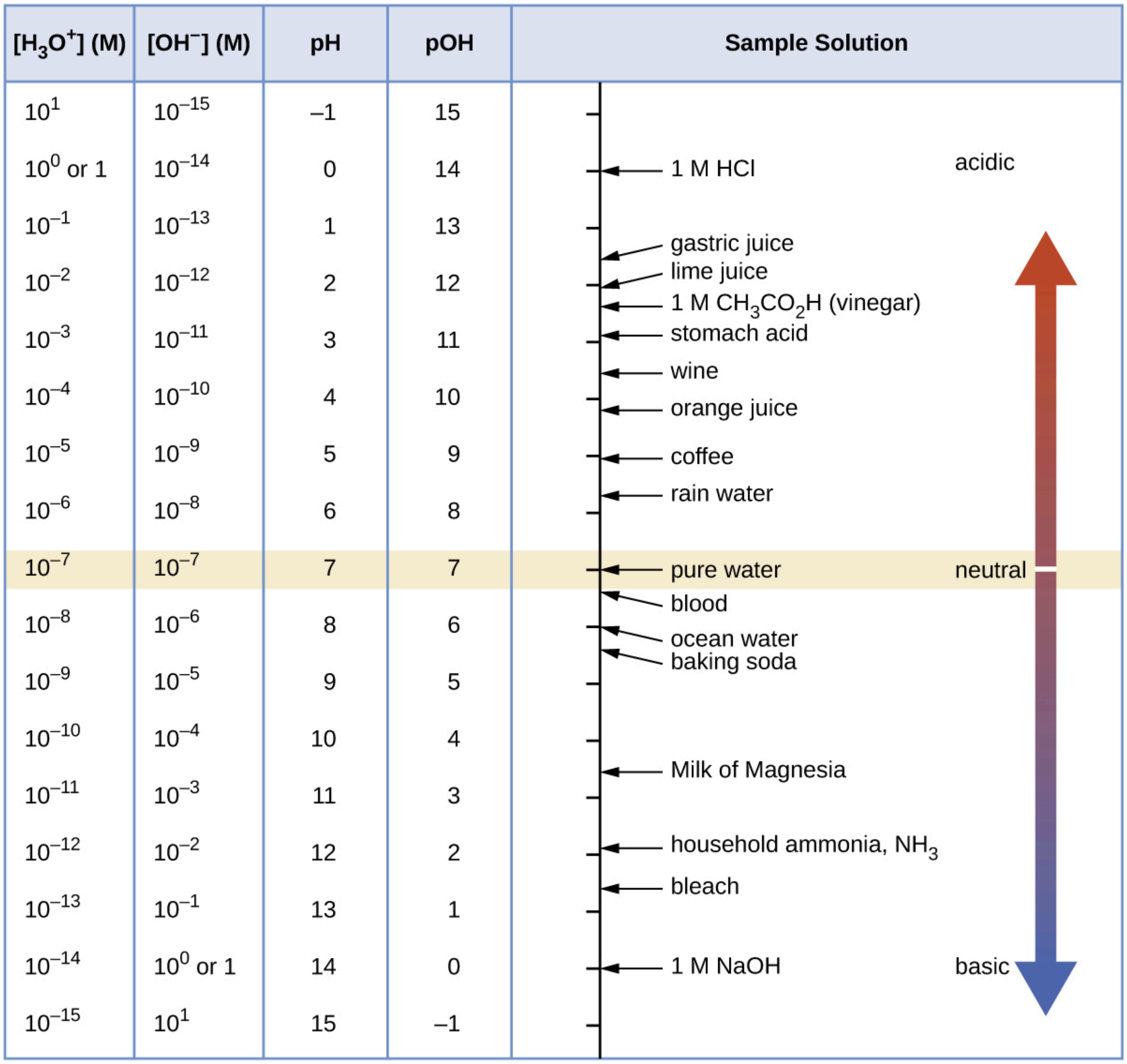
At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at other temperatures, such as enzyme reactions in warm-blooded organisms at a temperature around 36–40 °C. Unless otherwise noted, references to pH values are presumed to be those at 25 °C (**Table 14.1**).

Summary of Relations for Acidic, Basic and Neutral Solutions

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[\text{H}_3\text{O}^+] > [\text{OH}^-]$	$\text{pH} < 7$
neutral	$[\text{H}_3\text{O}^+] = [\text{OH}^-]$	$\text{pH} = 7$
basic	$[\text{H}_3\text{O}^+] < [\text{OH}^-]$	$\text{pH} > 7$

Table 14.1

Figure 14.2 shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH for solutions classified as acidic, basic, and neutral.



$[H_3O^+]$ (M)	$[OH^-]$ (M)	pH	pOH
10^{1}	10^{-15}	–1	15
10^{0} or 1	10^{-14}	0	14
10^{-1}	10^{-13}	1	13
10^{-2}	10^{-12}	2	12
10^{-3}	10^{-11}	3	11
10^{-4}	10^{-10}	4	10
10^{-5}	10^{-9}	5	9
10^{-6}	10^{-8}	6	8
10^{-7}	10^{-7}	7	7
10^{-8}	10^{-6}	8	6
10^{-9}	10^{-5}	9	5
10^{-10}	10^{-4}	10	4
10^{-11}	10^{-3}	11	3
10^{-12}	10^{-2}	12	2
10^{-13}	10^{-1}	13	1
10^{-14}	10^{0} or 1	14	0
10^{-15}	10^{1}	15	–1

Figure 14.2 The pH and pOH scales represent concentrations of H_3O^+ and OH^-, respectively. The pH and pOH values of some common substances at 25 °C are shown in this chart.

Example 14.4

Calculation of pH from $[H_3O^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of 1.2×10^{-3} *M*?

Solution

$$\text{pH} = -\log[H_3O^+]$$

$$= -\log(1.2 \times 10^{-3})$$

$$= -(-2.92) = 2.92$$

(The use of logarithms is explained in **Appendix B**. When taking the log of a value, keep as many decimal places in the result as there are significant figures in the value.)

Check Your Learning

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$\mathrm{CO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2CO_3}(aq)$$

Air-saturated water has a hydronium ion concentration caused by the dissolved CO_2 of 2.0×10^{-6} *M*, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer: 5.70

Example 14.5

Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3.

Solution

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = 7.3$$

$$\log[\mathrm{H_3O^+}] = -7.3$$

$$[\mathrm{H_3O^+}] = 10^{-7.3} \text{ or } [\mathrm{H_3O^+}] = \text{antilog of } -7.3$$

$$[\mathrm{H_3O^+}] = 5 \times 10^{-8}\ M$$

(On a calculator take the antilog, or the “inverse” log, of −7.3, or calculate $10^{-7.3}$.)

Check Your Learning

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

Answer: 12 *M*

How Sciences Interconnect

Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$\mathrm{H_2O}(l) + \mathrm{CO_2}(g) \longrightarrow \mathrm{H_2CO_3}(aq)$$
$$\mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{HCO_3}^-(aq)$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$\mathrm{H_2O}(l) + \mathrm{SO_3}(g) \longrightarrow \mathrm{H_2SO_4}(aq)$$
$$\mathrm{H_2SO_4}(aq) \longrightarrow \mathrm{H^+}(aq) + \mathrm{HSO_4}^-(aq)$$

Carbon dioxide is naturally present in the atmosphere because most organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also originates from burning fossil fuels, which have traces of sulfur, and from the process of “roasting” ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (**Figure 14.3**). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

For further information on acid rain, visit this **website (http://openstaxcollege.org/l/16EPA)** hosted by the US Environmental Protection Agency.

Figure 14.3 (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr)

Example 14.6

Calculation of pOH

What are the pOH and the pH of a 0.0125-*M* solution of potassium hydroxide, KOH?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[OH^-] = 0.0125\ M$:

$$\begin{aligned} \text{pOH} &= -\log[\text{OH}^-] = -\log 0.0125 \\ &= -(-1.903) = 1.903 \end{aligned}$$

The pH can be found from the pOH:

$$\text{pH} + \text{pOH} = 14.00$$
$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.903 = 12.10$$

Check Your Learning

The hydronium ion concentration of vinegar is approximately 4×10^{-3} *M*. What are the corresponding values of pOH and pH?

Answer: pOH = 11.6, pH = 2.4

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (**Figure 14.4**).

(a) (b)

Figure 14.4 (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

The pH of a solution may also be visually estimated using colored indicators (**Figure 14.5**). The acid-base equilibria that enable use of these indicator dyes for pH measurements are described in a later section of this chapter.

(a) (b)

Figure 14.5 (a) A solution containing a dye mixture, called universal indicator, takes on different colors depending upon its pH. (b) Convenient test strips, called pH paper, contain embedded indicator dyes that yield pH-dependent color changes on contact with aqueous solutions.(credit: modification of work by Sahar Atwa)

14.3 Relative Strengths of Acids and Bases

By the end of this section, you will be able to:

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

Acid and Base Ionization Constants

The relative strength of an acid or base is the extent to which it ionizes when dissolved in water. If the ionization reaction is essentially complete, the acid or base is termed *strong*; if relatively little ionization occurs, the acid or base is weak. As will be evident throughout the remainder of this chapter, there are many more weak acids and bases than strong ones. The most common strong acids and bases are listed in **Figure 14.6**.

6 Strong Acids		6 Strong Bases	
$HClO_4$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$Ca(OH)_2$	calcium hydroxide
HNO_3	nitric acid	$Sr(OH)_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	barium hydroxide

Figure 14.6 Some of the common strong acids and bases are listed here.

The relative strengths of acids may be quantified by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the **acid-ionization constant, K_a**. For the reaction of an acid HA:

$$\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq),$$

the acid ionization constant is written

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

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include $[H_2O]$ in the equation. The larger the K_a of an acid, the larger the concentration of H_3O^+ and A^- relative to the concentration of the nonionized acid, HA, in an equilibrium mixture, and the stronger the acid. An acid is classified as “strong” when it undergoes complete ionization, in which case the concentration of HA is zero and the acid ionization constant is immeasurably large ($K_a \approx \infty$). Acids that are partially ionized are called “weak,” and their acid ionization constants may be experimentally measured. A table of ionization constants for weak acids is provided in Appendix H.

To illustrate this idea, three acid ionization equations and K_a values are shown below. The ionization constants increase from first to last of the listed equations, indicating the relative acid strength increases in the order $CH_3CO_2H < HNO_2 < HSO_4{}^-$:

$$\begin{array}{rcl} \text{CH}_3\text{CO}_2\text{H}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{CO}_2{}^-(aq) & & K_a = 1.8 \times 10^{-5} \\ \text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NO}_2{}^-(aq) & & K_a = 4.6 \times 10^{-4} \\ \text{HSO}_4{}^-(aq) + \text{H}_2\text{O}(aq) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{SO}_4{}^{2-}(aq) & & K_a = 1.2 \times 10^{-2} \end{array}$$

Another measure of the strength of an acid is its percent ionization. The **percent ionization** of a weak acid is defined in terms of the composition of an equilibrium mixture:

$$\%\ \text{ionization} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HA}]_0} \times 100$$

where the numerator is equivalent to the concentration of the acid's conjugate base (per stoichiometry, $[A^-] = [H_3O^+]$). Unlike the K_a value, the percent ionization of a weak acid varies with the initial concentration of acid, typically decreasing as concentration increases. Equilibrium calculations of the sort described later in this chapter can be used to confirm this behavior.

Example 14.7

Calculation of Percent Ionization from pH

Calculate the percent ionization of a 0.125-*M* solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is:

$$\frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{HNO}_2]_0} \times 100$$

Converting the provided pH to hydronium ion molarity yields

$$[\text{H}_3\text{O}^+] = 10^{-2.09} = 0.0081\ M$$

Substituting this value and the provided initial acid concentration into the percent ionization equation gives

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

(Recall the provided pH value of 2.09 is logarithmic, and so it contains just two significant digits, limiting the certainty of the computed percent ionization.)

Check Your Learning

Calculate the percent ionization of a 0.10-*M* solution of acetic acid with a pH of 2.89.

Answer: 1.3% ionized

Link to Learning

View the simulation (http://openstaxcollege.org/l/16AcidBase) of strong and weak acids and bases at the molecular level.

Just as for acids, the relative strength of a base is reflected in the magnitude of its **base-ionization constant (K_b)** in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

$$\text{B}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HB}^+(aq) + \text{OH}^-(aq),$$

the ionization constant is written as

$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

Inspection of the data for three weak bases presented below shows the base strength increases in the order $\text{NO}_2{}^- < \text{CH}_2\text{CO}_2{}^- < \text{NH}_3$.

$$\begin{array}{lrcl}
\text{NO}_2{}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HNO}_2(aq) + \text{OH}^-(aq) & K_b & = & 2.17 \times 10^{-11} \\
\text{CH}_3\text{CO}_2{}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{CO}_2\text{H}(aq) + \text{OH}^-(aq) & K_b & = & 5.6 \times 10^{-10} \\
\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4{}^+(aq) + \text{OH}^-(aq) & K_b & = & 1.8 \times 10^{-5}
\end{array}$$

A table of ionization constants for weak bases appears in **Appendix I**. As for acids, the relative strength of a base is also reflected in its percent ionization, computed as

$$\%\ \text{ionization} = [\text{OH}^-]_{eq}/[\text{B}]_0 \times 100\%$$

but will vary depending on the base ionization constant and the initial concentration of the solution.

Relative Strengths of Conjugate Acid-Base Pairs

Brønsted-Lowry acid-base chemistry is the transfer of protons; thus, logic suggests a relation between the relative strengths of conjugate acid-base pairs. The strength of an acid or base is quantified in its ionization constant, K_a or K_b, which represents the extent of the acid or base ionization reaction. For the conjugate acid-base pair HA / A^-, ionization equilibrium equations and ionization constant expressions are

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \qquad K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$\mathrm{A^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{OH^-}(aq) + \mathrm{HA}(aq) \qquad K_\mathrm{b} = \frac{[\mathrm{HA}][\mathrm{OH}]}{[\mathrm{A^-}]}$$

Adding these two chemical equations yields the equation for the autoionization for water:

$$\cancel{\mathrm{HA}(aq)} + \mathrm{H_2O}(l) + \cancel{\mathrm{A^-}(aq)} + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \cancel{\mathrm{A^-}(aq)} + \mathrm{OH^-}(aq) + \cancel{\mathrm{HA}(aq)}$$
$$2\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq)$$

As discussed in another chapter on equilibrium, the equilibrium constant for a summed reaction is equal to the mathematical product of the equilibrium constants for the added reactions, and so

$$K_\mathrm{a} \times K_\mathrm{b} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \times \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = K_\mathrm{w}$$

This equation states the relation between ionization constants for any conjugate acid-base pair, namely, their mathematical product is equal to the ion product of water, K_w. By rearranging this equation, a reciprocal relation between the strengths of a conjugate acid-base pair becomes evident:

$$K_\mathrm{a} = K_\mathrm{w}/K_\mathrm{b} \text{ or } K_\mathrm{b} = K_\mathrm{w}/K_\mathrm{a}$$

The inverse proportional relation between K_a and K_b means *the stronger the acid or base, the weaker its conjugate partner*. **Figure 14.7** illustrates this relation for several conjugate acid-base pairs.

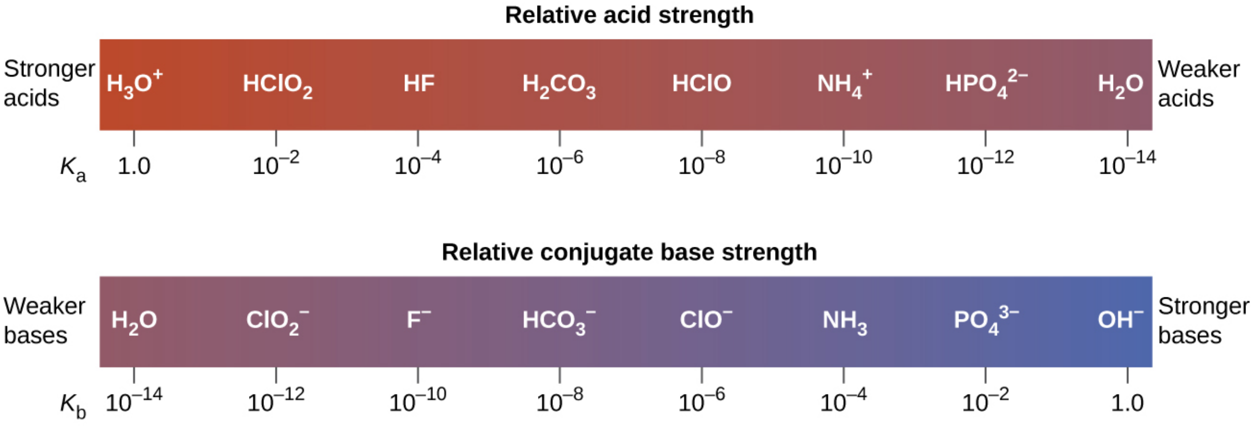
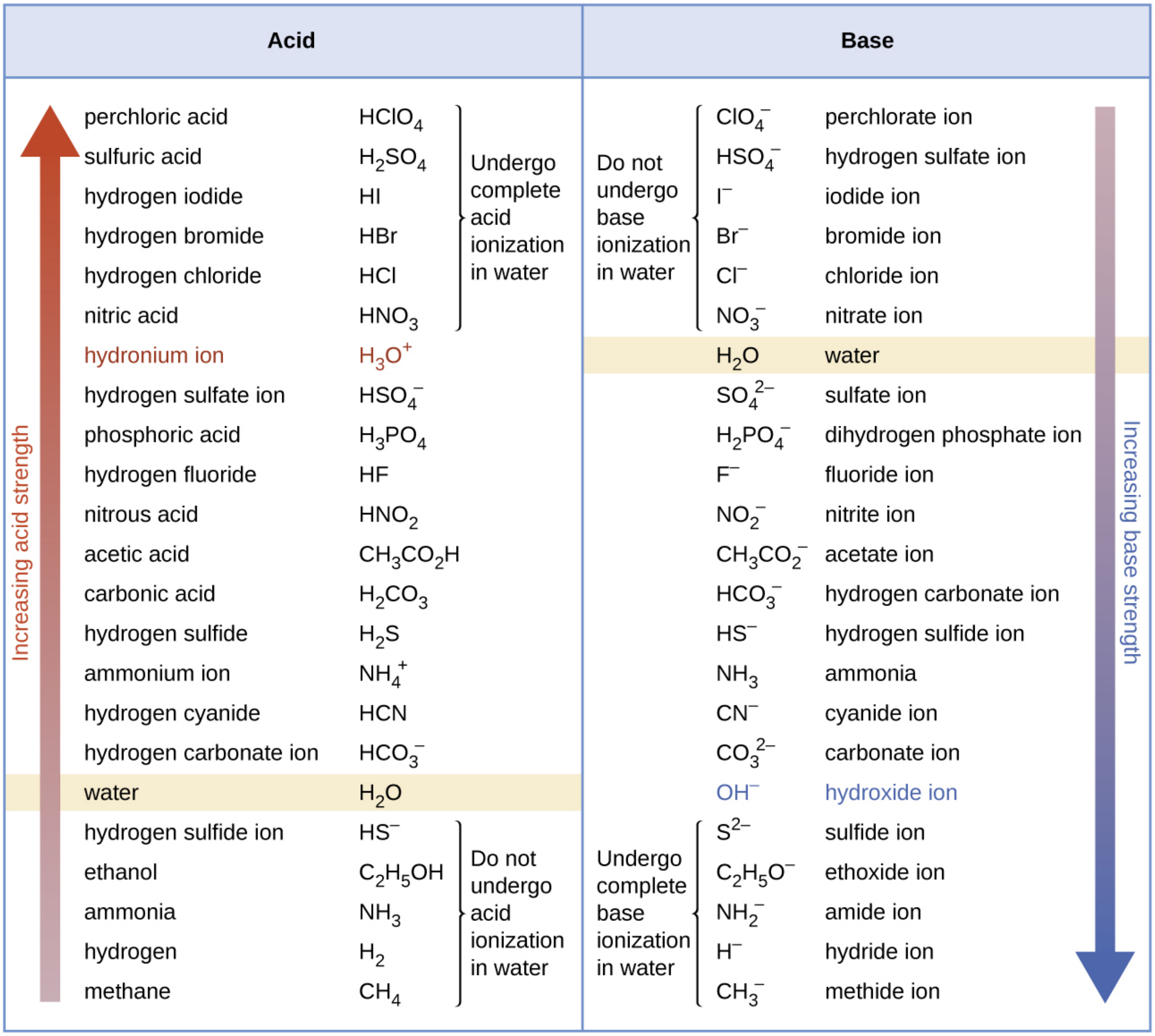


Figure 14.7 Relative strengths of several conjugate acid-base pairs are shown.



Acid					Base
perchloric acid	$HClO_4$	Undergo complete acid ionization in water	Do not undergo base ionization in water	ClO_4^-	perchlorate ion
sulfuric acid	H_2SO_4			HSO_4^-	hydrogen sulfate ion
hydrogen iodide	HI			I^-	iodide ion
hydrogen bromide	HBr			Br^-	bromide ion
hydrogen chloride	HCl			Cl^-	chloride ion
nitric acid	HNO_3			NO_3^-	nitrate ion
hydronium ion	H_3O^+			H_2O	water
hydrogen sulfate ion	HSO_4^-			SO_4^{2-}	sulfate ion
phosphoric acid	H_3PO_4			$H_2PO_4^-$	dihydrogen phosphate ion
hydrogen fluoride	HF			F^-	fluoride ion
nitrous acid	HNO_2			NO_2^-	nitrite ion
acetic acid	CH_3CO_2H			$CH_3CO_2^-$	acetate ion
carbonic acid	H_2CO_3			HCO_3^-	hydrogen carbonate ion
hydrogen sulfide	H_2S			HS^-	hydrogen sulfide ion
ammonium ion	NH_4^+			NH_3	ammonia
hydrogen cyanide	HCN			CN^-	cyanide ion
hydrogen carbonate ion	HCO_3^-			CO_3^{2-}	carbonate ion
water	H_2O			OH^-	hydroxide ion
hydrogen sulfide ion	HS^-	Do not undergo acid ionization in water	Undergo complete base ionization in water	S^{2-}	sulfide ion
ethanol	C_2H_5OH			$C_2H_5O^-$	ethoxide ion
ammonia	NH_3			NH_2^-	amide ion
hydrogen	H_2			H^-	hydride ion
methane	CH_4			CH_3^-	methide ion

Figure 14.8 This figure shows strengths of conjugate acid-base pairs relative to the strength of water as the reference substance.

The listing of conjugate acid–base pairs shown in **Figure 14.8** is arranged to show the relative strength of each species as compared with water, whose entries are highlighted in each of the table's columns. In the acid column, those species listed below water are weaker acids than water. These species do not undergo acid ionization in water; they are not Bronsted-Lowry acids. All the species listed above water are stronger acids, transferring protons to water to some extent when dissolved in an aqueous solution to generate hydronium ions. Species above water but below hydronium ion are *weak acids*, undergoing partial acid ionization, wheres those above hydronium ion are *strong acids* that are completely ionized in aqueous solution.

If all these strong acids are completely ionized in water, why does the column indicate they vary in strength, with nitric acid being the weakest and perchloric acid the strongest? Notice that the sole acid species present in an aqueous solution of any strong acid is $H_3O^+(aq)$, meaning that hydronium ion is the strongest acid that may exist in water; any stronger acid will react completely with water to generate hydronium ions. This limit on the acid strength of solutes in a solution is called a **leveling effect**. To measure the differences in acid strength for "strong" acids, the acids must be dissolved in a solvent that is *less basic* than water. In such solvents, the acids will be "weak," and so any differences in the extent of their ionization can be determined. For example, the binary hydrogen halides HCl, HBr, and HI are strong acids in water but weak acids in ethanol (strength increasing HCl < HBr < HI).

The right column of **Figure 14.8** lists a number of substances in order of increasing base strength from top to bottom. Following the same logic as for the left column, species listed above water are weaker bases and so they don't undergo base ionization when dissolved in water. Species listed between water and its conjugate base, hydroxide ion, are weak bases that partially ionize. Species listed below hydroxide ion are strong bases that completely ionize in water to yield hydroxide ions (i.e., they are *leveled* to hydroxide). A comparison of the acid and base columns in this table supports the reciprocal relation between the strengths of conjugate acid-base pairs. For example, the conjugate bases of the strong acids (top of table) are all of negligible strength. A strong acid exhibits an immeasurably large K_a, and so its conjugate base will exhibit a K_b that is essentially zero:

$$\begin{aligned} &\text{strong acid}: && K_a \approx \infty \\ &\text{conjugate base}: && K_b = K_w/K_a = K_w/\infty \approx 0 \end{aligned}$$

A similar approach can be used to support the observation that conjugate acids of strong bases ($K_b \approx \infty$) are of negligible strength ($K_a \approx 0$).

Example 14.8

Calculating Ionization Constants for Conjugate Acid-Base Pairs

Use the K_b for the nitrite ion, $NO_2{}^-$, to calculate the K_a for its conjugate acid.

Solution

K_b for $NO_2{}^-$ is given in this section as 2.17×10^{-11}. The conjugate acid of $NO_2{}^-$ is HNO_2; K_a for HNO_2 can be calculated using the relationship:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for K_a yields

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}} = 4.6 \times 10^{-4}$$

This answer can be verified by finding the K_a for HNO_2 in **Appendix H**.

Check Your Learning

Determine the relative acid strengths of $NH_4{}^+$ and HCN by comparing their ionization constants. The ionization constant of HCN is given in **Appendix H** as 4.9×10^{-10}. The ionization constant of $NH_4{}^+$ is not listed, but the ionization constant of its conjugate base, NH_3, is listed as 1.8×10^{-5}.

Answer: $NH_4{}^+$ is the slightly stronger acid (K_a for $NH_4{}^+ = 5.6 \times 10^{-10}$).

Acid-Base Equilibrium Calculations

The chapter on chemical equilibria introduced several types of equilibrium calculations and the various mathematical strategies that are helpful in performing them. These strategies are generally useful for equilibrium systems regardless of chemical reaction class, and so they may be effectively applied to acid-base equilibrium problems. This section presents several example exercises involving equilibrium calculations for acid-base systems.

Example 14.9

Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar (**Figure 14.9**) that provides its sour taste. At equilibrium, a solution contains $[CH_3CO_2H] = 0.0787\ M$ and $[H_3O^+] = [CH_3CO_2^-] = 0.00118\ M$. What is the value of K_a for acetic acid?

Figure 14.9 Vinegar contains acetic acid, a weak acid. (credit: modification of work by "HomeSpot HQ"/Flickr)

Solution

The relevant equilibrium equation and its equilibrium constant expression are shown below. Substitution of the provided equilibrium concentrations permits a straightforward calculation of the K_a for acetic acid.

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2{}^-(aq)$$

$$K_a = \frac{[H_3O^+][CH_3CO_2{}^-]}{[CH_3CO_2H]} = \frac{(0.00118)(0.00118)}{0.0787} = 1.77 \times 10^{-5}$$

Check Your Learning

The $HSO_4{}^-$ ion, weak acid used in some household cleansers:

$$HSO_4{}^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4{}^{2-}(aq)$$

What is the acid ionization constant for this weak acid if an equilibrium mixture has the following composition: $[H_3O^+] = 0.027\ M$; $[HSO_4{}^-] = 0.29\ M$; and $[SO_4{}^{2-}] = 0.13\ M$?

Answer: K_a for $HSO_4{}^- = 1.2 \times 10^{-2}$

Example 14.10

Determination of K_b from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2] = 0.050\ M$, $[C_8H_{10}N_4O_2H^+] = 5.0 \times 10^{-3}\ M$, and $[OH^-] = 2.5 \times 10^{-3}\ M$?

Solution

The relevant equilibrium equation and its equilibrium constant expression are shown below. Substitution of the provided equilibrium concentrations permits a straightforward calculation of the K_b for caffeine.

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq)$$

$$K_b = \frac{[C_8H_{10}N_4O_2H^+][OH^-]}{[C_8H_{10}N_4O_2]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

Check Your Learning

What is the equilibrium constant for the ionization of the $HPO_4{}^{2-}$ ion, a weak base

$$HPO_4{}^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4{}^-(aq) + OH^-(aq)$$

if the composition of an equilibrium mixture is as follows: $[OH^-] = 1.3 \times 10^{-6}\ M$; $[H_2PO_4{}^-] = 0.042\ M$; and $[HPO_4{}^{2-}] = 0.341\ M$?

Answer: K_b for $HPO_4{}^{2-} = 1.6 \times 10^{-7}$

Example 14.11

Determination of K_a or K_b from pH

The pH of a 0.0516-*M* solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2{}^-(aq)$$

Solution

The nitrous acid concentration provided is a *formal* concentration, one that does not account for any chemical equilibria that may be established in solution. Such concentrations are treated as “initial” values for equilibrium calculations using the ICE table approach. Notice the initial value of hydronium ion is listed as *approximately* zero because a small concentration of H_3O^+ is present (1×10^{-7} *M*) due to the autoprotolysis of water. In many cases, such as all the ones presented in this chapter, this concentration is much less than that generated by ionization of the acid (or base) in question and may be neglected.

The pH provided is a logarithmic measure of the hydronium ion concentration resulting from the acid ionization of the nitrous acid, and so it represents an “equilibrium” value for the ICE table:

$$[H_3O^+] = 10^{-2.34} = 0.0046\ M$$

The ICE table for this system is then

	HNO_2 +	H_2O $\rightleftharpoons$	H_3O^+ +	NO_2^-
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	−0.0046		+0.0046	+0.0046
Equilibrium concentration (*M*)	0.0470		0.0046	0.0046

Finally, calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[H_3O^+][NO_2{}^-]}{[HNO_2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.6 \times 10^{-4}$$

Check Your Learning.

The pH of a solution of household ammonia, a 0.950-*M* solution of NH_3, is 11.612. What is K_b for NH_3.

Answer: $K_b = 1.8 \times 10^{-5}$

Example 14.12

Calculating Equilibrium Concentrations in a Weak Acid Solution

Formic acid, HCO_2H, is one irritant that causes the body's reaction to some ant bites and stings (**Figure 14.10**).

Figure 14.10 The pain of some ant bites and stings is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH of a 0.534-*M* solution of formic acid?

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq) \qquad K_a = 1.8 \times 10^{-4}$$

Solution

The ICE table for this system is

	HCO_2H +	H_2O $\rightleftharpoons$	H_3O^+ +	HCO_2^-
Initial concentration (*M*)	0.534		~0	0
Change (*M*)			$+x$	$+x$
Equilibrium concentration (*M*)	$0.534 - x$		x	x

Substituting the equilibrium concentration terms into the K_a expression gives

$$K_a = 1.8 \times 10^{-4} = \frac{[H_3O^+][HCO_2^-]}{[HCO_2H]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

The relatively large initial concentration and small equilibrium constant permits the simplifying assumption that x will be much lesser than 0.534, and so the equation becomes

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solving the equation for x yields

$$x^2 = 0.534 \times \left(1.8 \times 10^{-4}\right) = 9.6 \times 10^{-5}$$

$$x = \sqrt{9.6 \times 10^{-5}}$$

$$= 9.8 \times 10^{-3}\ M$$

To check the assumption that x is small compared to 0.534, its relative magnitude can be estimated:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534} = 1.8 \times 10^{-2}\ (1.8\%\text{ of }0.534)$$

Because x is less than 5% of the initial concentration, the assumption is valid.

As defined in the ICE table, x is equal to the equilibrium concentration of hydronium ion:

$$x = [H_3O^+] = 0.0098\ M$$

Finally, the pH is calculated to be

$$\text{pH} = -\log[H_3O^+] = -\log(0.0098) = 2.01$$

Check Your Learning

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of a 0.100-M solution of acetic acid, CH_3CO_2H?

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2{}^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$

Answer: percent ionization = 1.3%

Example 14.13

Calculating Equilibrium Concentrations in a Weak Base Solution

Find the concentration of hydroxide ion, the pOH, and the pH of a 0.25-M solution of trimethylamine, a weak base:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq) \qquad K_b = 6.3 \times 10^{-5}$$

Solution

The ICE table for this system is

	$(CH_3)_3N$	$+ H_2O$	$\rightleftharpoons (CH_3)_3NH^+$	$+ OH^-$
Initial concentration (*M*)	0.25		0	~0
Change (*M*)	$-x$		x	x
Equilibrium concentration (*M*)	$0.25 + (-x)$		$0 + x$	$\sim 0 + x$

Substituting the equilibrium concentration terms into the K_b expression gives

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(x)(x)}{0.25 - x} = 6.3 \times 10^{-5}$$

Assuming $x << 0.25$ and solving for x yields

$$x = 4.0 \times 10^{-3}\ M$$

This value is less than 5% of the initial concentration (0.25), so the assumption is justified.
As defined in the ICE table, x is equal to the equilibrium concentration of hydroxide ion:

$$[\text{OH}^-] = \sim 0 + x = x = 4.0 \times 10^{-3}\ M$$

$$= 4.0 \times 10^{-3}\ M$$

The pOH is calculated to be

$$\text{pOH} = -\log\left(4.0 \times 10^{-3}\right) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$\text{pH} + \text{pOH} = \text{p}K_\text{w} = 14.00$$

permits the computation of pH:

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.40 = 11.60$$

Check Your Learning

Calculate the hydroxide ion concentration and the percent ionization of a 0.0325-M solution of ammonia, a weak base with a K_b of 1.76×10^{-5}.

Answer: $7.56 \times 10^{-4}\ M$, 2.33%

In some cases, the strength of the weak acid or base and its formal (initial) concentration result in an appreciable ionization. Though the ICE strategy remains effective for these systems, the algebra is a bit more involved because the simplifying assumption that x is negligible can not be made. Calculations of this sort are demonstrated in **Example 14.14** below.

Example 14.14

Calculating Equilibrium Concentrations without Simplifying Assumptions

Sodium bisulfate, NaHSO_4, is used in some household cleansers as a source of the $\text{HSO}_4{}^-$ ion, a weak acid. What is the pH of a 0.50-M solution of $\text{HSO}_4{}^-$?

$$\text{HSO}_4{}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{SO}_4{}^{2-}(aq) \qquad K_\text{a} = 1.2 \times 10^{-2}$$

Solution

The ICE table for this system is

	HSO_4^-	$+ \quad H_2O \rightleftharpoons$	H_3O^+	$+ \quad SO_4^{2-}$
Initial concentration (*M*)	0.50		~0	0
Change (*M*)	$-x$		$+x$	$+x$
Equilibrium concentration (*M*)	$0.50 - x$		x	x

Substituting the equilibrium concentration terms into the K_a expression gives

$$K_a = 1.2 \times 10^{-2} = \frac{[H_3O^+][SO_4{}^{2-}]}{[HSO_4{}^-]} = \frac{(x)(x)}{0.50 - x}$$

If the assumption that $x << 0.5$ is made, simplifying and solving the above equation yields

$$x = 0.077\ M$$

This value of x is clearly not significantly less than 0.50 *M*; rather, it is approximately 15% of the initial concentration:
When we check the assumption, we calculate:

$$\frac{x}{[HSO_4{}^-]_i}$$

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15\ (15\%)$$

Because the simplifying assumption is not valid for this system, the equilibrium constant expression is solved as follows:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

Rearranging this equation yields

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2} x = x^2$$

Writing the equation in quadratic form gives

$$x^2 + 1.2 \times 10^{-2} x - 6.0 \times 10^{-3} = 0$$

Solving for the two roots of this quadratic equation results in a negative value that may be discarded as physically irrelevant and a positive value equal to x. As defined in the ICE table, x is equal to the hydronium concentration.

$$x = [H_3O^+] = 0.072\ M$$

$$\text{pH} = -\log[H_3O^+] = -\log(0.072) = 1.14$$

Check Your Learning

Calculate the pH in a 0.010-M solution of caffeine, a weak base:

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq) \qquad K_b = 2.5 \times 10^{-4}$$

Answer: pH 11.16

Effect of Molecular Structure on Acid-Base Strength

Binary Acids and Bases

In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is HF < HCl < HBr < HI. Likewise, for group 16, the order of increasing acid strength is $H_2O < H_2S < H_2Se < H_2Te$.

Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is $CH_4 < NH_3 < H_2O < HF$; across the third row, it is $SiH_4 < PH_3 < H_2S < HCl$ (see **Figure 14.11**).

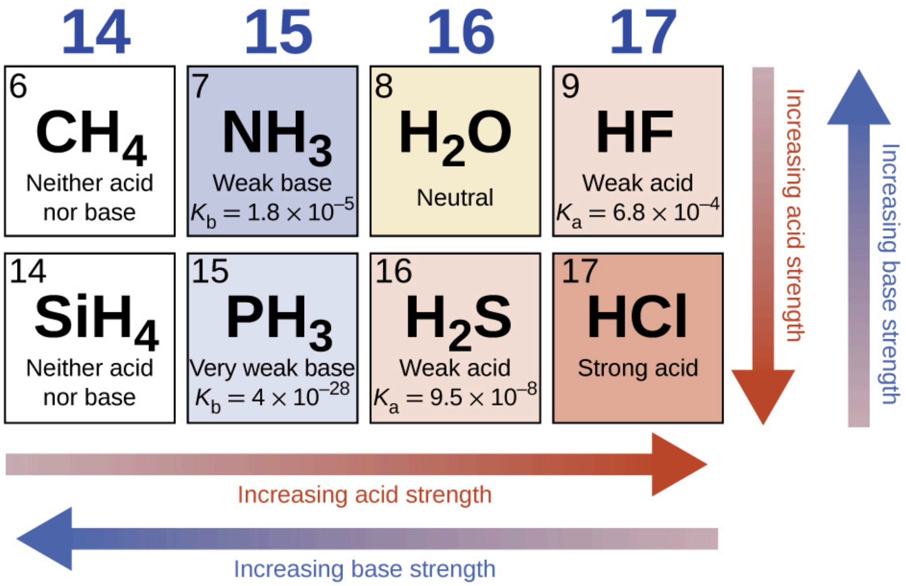
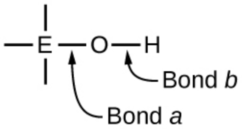


Figure 14.11 The figure shows trends in the strengths of binary acids and bases.

Ternary Acids and Bases

Ternary compounds composed of hydrogen, oxygen, and some third element ("E") may be structured as depicted in the image below. In these compounds, the central E atom is bonded to one or more O atoms, and at least one of the O atoms is also bonded to an H atom, corresponding to the general molecular formula $O_mE(OH)_n$. These compounds may be acidic, basic, or amphoteric depending on the properties of the central E atom. Examples of such compounds include sulfuric acid, $O_2S(OH)_2$, sulfurous acid, $OS(OH)_2$, nitric acid, O_2NOH, perchloric acid, O_3ClOH, aluminum hydroxide, $Al(OH)_3$, calcium hydroxide, $Ca(OH)_2$, and potassium hydroxide, KOH:



If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic −OH groups that are called **oxyacids**.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H_2SO_4, or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3, or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO_3, or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO_2, or ONOH (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (**Figure 14.12**).

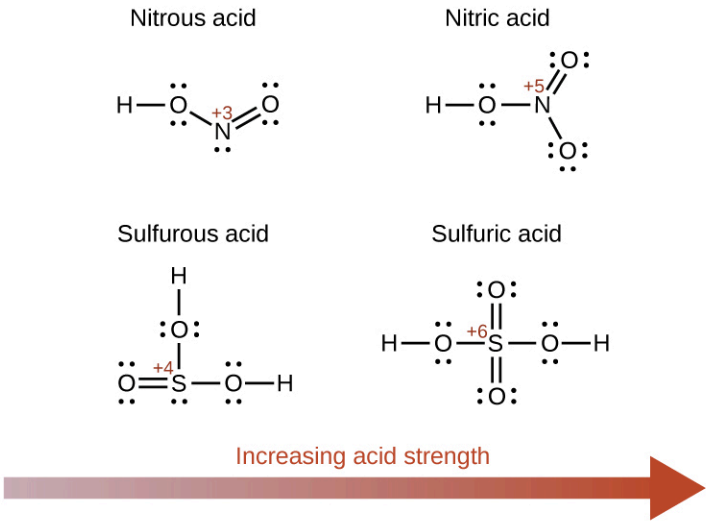


Figure 14.12 As the oxidation number of the central atom E increases, the acidity also increases.

Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate $Al(H_2O)_3(OH)_3$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $Al(H_2O)_3(OH)_3$, is converted into the soluble ion, $[Al(H_2O)_2(OH)_4]^-$, by reaction with hydroxide ion:

$$Al(H_2O)_3(OH)_3(aq) + OH^-(aq) \rightleftharpoons H_2O(l) + [Al(H_2O)_2(OH)_4]^-(aq)$$

In this reaction, a proton is transferred from one of the aluminum-bound H_2O molecules to a hydroxide ion in solution. The $Al(H_2O)_3(OH)_3$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion $[Al(H_2O)_6]^{3+}$ by reaction with hydronium ion:

$$3H_3O^+(aq) + Al(H_2O)_3(OH)_3(aq) \rightleftharpoons Al(H_2O)_6{}^{3+}(aq) + 3H_2O(l)$$

In this case, protons are transferred from hydronium ions in solution to $Al(H_2O)_3(OH)_3$, and the compound functions as a base.

14.4 Hydrolysis of Salts

By the end of this section, you will be able to:

- Predict whether a salt solution will be acidic, basic, or neutral
- Calculate the concentrations of the various species in a salt solution
- Describe the acid ionization of hydrated metal ions

Salts with Acidic Ions

Salts are ionic compounds composed of cations and anions, either of which may be capable of undergoing an acid or base ionization reaction with water. Aqueous salt solutions, therefore, may be acidic, basic, or neutral, depending on the relative acid-base strengths of the salt's constituent ions. For example, dissolving ammonium chloride in water results in its dissociation, as described by the equation

$$NH_4Cl(s) \rightleftharpoons NH_4{}^+(aq) + Cl^-(aq)$$

The ammonium ion is the conjugate acid of the weak base ammonia, NH_3, and so it will undergo acid ionization (or *acid hydrolysis*):

$$NH_4{}^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

Salts are ionic compounds composed of cations and anions, either of which may be capable of undergoing an acid or base ionization reaction with water. Aqueous salt solutions, therefore, may be acidic, basic, or neutral, depending on the relative acid-base strengths of the salt’s constituent ions. For example, dissolving the ammonium chloride in water results in its dissociation, as described by the equation

$$NH_4Cl(s) \rightleftharpoons NH_4{}^+(aq) + Cl^-(aq)$$

The ammonium ion is the conjugate acid of the base ammonia, NH3; its acid ionization (or acid hydrolysis) reaction is represented by

$$NH_4{}^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq) \qquad K_a = K_w/K_b$$

Since ammonia is a weak base, K_b is measurable and $K_a > 0$ (ammonium ion is a weak acid).

The chloride ion is the conjugate base of hydrochloric acid, and so its base ionization (or *base hydrolysis*) reaction is represented by

$$Cl^-(aq) + H_2O(l) \rightleftharpoons HCl(aq) + OH^-(aq) \qquad K_b = K_w/K_a$$

Since HCl is a strong acid, K_a is immeasurably large and $K_b \approx 0$ (chloride ions don’t undergo appreciable hydrolysis).

Thus, dissolving ammonium chloride in water yields a solution of weak acid cations ($NH_4{}^+$) and inert anions (Cl^-), resulting in an acidic solution.

Example 14.15

Calculating the pH of an Acidic Salt Solution

Aniline is an amine that is used to manufacture dyes. It is isolated as anilinium chloride, $[C_6H_5NH_3{}^+]Cl$, a salt prepared by the reaction of the weak base aniline and hydrochloric acid. What is the pH of a 0.233 *M* solution of anilinium chloride

$$C_6H_5NH_3{}^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5NH_2(aq)$$

Solution

The K_a for anilinium ion is derived from the K_b for its conjugate base, aniline (see **Appendix H**):

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-10}} = 2.3 \times 10^{-5}$$

Using the provided information, an ICE table for this system is prepared:

	$C_6H_5NH_3^+$ +	H_2O ⇌	$C_6H_5NH_2$ +	H_3O^+
Initial concentration (*M*)	0.233		0	~0
Change (*M*)	$-x$		$+x$	$+x$
Equilibrium concentration (*M*)	$0.233 - x$		x	x

Substituting these equilibrium concentration terms into the K_a expression gives

$$K_a = [C_6H_5NH_2][H_3O^+]/[C_6H_5NH_3{}^+]$$
$$2.3 \times 10^{-5} = (x)(x)/0.233 - x)$$

Assuming $x << 0.233$, the equation is simplified and solved for x:

$$2.3 \times 10^{-5} = x^2/0.233$$
$$x = 0.0023\ M$$

The ICE table defines x as the hydronium ion molarity, and so the pH is computed as

$$\text{pH} = -\log[H_3O^+] = -\log(0.0023) = 2.64$$

Check Your Learning

What is the hydronium ion concentration in a 0.100-*M* solution of ammonium nitrate, NH_4NO_3, a salt composed of the ions $NH_4{}^+$ and $NO_3{}^-$. Which is the stronger acid $C_6H_5NH_3{}^+$ or $NH_4{}^+$?

Answer: $[H_3O^+] = 7.5 \times 10^{-6}\ M$; $C_6H_5NH_3{}^+$ is the stronger acid.

Salts with Basic Ions

As another example, consider dissolving sodium acetate in water:

$$NaCH_3CO_2(s)\ Na + (aq) + CH_3CO_2{}^-(aq)$$

The sodium ion does not undergo appreciable acid or base ionization and has no effect on the solution pH. This may seem obvious from the ion's formula, which indicates no hydrogen or oxygen atoms, but some dissolved metal ions function as weak acids, as addressed later in this section.

The acetate ion, $CH_3CO_2{}^-$, is the conjugate base of acetic acid, CH_3CO_2H, and so its base ionization (or *base hydrolysis*) reaction is represented by

$$CH_3CO_2{}^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH-(aq) \qquad K_b = K_w/K_a$$

Because acetic acid is a weak acid, its K_a is measurable and $K_b > 0$ (acetate ion is a weak base).

Dissolving sodium acetate in water yields a solution of inert cations (Na^+) and weak base anions $(CH_3CO_2{}^-)$, resulting in a basic solution.

Example 14.16

Equilibrium in a Solution of a Salt of a Weak Acid and a Strong Base

Determine the acetic acid concentration in a solution with $[CH_3CO_2{}^-] = 0.050\ M$ and $[OH^-] = 2.5 \times 10^{-6}\ M$ at equilibrium. The reaction is:

$$CH_3CO_2{}^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$

Solution

The provided equilibrium concentrations and a value for the equilibrium constant will permit calculation of the missing equilibrium concentration. The process in question is the base ionization of acetate ion, for which

$$K_b \text{ (for } CH_3CO_2{}^-) = \frac{K_w}{K_a \text{ (for } CH_3CO_2H)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Substituting the available values into the K_b expression gives

$$K_b = \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2{}^-]} = 5.6 \times 10^{-10}$$

$$= \frac{[CH_3CO_2H](2.5 \times 10^{-6})}{(0.050)} = 5.6 \times 10^{-10}$$

Solving the above equation for the acetic acid molarity yields $[CH_3CO_2H] = 1.1 \times 10^{-5}\ M$.

Check Your Learning

What is the pH of a 0.083-*M* solution of NaCN?

Answer: 11.11

Salts with Acidic and Basic Ions

Some salts are composed of both acidic and basic ions, and so the pH of their solutions will depend on the relative strengths of these two species. Likewise, some salts contain a single ion that is amphiprotic, and so the relative strengths of this ion’s acid and base character will determine its effect on solution pH. For both types of salts, a comparison of the K_a and K_b values allows prediction of the solution’s acid-base status, as illustrated in the following example exercise.

Example 14.17

Determining the Acidic or Basic Nature of Salts

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) KBr

(b) $NaHCO_3$

(c) Na_2HPO_4

(d) NH_4F

Solution

Consider each of the ions separately in terms of its effect on the pH of the solution, as shown here:

(a) The K^+ cation is inert and will not affect pH. The bromide ion is the conjugate base of a strong acid, and so it is of negligible base strength (no appreciable base ionization). The solution is neutral.

(b) The Na^+ cation is inert and will not affect the pH of the solution; while the $HCO_3{}^-$ anion is amphiprotic. The K_a of $HCO_3{}^-$ is 4.7 × 10^{-11},and its K_b is $\frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$.

Since $K_b >> K_a$, the solution is basic.

(c) The Na^+ cation is inert and will not affect the pH of the solution, while the $HPO_4{}^{2-}$ anion is amphiprotic. The K_a of $HPO_4{}^{2-}$ is 4.2 × 10^{-13},

and its K_b is $\frac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7}$. Because $K_b >> K_a$, the solution is basic.

(d) The $NH_4{}^+$ ion is acidic (see above discussion) and the F^- ion is basic (conjugate base of the weak acid HF). Comparing the two ionization constants: K_a of $NH_4{}^+$ is 5.6 × 10^{-10} and the K_b of F^- is 1.4 × 10^{-11}, so the solution is acidic, since $K_a > K_b$.

Check Your Learning

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) K_2CO_3

(b) $CaCl_2$

(c) KH_2PO_4

(d) $(NH_4)_2CO_3$

Answer: (a) basic; (b) neutral; (c) acidic; (d) basic

The Ionization of Hydrated Metal Ions

Unlike the group 1 and 2 metal ions of the preceding examples (Na^+, Ca^{2+}, etc.), some metal ions function as acids in aqueous solutions. These ions are not just loosely solvated by water molecules when dissolved, instead they are covalently bonded to a fixed number of water molecules to yield a complex ion (see chapter on coordination chemistry). As an example, the dissolution of aluminum nitrate in water is typically represented as

$$Al(NO_3)(s) \rightleftharpoons Al^3 + (aq) + 3NO_3{}^-(aq)$$

However, the aluminum(III) ion actually reacts with six water molecules to form a stable complex ion, and so the more explicit representation of the dissolution process is

$$Al(NO_3)_3(s) + 6H_2O(l) \rightleftharpoons Al(H_2O)_6{}^{3+}(aq) + 3NO_3{}^-(aq)$$

As shown in **Figure 14.13**, the $Al(H_2O)_6{}^{3+}$ ions involve bonds between a central Al atom and the O atoms of the six water molecules. Consequently, the bonded water molecules' O–H bonds are more polar than in nonbonded water molecules, making the bonded molecules more prone to donation of a hydrogen ion:

$$Al(H_2O)_6{}^{3+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Al(H_2O)_5(OH)^{2+}(aq) \qquad K_a = 1.4 \times 10^{-5}$$

The conjugate base produced by this process contains five other bonded water molecules capable of acting as acids, and so the sequential or step-wise transfer of protons is possible as depicted in few equations below:

$$\text{Al(H}_2\text{O)}_6{}^{3+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Al(H}_2\text{O)}_5\text{(OH)}^{2+}(aq)$$
$$\text{Al(H}_2\text{O)}_5\text{(OH)}^{2+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Al(H}_2\text{O)}_4\text{(OH)}_2{}^+(aq)$$
$$\text{Al(H}_2\text{O)}_4\text{(OH)}_2{}^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Al(H}_2\text{O)}_3\text{(OH)}_3(aq)$$

This is an example of a polyprotic acid, the topic of discussion in a later section of this chapter.

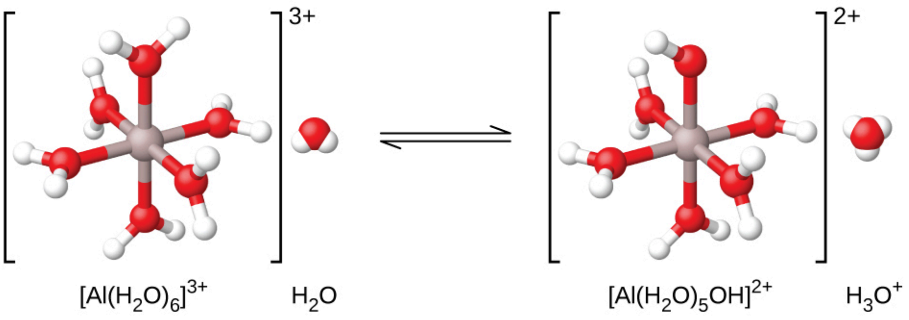


Figure 14.13 When an aluminum ion reacts with water, the hydrated aluminum ion becomes a weak acid.

Aside from the alkali metals (group 1) and some alkaline earth metals (group 2), most other metal ions will undergo acid ionization to some extent when dissolved in water. The acid strength of these complex ions typically increases with increasing charge and decreasing size of the metal ions. The first-step acid ionization equations for a few other acidic metal ions are shown below:

$$\text{Fe(H}_2\text{O)}_6{}^{3+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Fe(H}_2\text{O)}_5\text{(OH)}^{2+}(aq) \qquad pK_a = 2.74$$
$$\text{Cu(H}_2\text{O)}_6{}^{2+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Cu(H}_2\text{O)}_5\text{(OH)}^{+}(aq) \qquad pK_a = \sim 6.3$$
$$\text{Zn(H}_2\text{O)}_4{}^{2+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Zn(H}_2\text{O)}_3\text{(OH)}^{+}(aq) \qquad pK_a = 9.6$$

Example 14.18

Hydrolysis of $[Al(H_2O)_6]^{3+}$

Calculate the pH of a 0.10-*M* solution of aluminum chloride, which dissolves completely to give the hydrated aluminum ion $[\text{Al(H}_2\text{O)}_6]^{3+}$ in solution.

Solution

The equation for the reaction and K_a are:

$$\text{Al(H}_2\text{O)}_6{}^{3+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Al(H}_2\text{O)}_5\text{(OH)}^{2+}(aq) \qquad K_a = 1.4 \times 10^{-5}$$

An ICE table with the provided information is

	$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons$	H_3O^+ +	$Al(H_2O)_5(OH)^{2+}$
Initial concentration (*M*)	0.10	~0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$0.10 - x$	x	x

Substituting the expressions for the equilibrium concentrations into the equation for the ionization constant yields:

$$K_a = \frac{[H_3O^+][Al(H_2O)_5(OH)^{2+}]}{[Al(H_2O)_6{}^{3+}]}$$

$$= \frac{(x)(x)}{0.10 - x} = 1.4 \times 10^{-5}$$

Assuming x << 0.10 and solving the simplified equation gives:

$$x = 1.2 \times 10^{-3}\ M$$

The ICE table defined x as equal to the hydronium ion concentration, and so the pH is calculated to be

$$[H_3O^+] = 0 + x = 1.2 \times 10^{-3}\ M$$

$$\text{pH} = -\log[H_3O^+] = 2.92 \text{ (an acidic solution)}$$

Check Your Learning

What is $[Al(H_2O)_5(OH)^{2+}]$ in a 0.15-M solution of $Al(NO_3)_3$ that contains enough of the strong acid HNO_3 to bring $[H_3O^+]$ to 0.10 M?

Answer: $2.1 \times 10^{-5}\ M$

14.5 Polyprotic Acids

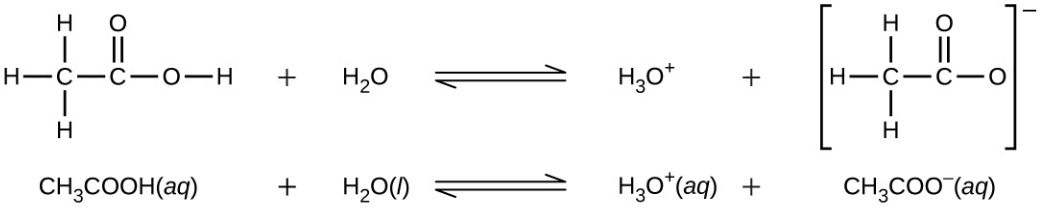
By the end of this section, you will be able to:

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

Acids are classified by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, HNO_3, and HCN that contain one ionizable hydrogen atom in each molecule are called **monoprotic acids**. Their reactions with water are:

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3{}^-(aq)$$
$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

Even though it contains four hydrogen atoms, acetic acid, CH_3CO_2H, is also monoprotic because only the hydrogen atom from the carboxyl group (COOH) reacts with bases:



Similarly, monoprotic bases are bases that will accept a single proton.

Diprotic acids contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

$$\text{First ionization: } H_2SO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_4^{\;-}(aq) \qquad K_{a1} = \text{more than } 10^2\text{; complete dissociation}$$

$$\text{Second ionization: } HSO_4^{\;-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{\;2-}(aq) \qquad K_{a2} = 1.2 \times 10^{-2}$$

This **stepwise ionization** process occurs for all polyprotic acids. Carbonic acid, H_2CO_3, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

First ionization:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^{\;-}(aq) \qquad K_{H_2CO_3} = \frac{[H_3O^+][HCO_3^{\;-}]}{[H_2CO_3]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

Second ionization:

$$HCO_3^{\;-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{\;2-}(aq) \qquad K_{HCO_3^{\;-}} = \frac{[H_3O^+][CO_3^{\;2-}]}{[HCO_3^{\;-}]} = 4.7 \times 10^{-11}$$

$K_{H_2CO_3}$ is larger than $K_{HCO_3^{\;-}}$ by a factor of 10^4, so H_2CO_3 is the dominant producer of hydronium ion in the solution. This means that little of the $HCO_3^{\;-}$ formed by the ionization of H_2CO_3 ionizes to give hydronium ions (and carbonate ions), and the concentrations of H_3O^+ and $HCO_3^{\;-}$ are practically equal in a pure aqueous solution of H_2CO_3.

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This approach is demonstrated in the following example exercise.

Example 14.19

Ionization of a Diprotic Acid

"Carbonated water" contains a palatable amount of dissolved carbon dioxide. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are $[H_3O^+]$, $[HCO_3^{\;-}]$, and $[CO_3^{\;2-}]$ in a saturated solution of CO_2 with an initial $[H_2CO_3] = 0.033$ M?

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^{\;-}(aq) \qquad K_{a1} = 4.3 \times 10^{-7}$$
$$HCO_3^{\;-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{\;2-}(aq) \qquad K_{a2} = 4.7 \times 10^{-11}$$

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than $HCO_3^{\;-}$, so the stepwise ionization reactions may be treated separately.

The first ionization reaction is

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^{\;-}(aq) \qquad K_{a1} = 4.3 \times 10^{-7}$$

Using provided information, an ICE table for this first step is prepared:

	H_2CO_3 +	H_2O ⇌	H_3O^+ +	HCO_3^-
Initial concentration (*M*)	0.033		~0	0
Change (*M*)	$-x$		$+x$	$+x$
Equilibrium concentration (*M*)	$0.033 - x$		x	x

Substituting the equilibrium concentrations into the equilibrium equation gives

$$K_{H_2CO_3} = \frac{[H_3O^+][HCO_3^{\,-}]}{[H_2CO_3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Assuming $x << 0.033$ and solving the simplified equation yields

$$x = 1.2 \times 10^{-4}$$

The ICE table defined x as equal to the bicarbonate ion molarity and the hydronium ion molarity:

$$[H_2CO_3] = 0.033\ M$$

$$[H_3O^+] = [HCO_3^{\,-}] = 1.2 \times 10^{-4}\ M$$

Using the bicarbonate ion concentration computed above, the second ionization is subjected to a similar equilibrium calculation:

$$HCO_3^{\,-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{\,2-}(aq)$$

$$K_{HCO_3^{\,-}} = \frac{[H_3O^+][CO_3^{\,2-}]}{[HCO_3^{\,-}]} = \frac{(1.2 \times 10^{-4})[CO_3^{\,2-}]}{1.2 \times 10^{-4}}$$

$$[CO_3^{\,2-}] = \frac{(4.7 \times 10^{-11})(1.2 \times 10^{-4})}{1.2 \times 10^{-4}} = 4.7 \times 10^{-11}\ M$$

To summarize: at equilibrium $[H_2CO_3] = 0.033\ M$; $[H_3O^+] = 1.2 \times 10^{-4}$; $[HCO_3^{\,-}] = 1.2 \times 10^{-4}\ M$; $[CO_3^{\,2-}] = 5.6 \times 10^{-11}\ M$.

Check Your Learning

The concentration of H_2S in a saturated aqueous solution at room temperature is approximately 0.1 *M*. Calculate $[H_3O^+]$, $[HS^-]$, and $[S^{2-}]$ in the solution:

$$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq) \qquad K_{a1} = 8.9 \times 10^{-8}$$

$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq) \qquad K_{a2} = 1.0 \times 10^{-19}$$

Answer: $[H_2S] = 0.1\ M$; $[H_3O^+] = [HS^-] = 0.000094\ M$; $[S^{2-}] = 1 \times 10^{-19}\ M$

A **triprotic acid** is an acid that has three ionizable H atoms. Phosphoric acid is one example:

$$\text{First ionization: } H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4{}^-(aq) \qquad K_{a1} = 7.5 \times 10^{-3}$$
$$\text{Second ionization: } H_2PO_4{}^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4{}^{2-}(aq) \qquad K_{a2} = 6.2 \times 10^{-8}$$
$$\text{Third ionization: } HPO_4{}^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4{}^{3-}(aq) \qquad K_{a3} = 4.2 \times 10^{-13}$$

As for the diprotic acid examples, each successive ionization reaction is less extensive than the former, reflected in decreasing values for the stepwise acid ionization constants. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6.

This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of H_3PO_4 complicated. However, because the successive ionization constants differ by a factor of 10^5 to 10^6, large differences exist in the small changes in concentration accompanying the ionization reactions. This allows the use of math-simplifying assumptions and processes, as demonstrated in the examples above.

Polyprotic bases are capable of accepting more than one hydrogen ion. The carbonate ion is an example of a **diprotic base**, because it can accept two protons, as shown below. Similar to the case for polyprotic acids, note the ionization constants decrease with ionization step. Likewise, equilibrium calculations involving polyprotic bases follow the same approaches as those for polyprotic acids.

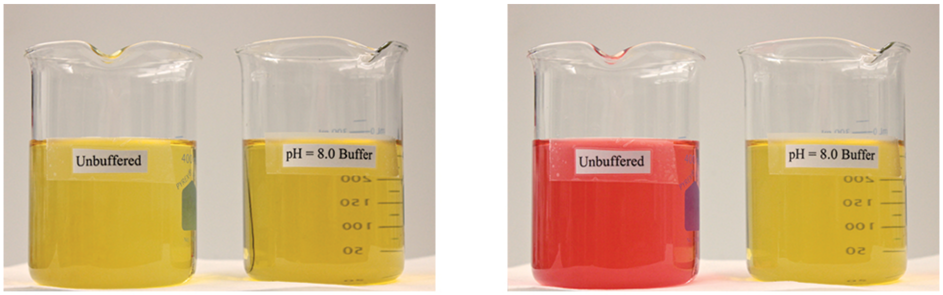
$$H_2O(l) + CO_3{}^{2-}(aq) \rightleftharpoons HCO_3{}^-(aq) + OH^-(aq) \qquad K_{b1} = 2.1 \times 10^{-4}$$
$$H_2O(l) + HCO^{3-}(aq) \rightleftharpoons H_2CO_3(aq) + OH^-(aq) \qquad K_{b2} = 2.3 \times 10^{-8}$$

14.6 Buffers

By the end of this section, you will be able to:

- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

A solution containing appreciable amounts of a weak conjugate acid-base pair is called a buffer solution, or a **buffer**. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (**Figure 14.14**). A solution of acetic acid and sodium acetate ($CH_3COOH + CH_3COONa$) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia and ammonium chloride ($NH_3(aq) + NH_4Cl(aq)$).



(a) (b)

Figure 14.14 (a) The buffered solution on the left and the unbuffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-*M* HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

How Buffers Work

To illustrate the function of a buffer solution, consider a mixture of roughly equal amounts of acetic acid and sodium acetate. The presence of a weak conjugate acid-base pair in the solution imparts the ability to neutralize modest amounts of added strong acid or base. For example, adding strong base to this solution will neutralize hydronium ion and shift the acetic acid ionization equilibrium to the right, partially restoring the decreased H_3O^+ concentration:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2{}^-(aq)$$

Likewise, adding strong acid to this buffer solution will neutralize acetate ion, shifting the above ionization equilibrium right and returning [H3O+] to near its original value. **Figure 14.15** provides a graphical illustration of the changes in conjugate-partner concentration that occur in this buffer solution when strong acid and base are added. The buffering action of the solution is essentially a result of the added strong acid and base being converted to the weak acid and base that make up the buffer's conjugate pair. The weaker acid and base undergo only slight ionization, as compared with the complete ionization of the strong acid and base, and the solution pH, therefore, changes much less drastically than it would in an unbuffered solution.

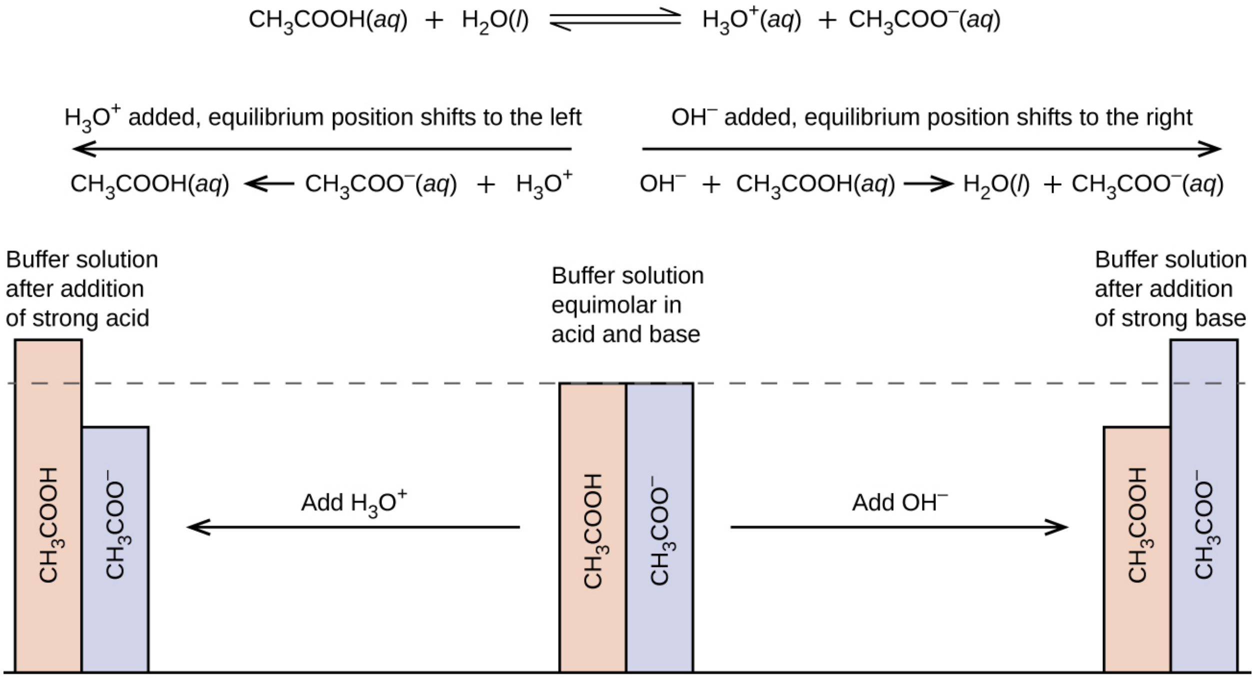


Figure 14.15 Buffering action in a mixture of acetic acid and acetate salt.

Example 14.20

pH Changes in Buffered and Unbuffered Solutions

Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might affect the biochemical activity of these compounds.

(a) Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.

(b) Calculate the pH after 1.0 mL of 0.10 NaOH is added to 100 mL of this buffer.

(c) For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74.

Solution

(a) Following the ICE approach to this equilibrium calculation yields the following:

	CH_3CO_2H +	H_2O $\rightleftharpoons$	H_3O^+ +	$CH_3CO_2^-$
Initial concentration (*M*)	0.10		~0	0.10
Change (*M*)	$-x$		$+x$	$+x$
Equilibrium concentration (*M*)	$0.10 - x$		x	$0.10 + x$

Substituting the equilibrium concentration terms into the K_a expression, assuming $x << 0.10$, and solving the simplified equation for x yields

$$\begin{aligned} x &= 1.8 \times 10^{-5}\,M \\ [H_3O^+] &= 0 + x = 1.8 \times 10^{-5}\ M \\ pH = -\log[H_3O^+] &= -\log(1.8 \times 10^{-5}) \\ &= 4.74 \end{aligned}$$

(b) Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer.

Adding strong acid will neutralize some of the acetic acid, yielding the conjugate base acetate ion. Compute the new concentrations of these two buffer components, then repeat the equilibrium calculation of part (a) using these new concentrations.

$$0.0010\,\cancel{L} \times \left(\frac{0.10\text{ mol NaOH}}{1\,\cancel{L}}\right) = 1.0 \times 10^{-4}\text{ mol NaOH}$$

The initial molar amount of acetic acid is

$$0.100\,\cancel{L} \times \left(\frac{0.100\text{ mol }CH_3CO_2H}{1\,\cancel{L}}\right) = 1.00 \times 10^{-2}\text{ mol }CH_3CO_2H$$

The amount of acetic acid remaining after some is neutralized by the added base is

$$(1.0 \times 10^{-2}) - (0.01 \times 10^{-2}) = 0.99 \times 10^{-2}\text{ mol }CH_3CO_2H$$

The newly formed acetate ion, along with the initially present acetate, gives a final acetate concentration of

$$(1.0 \times 10^{-2}) + (0.01 \times 10^{-2}) = 1.01 \times 10^{-2}\text{ mol }NaCH_3CO_2$$

Compute molar concentrations for the two buffer components:

$$\begin{aligned} [CH_3CO_2H] &= \frac{9.9 \times 10^{-3}\text{ mol}}{0.101\text{ L}} = 0.098\,M \\ [NaCH_3CO_2] &= \frac{1.01 \times 10^{-2}\text{ mol}}{0.101\text{ L}} = 0.100\,M \end{aligned}$$

Using these concentrations, the pH of the solution may be computed as in part (a) above, yielding pH = 4.75 (only slightly different from that prior to adding the strong base).

(c) For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74.

The amount of hydrogen ion initially present in the solution is

$$\begin{aligned} [H_3O^+] &= 10^{-4.74} = 1.8 \times 10^{-5}\ M \\ \text{mol }H_3O^+ &= (0.100\,L)(1.8 \times 10^{-5}\ M) = 1.8 \times 10^{-6}\text{ mol }H_3O^+ \end{aligned}$$

The amount of hydroxide ion added to the solution is

$$\text{mol OH}^- = (0.0010\,L)(0.10\,M) = 1.0 \times 10^{-4}\ \text{mol OH}^-$$

The added hydroxide will neutralize hydronium ion via the reaction

$$\text{H}_3\text{O}^+\,(aq) + \text{OH}^-\,(aq)\ 2\text{H}_2\text{O}(l)$$

The 1:1 stoichiometry of this reaction shows that an excess of hydroxide has been added (greater molar amount than the initially present hydronium ion).

The amount of hydroxide ion remaining is

$$1.0 \times 10^{-4}\ \text{mol} - 1.8 \times 10^{-6}\,\text{mol} = 9.8 \times 10^{-5}\ \text{mol OH}^-$$

corresponding to a hydroxide molarity of

$$9.8 \times 10^{-5}\ \text{mol OH}^-\ /0.101\,L = 9.7 \times 10^{-4}\ M$$

The pH of the solution is then calculated to be

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - \ -\log(9.7 \times 10^{-4}) = 10.99$$

In this unbuffered solution, addition of the base results in a significant rise in pH (from 4.74 to 10.99) compared with the very slight increase observed for the buffer solution in part (b) (from 4.74 to 4.75).

Check Your Learning

Show that adding 1.0 mL of 0.10 *M* HCl changes the pH of 100 mL of a 1.8×10^{-5} *M* HCl solution from 4.74 to 3.00.

Answer: Initial pH of 1.8×10^{-5} *M* HCl; pH = $-\log[\text{H}_3\text{O}^+] = -\log[1.8 \times 10^{-5}] = 4.74$
Moles of H_3O^+ in 100 mL 1.8×10^{-5} *M* HCl; 1.8×10^{-5} moles/L $\times$ 0.100 L = 1.8×10^{-6}
Moles of H_3O^+ added by addition of 1.0 mL of 0.10 *M* HCl: 0.10 moles/L $\times$ 0.0010 L = 1.0×10^{-4} moles;
final pH after addition of 1.0 mL of 0.10 *M* HCl:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log\left(\frac{\text{total moles H}_3\text{O}^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4}\ \text{mol} + 1.8 \times 10^{-6}\ \text{mol}}{101\ \text{mL}\left(\frac{1\,\text{L}}{1000\,\text{mL}}\right)}\right) = 3.00$$

Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (**Figure 14.16**). Instead, the ability of a buffer solution to resist changes in pH relies on the presence of appreciable amounts of its conjugate weak acid-base pair. When enough strong acid or base is added to substantially lower the concentration of either member of the buffer pair, the buffering action within the solution is compromised.

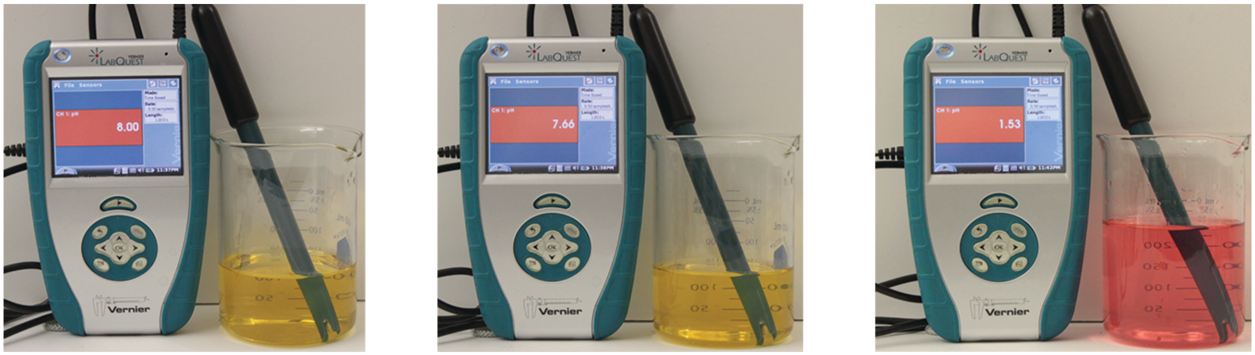


Figure 14.16 The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The **buffer capacity** is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 *M* in acetic acid and 1.0 *M* in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 *M* in acetic acid and 0.10 *M* in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. **Figure 14.17** shows how pH changes for an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

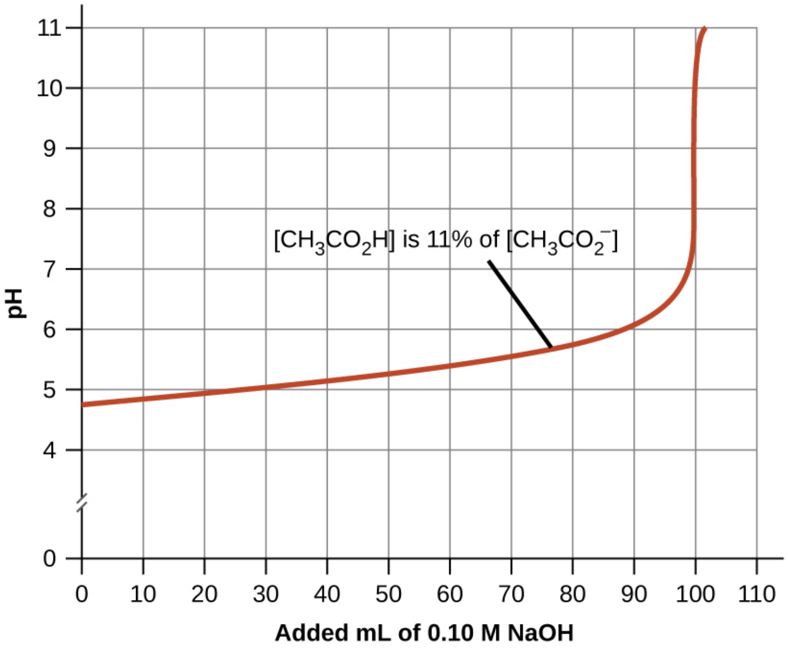


Figure 14.17 Change in pH as an increasing amount of a 0.10-*M* NaOH solution is added to 100 mL of a buffer solution in which, initially, $[CH_3CO_2H] = 0.10\ M$ and $[CH_3CO_2{}^-] = 0.10\ M$. Note the greatly diminished buffering action occurring after the buffer capacity has been reached, resulting in drastic rises in pH on adding more strong base.

2. Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, H_2CO_3, and the bicarbonate ion, $HCO_3{}^-$. When a hydronium ion is introduced to the blood stream, it is removed primarily by the reaction:

$$H_3O^+(aq) + HCO_3{}^-(aq) \longrightarrow H_2CO_3(aq) + H_2O(l)$$

An added hydroxide ion is removed by the reaction:

$$OH^-(aq) + H_2CO_3(aq) \longrightarrow HCO_3{}^-(aq) + H_2O(l)$$

The added strong acid or base is thus effectively converted to the much weaker acid or base of the buffer pair (H_3O^+ is converted to H_2CO_3 and OH^- is converted to $HCO_3{}^-$). The pH of human blood thus remains very near the value determined by the buffer pairs pKa, in this case, 7.35. Normal variations in blood pH are usually less than 0.1, and pH changes of 0.4 or greater are likely to be fatal.

The Henderson-Hasselbalch Equation

The ionization-constant expression for a solution of a weak acid can be written as:

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

Rearranging to solve for $[H_3O^+]$ yields:

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

Taking the negative logarithm of both sides of this equation gives

$$-\log[H_3O^+] = -\log K_a - \log\frac{[HA]}{[A^-]},$$

which can be written as

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

where pK_a is the negative of the logarithm of the ionization constant of the weak acid (pK_a = −log K_a). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak conjugate acid-base pair in a buffered solution. Scientists often use this expression, called the **Henderson-Hasselbalch equation**, to calculate the pH of buffer solutions. It is important to note that the "*x* is small" assumption must be valid to use this equation.

Portrait of a Chemist

Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

How Sciences Interconnect

Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$CO_2(g) + 2H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3{}^-(aq) + H_3O^+(aq)$$

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, $HCO_3{}^-$, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$pH = pK_a + \log\frac{[base]}{[acid]} = 6.4 + \log\frac{0.024}{0.0012} = 7.7$$

The fact that the H_2CO_3 concentration is significantly lower than that of the $HCO_3{}^-$ ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the $HCO_3{}^-$ ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

Link to Learning

View **information (http://openstaxcollege.org/l/16BufferSystem)** on the buffer system encountered in natural waters.

14.7 Acid-Base Titrations

By the end of this section, you will be able to:

- Interpret titration curves for strong and weak acid-base systems
- Compute sample pH at important stages of a titration
- Explain the function of acid-base indicators

As seen in the chapter on the stoichiometry of chemical reactions, titrations can be used to quantitatively analyze solutions for their acid or base concentrations. In this section, we will explore the underlying chemical equilibria that make acid-base titrimetry a useful analytical technique.

Titration Curves

A **titration curve** is a plot of some solution property versus the amount of added titrant. For acid-base titrations, solution pH is a useful property to monitor because it varies predictably with the solution composition and, therefore, may be used to monitor the titration's progress and detect its end point. The following example exercise demonstrates the computation of pH for a titration solution after additions of several specified titrant volumes. The first example involves a strong acid titration that requires only stoichiometric calculations to derive the solution pH. The second example addresses a weak acid titration requiring equilibrium calculations.

Example 14.21

Calculating pH for Titration Solutions: Strong Acid/Strong Base

A titration is carried out for 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* of a strong base NaOH (the titration curve is shown in **Figure 14.18**). Calculate the pH at these volumes of added base solution:

(a) 0.00 mL

(b) 12.50 mL

(c) 25.00 mL

(d) 37.50 mL

Solution

(a) Titrant volume = 0 mL. The solution pH is due to the acid ionization of HCl. Because this is a strong acid, the ionization is complete and the hydronium ion molarity is 0.100 *M*. The pH of the solution is then

$$\text{pH} = -\log(0.100) = 1.000$$

(b) Titrant volume = 12.50 mL. Since the acid sample and the base titrant are both monoprotic and equally concentrated, this titrant addition involves less than a stoichiometric amount of base, and so it is completely consumed by reaction with the excess acid in the sample. The concentration of acid remaining is computed by subtracting the consumed amount from the intial amount and then dividing by the solution volume:

$$[\text{H}_3\text{O}^+] = \frac{\text{n}(\text{H}^+)}{V} = \frac{0.002500\ \text{mol} \times \left(\frac{1000\ \text{mL}}{1\ \text{L}}\right) - 0.100\ M \times 12.50\ \text{mL}}{25.00\ \text{mL} + 12.50\ \text{mL}} = 0.0333\ M$$

(c) Titrant volume = 25.00 mL. This titrant addition involves a stoichiometric amount of base (the *equivalence point*), and so only products of the neutralization reaction are in solution (water and NaCl). Neither the cation nor the anion of this salt undergo acid-base ionization; the only process generating hydronium ions is the autoprotolysis of water. The solution is neutral, having a pH = 7.00.

(d) Titrant volume = 37.50 mL. This involves the addition of titrant in excess of the equivalence point. The solution pH is then calculated using the concentration of hydroxide ion:

$$\text{n}(\text{OH}^-)_0 > \text{n}(\text{H}^+)_0$$

$$[\text{OH}^-] = \frac{\text{n}(\text{OH}^-)}{V} = \frac{0.100\ M \times 35.70\ \text{mL} - 0.002500\ \text{mol} \times \left(\frac{1000\ \text{mL}}{1\ \text{L}}\right)}{25.00\ \text{mL} + 37.50\ \text{mL}} = 0.0200\ M$$

$\text{pH} = 14 - \text{pOH} = 14 + \log([\text{OH}^-]) = 14 + \log(0.0200) = 12.30$

Check Your Learning

Calculate the pH for the strong acid/strong base titration between 50.0 mL of 0.100 *M* $\text{HNO}_3(aq)$ and 0.200 *M* NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 40.0 mL.

Answer: 0.00: 1.000; 15.0: 1.5111; 25.0: 7; 40.0: 12.523

Example 14.22

Titration of a Weak Acid with a Strong Base

Consider the titration of 25.00 mL of 0.100 *M* $\text{CH}_3\text{CO}_2\text{H}$ with 0.100 *M* NaOH. The reaction can be represented as:

$$\text{CH}_3\text{CO}_2\text{H} + \text{OH}^- \longrightarrow \text{CH}_3\text{CO}_2{}^- + \text{H}_2\text{O}$$

Calculate the pH of the titration solution after the addition of the following volumes of NaOH titrant:

(a) 0.00 mL

(b) 25.00 mL

(c) 12.50 mL

(d) 37.50 mL

Solution

(a) The initial pH is computed for the acetic acid solution in the usual ICE approach:

$$K_a = \frac{[H_3O^+][CH_3CO_2{}^-]}{[CH_3CO_2H]} \approx \frac{[H_3O^+]^2}{[CH_3CO_2H]_0}, \quad \text{and}$$

$$[H_3O^+] = \sqrt{K_a \times [CH_3CO_2H]} = \sqrt{1.8 \times 10^{-5} \times 0.100} = 1.3 \times 10^{-3}$$

$$\text{pH} = -\log(1.3 \times 10^{-3}) = 2.87$$

(b) The acid and titrant are both monoprotic and the sample and titrant solutions are equally concentrated; thus, this volume of titrant represents the equivalence point. Unlike the strong-acid example above, however, the reaction mixture in this case contains a weak conjugate base (acetate ion). The solution pH is computed considering the base ionization of acetate, which is present at a concentration of

$$\frac{0.00250\ \text{mol}}{0.0500\ \text{L}} = 0.0500\ \text{M}CH_3CO_2{}^-$$

Base ionization of acetate is represented by the equation

$$CH_3CO_2{}^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$

$$K_b = \frac{[H^+][OH^-]}{K_a} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Assuming x << 0.0500, the pH may be calculated via the usual ICE approach: $K_b = \frac{x^2}{0.0500\ M}$

$$x = [OH^-] = 5.3 \times 10^{-6}$$

$$\text{pOH} = -\log(5.3 \times 10^{-6}) = 5.28$$

$$\text{pH} = 14.00 - 5.28 = 8.72$$

Note that the pH at the equivalence point of this titration is significantly greater than 7, as expected when titrating a weak acid with a strong base.

(c) Titrant volume = 12.50 mL. This volume represents one-half of the stoichiometric amount of titrant, and so one-half of the acetic acid has been neutralized to yield an equivalent amount of acetate ion. The concentrations of these conjugate acid-base partners, therefore, are equal. A convenient approach to computing the pH is use of the Henderson-Hasselbalch equation:

$$\text{pH} = pK_a + \log\frac{[\text{Base}]}{[\text{Acid}]} = -\log(K_a) + \log\frac{[CH_3CO_2{}^-]}{[CH_3CO_2H]} = -\log(1.8 \times 10^{-5}) + \log(1)$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$$

(pH = pK_a at the half-equivalence point in a titration of a weak acid)

(d) Titrant volume = 37.50 mL. This volume represents a stoichiometric excess of titrant, and a reaction solution containing both the titration product, acetate ion, and the excess strong titrant. In such solutions, the solution pH is determined primarily by the amount of excess strong base:

$$[OH^-] = \frac{(0.003750\ \text{mol} - 0.00250\ \text{mol})}{0.06250\ \text{L}} = 2.00 \times 10^{-2}\ M$$

$$\text{pOH} = -\log\left(2.00 \times 10^{-2}\right) = 1.70, \text{ and pH} = 14.00 - 1.70 = 12.30$$

Check Your Learning

Calculate the pH for the weak acid/strong base titration between 50.0 mL of 0.100 M HCOOH(aq) (formic acid) and 0.200 M NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 30.0 mL.

Answer: 0.00 mL: 2.37; 15.0 mL: 3.92; 25.00 mL: 8.29; 30.0 mL: 12.097

Performing additional calculations similar to those in the preceding example permits a more full assessment of titration curves. A summary of pH/volume data pairs for the strong and weak acid titrations is provided in **Table**

14.2 and plotted as titration curves in **Figure 14.18**. A comparison of these two curves illustrates several important concepts that are best addressed by identifying the four stages of a titration:

initial state (added titrant volume = 0 mL): pH is determined by the acid being titrated; because the two acid samples are equally concentrated, the weak acid will exhibit a greater initial pH

pre-equivalence point (0 mL < V < 25 mL): solution pH increases gradually and the acid is consumed by reaction with added titrant; composition includes unreacted acid and the reaction product, its conjugate base

equivalence point (V = 25 mL): a drastic rise in pH is observed as the solution composition transitions from acidic to either neutral (for the strong acid sample) or basic (for the weak acid sample), with pH determined by ionization of the conjugate base of the acid

postequivalence point (V > 25 mL): pH is determined by the amount of excess strong base titrant added; since both samples are titrated with the same titrant, both titration curves appear similar at this stage.

pH Values in the Titrations of a Strong Acid and of a Weak Acid

Volume of 0.100 *M* NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 *M* HCl[1]	pH Values 0.100 *M* CH_3CO_2H[2]
0.0	0.0	1.00	2.87
5.0	0.00050	1.18	4.14
10.0	0.00100	1.37	4.57
15.0	0.00150	1.60	4.92
20.0	0.00200	1.95	5.35
22.0	0.00220	2.20	5.61
24.0	0.00240	2.69	6.13
24.5	0.00245	3.00	6.44
24.9	0.00249	3.70	7.14
25.0	0.00250	7.00	8.72
25.1	0.00251	10.30	10.30
25.5	0.00255	11.00	11.00
26.0	0.00260	11.29	11.29
28.0	0.00280	11.75	11.75
30.0	0.00300	11.96	11.96
35.0	0.00350	12.22	12.22
40.0	0.00400	12.36	12.36
45.0	0.00450	12.46	12.46
50.0	0.00500	12.52	12.52

Table 14.2

---

1. Titration of 25.00 mL of 0.100 *M* HCl (0.00250 mol of HCI) with 0.100 *M* NaOH.
2. Titration of 25.00 mL of 0.100 *M* CH_3CO_2H (0.00250 mol of CH_3CO_2H) with 0.100 *M* NaOH.

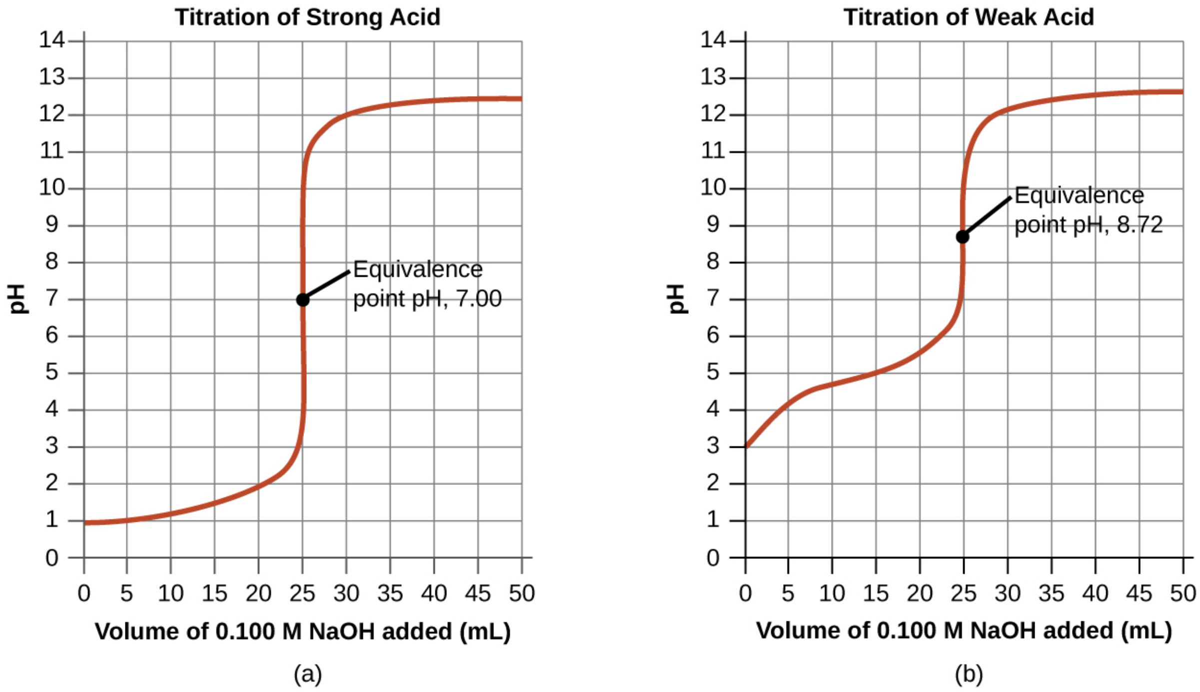


Figure 14.18 (a) The titration curve for the titration of 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 *M* acetic acid (weak acid) with 0.100 *M* NaOH (strong base) has an equivalence point of 8.72 pH.

Acid-Base Indicators

Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colorless substance in any aqueous solution with a hydronium ion concentration greater than 5.0×10^{-9} *M* (pH < 8.3). In more basic solutions where the hydronium ion concentration is less than 5.0×10^{-9} *M* (pH > 8.3), it is red or pink. Substances such as phenolphthalein, which can be used to determine the pH of a solution, are called **acid-base indicators**. Acid-base indicators are either weak organic acids or weak organic bases.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use HIn as a simple representation for the complex methyl orange molecule:

$$\underset{\text{red}}{\mathrm{HIn}(aq)} + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \underset{\text{yellow}}{\mathrm{In^-}(aq)}$$

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{In^-}]}{[\mathrm{HIn}]} = 4.0 \times 10^{-4}$$

The anion of methyl orange, $\mathrm{In^-}$, is yellow, and the nonionized form, HIn, is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the nonionized red form, in accordance with Le Châtelier’s principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

The perceived color of an indicator solution is determined by the ratio of the concentrations of the two species $\mathrm{In^-}$ and HIn. If most of the indicator (typically about 60−90% or more) is present as $\mathrm{In^-}$, the perceived color of the solution is yellow. If most is present as HIn, then the solution color appears red. The Henderson-Hasselbalch equation is useful for understanding the relationship between the pH of an indicator solution and its composition (thus, perceived color):

$$\text{pH} = \text{p}K\text{a} + \log\left(\frac{[\text{In}^-]}{[\text{HIn}]}\right)$$

In solutions where pH > pK_a, the logarithmic term must be positive, indicating an excess of the conjugate base form of the indicator (yellow solution). When pH > pK_a, the log term must be negative, indicating an excess of the conjugate acid (red solution). When the solution pH is close to the indicator pKa, appreciable amounts of both conjugate partners are present, and the solution color is that of an additive combination of each (yellow and red, yielding orange). The **color change interval** (or *pH interval*) for an acid-base indicator is defined as the range of pH values over which a change in color is observed, and for most indicators this range is approximately pK_a ± 1.

There are many different acid-base indicators that cover a wide range of pH values and can be used to determine the approximate pH of an unknown solution by a process of elimination. Universal indicators and pH paper contain a mixture of indicators and exhibit different colors at different pHs. **Figure 14.19** presents several indicators, their colors, and their color-change intervals.

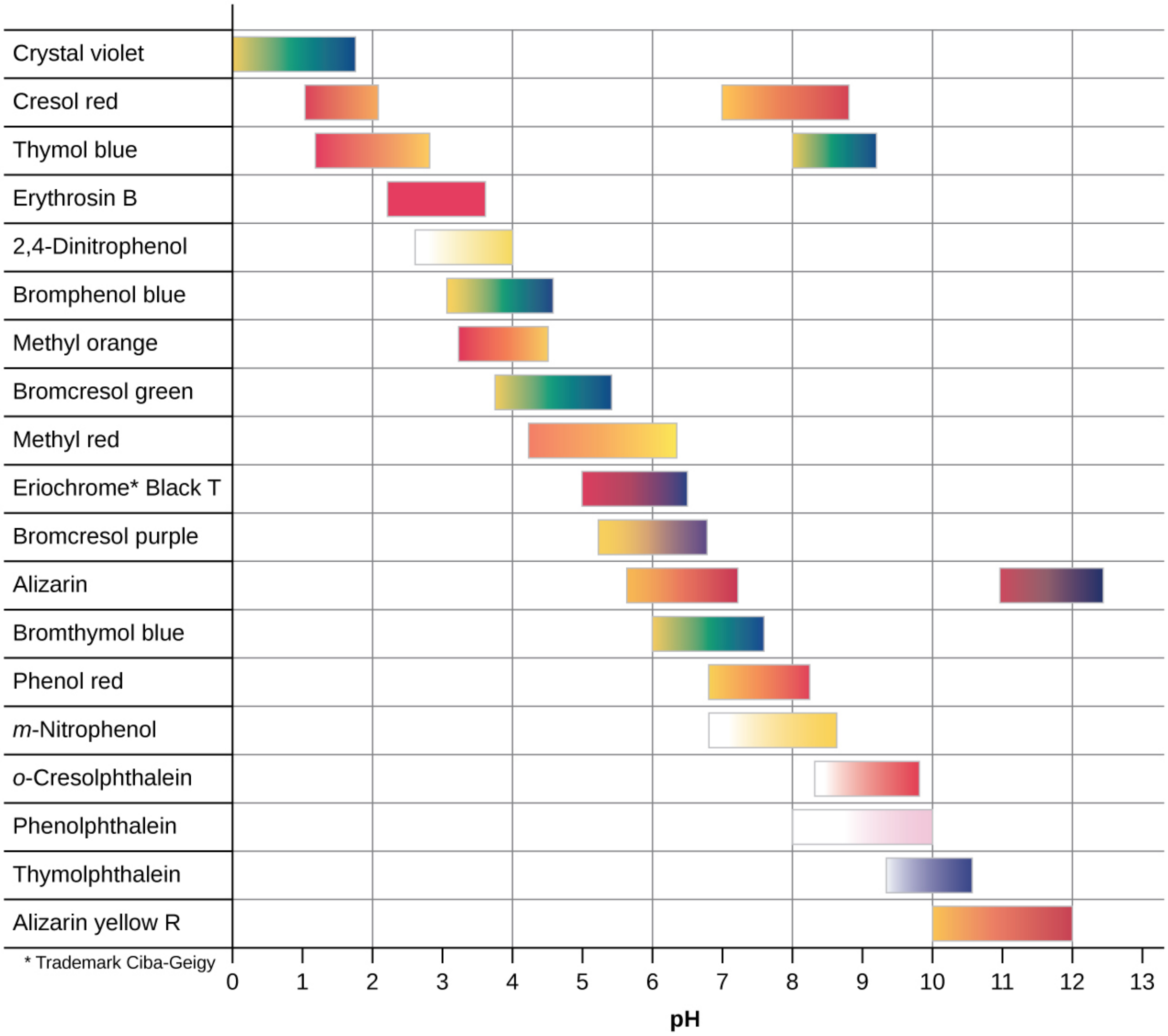


Figure 14.19 This chart illustrates the color change intervals for several acid-base indicators.

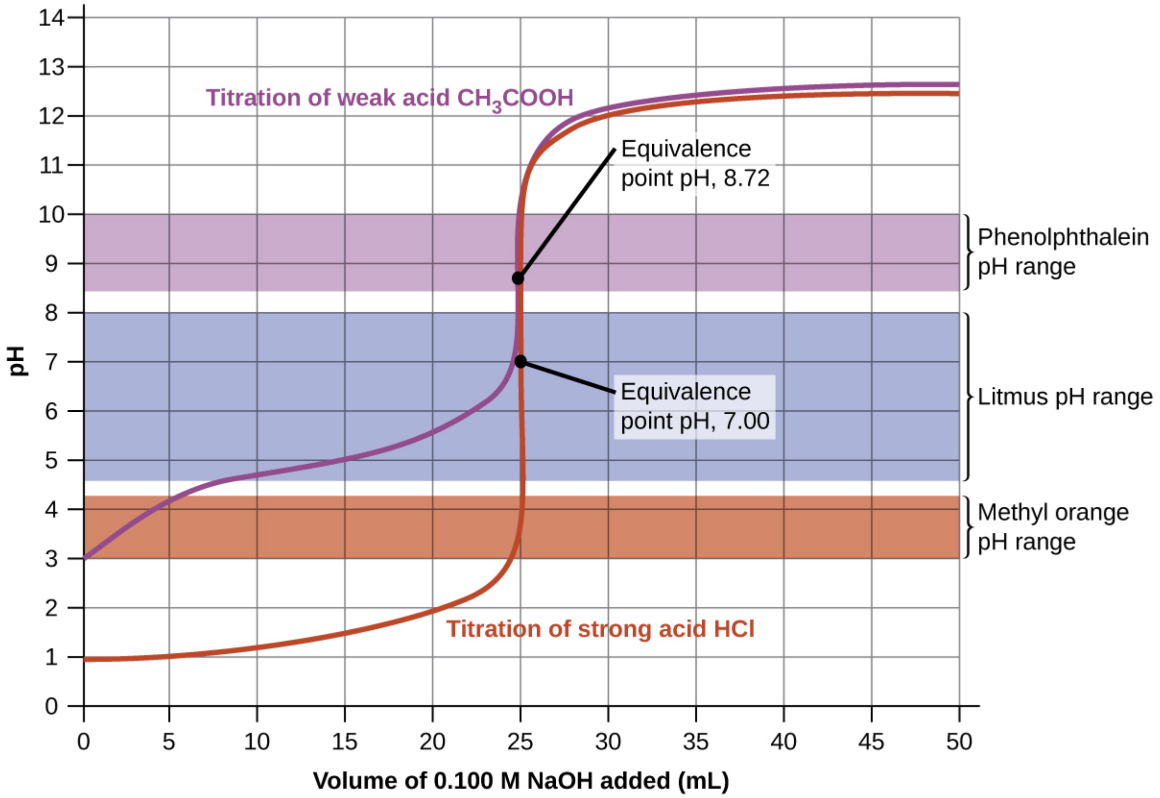


Figure 14.20 Titration curves for strong and weak acids illustrating the proper choice of acid-base indicator. Any of the three indicators will exhibit a reasonably sharp color change at the equivalence point of the strong acid titration, but only phenolphthalein is suitable for use in the weak acid titration.

The titration curves shown in **Figure 14.20** illustrate the choice of a suitable indicator for specific titrations. In the strong acid titration, use of any of the three indicators should yield reasonably sharp color changes and accurate end point determinations. For this titration, the solution pH reaches the lower limit of the methyl orange color change interval after addition of ~24 mL of titrant, at which point the initially red solution would begin to appear orange. When 25 mL of titrant has been added (the equivalence point), the pH is well above the upper limit and the solution will appear yellow. The titration's end point may then be estimated as the volume of titrant that yields a distinct orange-to-yellow color change. This color change would be challenging for most human eyes to precisely discern. More-accurate estimates of the titration end point are possible using either litmus or phenolphthalein, both of which exhibit color change intervals that are encompassed by the steep rise in pH that occurs around the 25.00 mL equivalence point.

The weak acid titration curve in **Figure 14.20** shows that only one of the three indicators is suitable for end point detection. If methyl orange is used in this titration, the solution will undergo a gradual red-to-orange-to-yellow color change over a relatively large volume interval (0–6 mL), completing the color change well before the equivalence point (25 mL) has been reached. Use of litmus would show a color change that begins after adding 7–8 mL of titrant and ends just before the equivalence point. Phenolphthalein, on the other hand, exhibits a color change interval that nicely brackets the abrupt change in pH occurring at the titration's equivalence point. A sharp color change from colorless to pink will be observed within a very small volume interval around the equivalence point.

Key Terms

acid ionization reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

acid ionization constant (K_a) equilibrium constant for an acid ionization reaction

acid-base indicator weak acid or base whose conjugate partner imparts a different solution color; used in visual assessments of solution pH

acidic a solution in which $[H_3O^+] > [OH^-]$

amphiprotic species that may either donate or accept a proton in a Bronsted-Lowry acid-base reaction

amphoteric species that can act as either an acid or a base

autoionization reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

base ionization constant (K_b) equilibrium constant for a base ionization reaction

basic a solution in which $[H_3O^+] < [OH^-]$

Brønsted-Lowry acid proton donor

Brønsted-Lowry base proton acceptor

buffer mixture of appreciable amounts of a weak acid-base pair the pH of a buffer resists change when small amounts of acid or base are added

buffer capacity amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

color-change interval range in pH over which the color change of an indicator is observed

conjugate acid substance formed when a base gains a proton

conjugate base substance formed when an acid loses a proton

diprotic acid acid containing two ionizable hydrogen atoms per molecule

diprotic base base capable of accepting two protons

Henderson-Hasselbalch equation logarithmic version of the acid ionization constant expression, conveniently formatted for calculating the pH of buffer solutions

ion-product constant for water (K_w) equilibrium constant for the autoionization of water

leveling effect observation that acid-base strength of solutes in a given solvent is limited to that of the solvent’s characteristic acid and base species (in water, hydronium and hydroxide ions, respectively)

monoprotic acid acid containing one ionizable hydrogen atom per molecule

neutral describes a solution in which $[H_3O^+] = [OH^-]$

oxyacid ternary compound with acidic properties, molecules of which contain a central nonmetallic atom bonded to one or more O atoms, at least one of which is bonded to an ionizable H atom

percent ionization ratio of the concentration of ionized acid to initial acid concentration expressed as a percentage

pH logarithmic measure of the concentration of hydronium ions in a solution

pOH logarithmic measure of the concentration of hydroxide ions in a solution

stepwise ionization process in which a polyprotic acid is ionized by losing protons sequentially

titration curve plot of some sample property (such as pH) versus volume of added titrant

triprotic acid acid that contains three ionizable hydrogen atoms per molecule

Key Equations

- $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ (at 25 °C)
- $\text{pH} = -\log[H_3O^+]$
- $\text{pOH} = -\log[OH^-]$
- $[H_3O^+] = 10^{-\text{pH}}$
- $[OH^-] = 10^{-\text{pOH}}$
- $\text{pH} + \text{pOH} = \text{p}K_w = 14.00$ at 25 °C
- $K_a = \frac{[H_3O^+][A^-]}{[HA]}$
- $K_b = \frac{[HB^+][OH^-]}{[B]}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w$
- $\text{Percent ionization} = \frac{[H_3O^+]_{eq}}{[HA]_0} \times 100$
- $\text{p}K_a = -\log K_a$
- $\text{p}K_b = -\log K_b$
- $\text{pH} = \text{p}K_a + \log\frac{[A^-]}{[HA]}$

Summary

14.1 Brønsted-Lowry Acids and Bases

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, OH^- when it undergoes autoionization:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25\ °C$$

14.2 pH and pOH

Concentrations of hydronium and hydroxide ions in aqueous media are often represented as logarithmic pH and pOH values, respectively. At 25 °C, the autoprotolysis equilibrium for water requires the sum of pH and pOH to equal 14 for any aqueous solution. The relative concentrations of hydronium and hydroxide ion in a solution define its status as acidic ($[H_3O^+] > [OH^-]$), basic ($[H_3O^+] < [OH^-]$), or neutral ($[H_3O^+] = [OH^-]$). At 25 °C, a $pH < 7$ indicates an acidic solution, a $pH > 7$ a basic solution, and a $pH = 7$ a neutral solution.

14.3 Relative Strengths of Acids and Bases

The relative strengths of acids and bases are reflected in the magnitudes of their ionization constants; the stronger the acid or base, the larger its ionization constant. A reciprocal relation exists between the strengths of a conjugate acid-base pair: the stronger the acid, the weaker its conjugate base. Water exerts a leveling effect on dissolved acids or bases, reacting completely to generate its characteristic hydronium and hydroxide ions (the strongest acid and base that may exist in water). The strengths of the binary acids increase from left to right across a period of the periodic table ($CH_4 < NH_3 < H_2O < HF$), and they increase down a group ($HF < HCl < HBr < HI$). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases ($H_2SO_3 < H_2SO_4$). The strengths of oxyacids also increase as the electronegativity of the central element increases [$H_2SeO_4 < H_2SO_4$].

14.4 Hydrolysis of Salts

The ions composing salts may possess acidic or basic character, ionizing when dissolved in water to yield acidic or basic solutions. Acidic cations are typically the conjugate partners of weak bases, and basic anions are the conjugate partners of weak acids. Many metal ions bond to water molecules when dissolved to yield complex ions that may function as acids.

14.5 Polyprotic Acids

An acid that contains more than one ionizable proton is a polyprotic acid. These acids undergo stepwise ionization reactions involving the transfer of single protons. The ionization constants for polyprotic acids decrease with each subsequent step; these decreases typically are large enough to permit simple equilibrium calculations that treat each step separately.

14.6 Buffers

Solutions that contain appreciable amounts of a weak conjugate acid-base pair are called buffers. A buffered solution will experience only slight changes in pH when small amounts of acid or base are added. Addition of large amounts of acid or base can exceed the buffer capacity, consuming most of one conjugate partner and preventing further buffering action.

14.7 Acid-Base Titrations

The titration curve for an acid-base titration is typically a plot of pH versus volume of added titrant. These curves are useful in selecting appropriate acid-base indicators that will permit accurate determinations of titration end points.

Exercises

14.1 Brønsted-Lowry Acids and Bases

1. Write equations that show NH_3 as both a conjugate acid and a conjugate base.

2. Write equations that show $H_2PO_4{}^-$ acting both as an acid and as a base.

3. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a) H_3O^+

(b) HCl

(c) NH_3

(d) CH_3CO_2H

(e) $NH_4{}^+$

(f) $HSO_4{}^-$

4. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a) HNO_3

(b) $PH_4{}^+$

(c) H_2S

(d) CH_3CH_2COOH

(e) $H_2PO_4{}^-$

(f) HS^-

5. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

(a) H_2O

(b) OH^-

(c) NH_3

(d) CN^-

(e) S^{2-}

(f) $H_2PO_4{}^-$

6. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

(a) HS^-

(b) $PO_4{}^{3-}$

(c) $NH_2{}^-$

(d) C_2H_5OH

(e) O^{2-}

(f) $H_2PO_4{}^-$

7. What is the conjugate acid of each of the following? What is the conjugate base of each?

(a) OH^-

(b) H_2O

(c) $HCO_3{}^-$

(d) NH_3

(e) $HSO_4{}^-$

(f) H_2O_2

(g) HS^-

(h) $H_5N_2{}^+$

8. What is the conjugate acid of each of the following? What is the conjugate base of each?

(a) H_2S

(b) $H_2PO_4{}^-$

(c) PH_3

(d) HS^-

(e) $HSO_3{}^-$

(f) $H_3O_2{}^+$

(g) H_4N_2

(h) CH_3OH

9. Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

(a) $HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3{}^-$

(b) $CN^- + H_2O \longrightarrow HCN + OH^-$

(c) $H_2SO_4 + Cl^- \longrightarrow HCl + HSO_4{}^-$

(d) $HSO_4{}^- + OH^- \longrightarrow SO_4{}^{2-} + H_2O$

(e) $O^{2-} + H_2O \longrightarrow 2OH^-$

(f) $[Cu(H_2O)_3(OH)]^+ + [Al(H_2O)_6]^{3+} \longrightarrow [Cu(H_2O)_4]^{2+} + [Al(H_2O)_5(OH)]^{2+}$

(g) $H_2S + NH_2{}^- \longrightarrow HS^- + NH_3$

10. Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

(a) $NO_2{}^- + H_2O \longrightarrow HNO_2 + OH^-$

(b) $HBr + H_2O \longrightarrow H_3O^+ + Br^-$

(c) $HS^- + H_2O \longrightarrow H_2S + OH^-$

(d) $H_2PO_4{}^- + OH^- \longrightarrow HPO_4{}^{2-} + H_2O$

(e) $H_2PO_4{}^- + HCl \longrightarrow H_3PO_4 + Cl^-$

(f) $[Fe(H_2O)_5(OH)]^{2+} + [Al(H_2O)_6]^{3+} \longrightarrow [Fe(H_2O)_6]^{3+} + [Al(H_2O)_5(OH)]^{2+}$

(g) $CH_3OH + H^- \longrightarrow CH_3O^- + H_2$

11. What are amphiprotic species? Illustrate with suitable equations.

12. State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species:

(a) H_2O

(b) $H_2PO_4{}^-$

(c) S^{2-}

(d) $CO_3{}^{2-}$

(e) $HSO_4{}^-$

13. State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.

(a) NH_3

(b) $HPO_4{}^-$

(c) Br^-

(d) $NH_4{}^+$

(e) $ASO_4{}^{3-}$

14. Is the self-ionization of water endothermic or exothermic? The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C and 9.3×10^{-14} at 60 °C.

14.2 pH and pOH

15. Explain why a sample of pure water at 40 °C is neutral even though $[H_3O^+] = 1.7 \times 10^{-7}$ *M*. K_w is 2.9×10^{-14} at 40 °C.

16. The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 40 °C.

17. The ionization constant for water (K_w) is 9.311×10^{-14} at 60 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 60 °C.

18. Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

(a) 0.200 *M* HCl

(b) 0.0143 *M* NaOH

(c) 3.0 *M* HNO_3

(d) 0.0031 *M* $Ca(OH)_2$

19. Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

(a) 0.000259 *M* $HClO_4$

(b) 0.21 *M* NaOH

(c) 0.000071 *M* $Ba(OH)_2$

(d) 2.5 *M* KOH

20. What are the pH and pOH of a solution of 2.0 M HCl, which ionizes completely?

21. What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

22. Calculate the hydrogen ion concentration and the hydroxide ion concentration in wine from its pH. See **Figure 14.2** for useful information.

23. Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See **Figure 14.2** for useful information.

24. The hydronium ion concentration in a sample of rainwater is found to be 1.7×10^{-6} *M* at 25 °C. What is the concentration of hydroxide ions in the rainwater?

25. The hydroxide ion concentration in household ammonia is 3.2×10^{-3} *M* at 25 °C. What is the concentration of hydronium ions in the solution?

14.3 Relative Strengths of Acids and Bases

26. Explain why the neutralization reaction of a strong acid and a weak base gives a weakly acidic solution.

27. Explain why the neutralization reaction of a weak acid and a strong base gives a weakly basic solution.

28. Use this list of important industrial compounds (and **Figure 14.8**) to answer the following questions regarding: CaO, $Ca(OH)_2$, CH_3CO_2H, CO_2, HCl, H_2CO_3, HF, HNO_2, HNO_3, H_3PO_4, H_2SO_4, NH_3, NaOH, Na_2CO_3.

(a) Identify the strong Brønsted-Lowry acids and strong Brønsted-Lowry bases.

(b) List those compounds in (a) that can behave as Brønsted-Lowry acids with strengths lying between those of H_3O^+ and H_2O.

(c) List those compounds in (a) that can behave as Brønsted-Lowry bases with strengths lying between those of H_2O and OH^-.

29. The odor of vinegar is due to the presence of acetic acid, CH_3CO_2H, a weak acid. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this acid.

30. Household ammonia is a solution of the weak base NH_3 in water. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this base.

31. Explain why the ionization constant, K_a, for H_2SO_4 is larger than the ionization constant for H_2SO_3.

32. Explain why the ionization constant, K_a, for HI is larger than the ionization constant for HF.

33. Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid $Mg(OH)_2$ in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction, and identify the conjugate acid-base pairs.

34. Nitric acid reacts with insoluble copper(II) oxide to form soluble copper(II) nitrate, $Cu(NO_3)_2$, a compound that has been used to prevent the growth of algae in swimming pools. Write the balanced chemical equation for the reaction of an aqueous solution of HNO_3 with CuO.

35. What is the ionization constant at 25 °C for the weak acid $CH_3NH_3{}^+$, the conjugate acid of the weak base CH_3NH_2, $K_b = 4.4 \times 10^{-4}$.

36. What is the ionization constant at 25 °C for the weak acid $(CH_3)_2NH_2{}^+$, the conjugate acid of the weak base $(CH_3)_2NH$, $K_b = 5.9 \times 10^{-4}$?

37. Which base, CH_3NH_2 or $(CH_3)_2NH$, is the stronger base? Which conjugate acid, $(CH_3)_2NH_2{}^+$ or $CH_3NH_3{}^+$, is the stronger acid?

38. Which is the stronger acid, $NH_4{}^+$ or HBrO?

39. Which is the stronger base, $(CH_3)_3N$ or $H_2BO_3{}^-$?

40. Predict which acid in each of the following pairs is the stronger and explain your reasoning for each.

(a) H_2O or HF

(b) $B(OH)_3$ or $Al(OH)_3$

(c) $HSO_3{}^-$ or $HSO_4{}^-$

(d) NH_3 or H_2S

(e) H_2O or H_2Te

41. Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.

(a) $HSO_4{}^-$ or $HSeO_4{}^-$

(b) NH_3 or H_2O

(c) PH_3 or HI

(d) NH_3 or PH_3

(e) H_2S or HBr

42. Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity: HCl, HBr, HI

(b) basicity: H_2O, OH^-, H^-, Cl^-

(c) basicity: $Mg(OH)_2$, $Si(OH)_4$, $ClO_3(OH)$ (Hint: Formula could also be written as $HClO_4$.)

(d) acidity: HF, H_2O, NH_3, CH_4

43. Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity: $NaHSO_3$, $NaHSeO_3$, $NaHSO_4$

(b) basicity: $BrO_2{}^-$, $ClO_2{}^-$, $IO_2{}^-$

(c) acidity: HOCl, HOBr, HOI

(d) acidity: HOCl, HOClO, $HOClO_2$, $HOClO_3$

(e) basicity: $NH_2{}^-$, HS^-, HTe^-, $PH_2{}^-$

(f) basicity: BrO^-, $BrO_2{}^-$, $BrO_3{}^-$, $BrO_4{}^-$

44. Both HF and HCN ionize in water to a limited extent. Which of the conjugate bases, F^- or CN^-, is the stronger base?

45. The active ingredient formed by aspirin in the body is salicylic acid, $C_6H_4OH(CO_2H)$. The carboxyl group ($-CO_2H$) acts as a weak acid. The phenol group (an OH group bonded to an aromatic ring) also acts as an acid but a much weaker acid. List, in order of descending concentration, all of the ionic and molecular species present in a 0.001-*M* aqueous solution of $C_6H_4OH(CO_2H)$.

46. Are the concentrations of hydronium ion and hydroxide ion in a solution of an acid or a base in water directly proportional or inversely proportional? Explain your answer.

47. What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid or base?

48. Which of the following will increase the percent of NH_3 that is converted to the ammonium ion in water?

(a) addition of NaOH

(b) addition of HCl

(c) addition of NH_4Cl

49. Which of the following will increase the percentage of HF that is converted to the fluoride ion in water?

(a) addition of NaOH

(b) addition of HCl

(c) addition of NaF

50. What is the effect on the concentrations of NO_2^-, HNO_2, and OH^- when the following are added to a solution of KNO_2 in water:

(a) HCl

(b) HNO_2

(c) NaOH

(d) NaCl

(e) KNO

51. What is the effect on the concentration of hydrofluoric acid, hydronium ion, and fluoride ion when the following are added to separate solutions of hydrofluoric acid?

(a) HCl

(b) KF

(c) NaCl

(d) KOH

(e) HF

52. Why is the hydronium ion concentration in a solution that is 0.10 *M* in HCl and 0.10 *M* in HCOOH determined by the concentration of HCl?

53. From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

(a) CH_3CO_2H: $[H_3O^+] = 1.34 \times 10^{-3}\ M$;
$[CH_3CO_2^-] = 1.34 \times 10^{-3}\ M$;

$[CH_3CO_2H] = 9.866 \times 10^{-2}\ M$;

(b) ClO^-: $[OH^-] = 4.0 \times 10^{-4}\ M$;

$[HClO] = 2.38 \times 10^{-4}\ M$;

$[ClO^-] = 0.273\ M$;

(c) HCO_2H: $[HCO_2H] = 0.524\ M$;
$[H_3O^+] = 9.8 \times 10^{-3}\ M$;
$[HCO_2^-] = 9.8 \times 10^{-3}\ M$;

(d) $C_6H_5NH_3^+$: $[C_6H_5NH_3^+] = 0.233\ M$;

$[C_6H_5NH_2] = 2.3 \times 10^{-3}\ M$;
$[H_3O^+] = 2.3 \times 10^{-3}\ M$

54. From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

(a) NH_3: $[OH^-] = 3.1 \times 10^{-3}\ M$;
$[NH_4^+] = 3.1 \times 10^{-3}\ M$;

$[NH_3] = 0.533\ M$;

(b) HNO_2: $[H_3O^+] = 0.011\ M$;
$[NO_2^-] = 0.0438\ M$;

$[HNO_2] = 1.07\ M$;

(c) $(CH_3)_3N$: $[(CH_3)_3N] = 0.25\ M$;
$[(CH_3)_3NH^+] = 4.3 \times 10^{-3}\ M$;

$[OH^-] = 3.7 \times 10^{-3}\ M$;

(d) NH_4^+: $[NH_4^+] = 0.100\ M$;

$[NH_3] = 7.5 \times 10^{-6}\ M$;
$[H_3O^+] = 7.5 \times 10^{-6}\ M$

55. Determine K_b for the nitrite ion, NO_2^-. In a 0.10-M solution this base is 0.0015% ionized.

56. Determine K_a for hydrogen sulfate ion, HSO_4^-. In a 0.10-M solution the acid is 29% ionized.

57. Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

(a) F^-

(b) NH_4^+

(c) AsO_4^{3-}

(d) $(CH_3)_2NH_2^+$

(e) NO_2^-

(f) $HC_2O_4^-$ (as a base)

58. Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

(a) HTe^- (as a base)

(b) $(CH_3)_3NH^+$

(c) $HAsO_4^{3-}$ (as a base)

(d) HO_2^- (as a base)

(e) $C_6H_5NH_3^+$

(f) HSO_3^- (as a base)

59. Using the K_a value of 1.4×10^{-5}, place $Al(H_2O)_6^{3+}$ in the correct location in **Figure 14.7**.

60. Calculate the concentration of all solute species in each of the following solutions of acids or bases. Assume that the ionization of water can be neglected, and show that the change in the initial concentrations can be neglected.

(a) 0.0092 *M* HClO, a weak acid

(b) 0.0784 *M* $C_6H_5NH_2$, a weak base

(c) 0.0810 *M* HCN, a weak acid

(d) 0.11 *M* $(CH_3)_3N$, a weak base

(e) 0.120 *M* $Fe(H_2O)_6{}^{2+}$ a weak acid, $K_a = 1.6 \times 10^{-7}$

61. Propionic acid, $C_2H_5CO_2H$ ($K_a = 1.34 \times 10^{-5}$), is used in the manufacture of calcium propionate, a food preservative. What is the pH of a 0.698-*M* solution of $C_2H_5CO_2H$?

62. White vinegar is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is 1.007 g/cm^3, what is the pH?

63. The ionization constant of lactic acid, $CH_3CH(OH)CO_2H$, an acid found in the blood after strenuous exercise, is 1.36×10^{-4}. If 20.0 g of lactic acid is used to make a solution with a volume of 1.00 L, what is the concentration of hydronium ion in the solution?

64. Nicotine, $C_{10}H_{14}N_2$, is a base that will accept two protons ($K_{b1} = 7 \times 10^{-7}$, $K_{b2} = 1.4 \times 10^{-11}$). What is the concentration of each species present in a 0.050-*M* solution of nicotine?

65. The pH of a 0.23-*M* solution of HF is 1.92. Determine K_a for HF from these data.

66. The pH of a 0.15-*M* solution of $HSO_4{}^-$ is 1.43. Determine K_a for $HSO_4{}^-$ from these data.

67. The pH of a 0.10-*M* solution of caffeine is 11.70. Determine K_b for caffeine from these data:

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq)$$

68. The pH of a solution of household ammonia, a 0.950 M solution of NH_3, is 11.612. Determine K_b for NH_3 from these data.

14.4 Hydrolysis of Salts

69. Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) $Al(NO_3)_3$

(b) RbI

(c) $KHCO_2$

(d) CH_3NH_3Br

70. Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) $FeCl_3$

(b) K_2CO_3

(c) NH_4Br

(d) $KClO_4$

71. Novocaine, $C_{13}H_{21}O_2N_2Cl$, is the salt of the base procaine and hydrochloric acid. The ionization constant for procaine is 7×10^{-6}. Is a solution of novocaine acidic or basic? What are $[H_3O^+]$, $[OH^-]$, and pH of a 2.0% solution by mass of novocaine, assuming that the density of the solution is 1.0 g/mL.

14.5 Polyprotic Acids

72. Which of the following concentrations would be practically equal in a calculation of the equilibrium concentrations in a 0.134-*M* solution of H_2CO_3, a diprotic acid: $[H_3O^+]$, $[OH^-]$, $[H_2CO_3]$, $[HCO_3{}^-]$, $[CO_3{}^{2-}]$? No calculations are needed to answer this question.

73. Calculate the concentration of each species present in a 0.050-*M* solution of H_2S.

74. Calculate the concentration of each species present in a 0.010-*M* solution of phthalic acid, $C_6H_4(CO_2H)_2$.

$$C_6H_4(CO_2H)_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_4(CO_2H)(CO_2)^-(aq) \qquad K_a = 1.1 \times 10^{-3}$$

$$C_6H_4(CO_2H)(CO_2)(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_4(CO_2)_2{}^{2-}(aq) \qquad K_a = 3.9 \times 10^{-6}$$

75. Salicylic acid, $HOC_6H_4CO_2H$, and its derivatives have been used as pain relievers for a long time. Salicylic acid occurs in small amounts in the leaves, bark, and roots of some vegetation (most notably historically in the bark of the willow tree). Extracts of these plants have been used as medications for centuries. The acid was first isolated in the laboratory in 1838.

(a) Both functional groups of salicylic acid ionize in water, with $K_a = 1.0 \times 10^{-3}$ for the—CO_2H group and 4.2×10^{-13} for the −OH group. What is the pH of a saturated solution of the acid (solubility = 1.8 g/L).

(b) Aspirin was discovered as a result of efforts to produce a derivative of salicylic acid that would not be irritating to the stomach lining. Aspirin is acetylsalicylic acid, $CH_3CO_2C_6H_4CO_2H$. The $-CO_2H$ functional group is still present, but its acidity is reduced, $K_a = 3.0 \times 10^{-4}$. What is the pH of a solution of aspirin with the same concentration as a saturated solution of salicylic acid (See Part a).

76. The ion HTe^- is an amphiprotic species; it can act as either an acid or a base.

(a) What is K_a for the acid reaction of HTe^- with H_2O?

(b) What is K_b for the reaction in which HTe^- functions as a base in water?

(c) Demonstrate whether or not the second ionization of H_2Te can be neglected in the calculation of $[HTe^-]$ in a 0.10 M solution of H_2Te.

14.6 Buffers

77. Explain why a buffer can be prepared from a mixture of NH_4Cl and NaOH but not from NH_3 and NaOH.

78. Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the acid H_3PO_4 and a salt of its conjugate base NaH_2PO_4.

79. Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the base NH_3 and a salt of its conjugate acid NH_4Cl.

80. What is $[H_3O^+]$ in a solution of 0.25 *M* CH_3CO_2H and 0.030 *M* $NaCH_3CO_2$?

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2{}^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$

81. What is $[H_3O^+]$ in a solution of 0.075 *M* HNO_2 and 0.030 *M* $NaNO_2$?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2{}^-(aq) \qquad K_a = 4.5 \times 10^{-5}$$

82. What is $[OH^-]$ in a solution of 0.125 *M* CH_3NH_2 and 0.130 *M* CH_3NH_3Cl?

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3{}^+(aq) + OH^-(aq) \qquad K_b = 4.4 \times 10^{-4}$$

83. What is $[OH^-]$ in a solution of 1.25 *M* NH_3 and 0.78 *M* NH_4NO_3?

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4{}^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$

84. What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:

(a) HCl

(b) KCH_3CO_2

(c) NaCl

(d) KOH

(e) CH_3CO_2H

85. What is the effect on the concentration of ammonia, hydroxide ion, and ammonium ion when the following are added to a basic buffer solution of equal concentrations of ammonia and ammonium nitrate:

(a) KI

(b) NH_3

(c) HI

(d) NaOH

(e) NH_4Cl

86. What will be the pH of a buffer solution prepared from 0.20 mol NH_3, 0.40 mol NH_4NO_3, and just enough water to give 1.00 L of solution?

87. Calculate the pH of a buffer solution prepared from 0.155 mol of phosphoric acid, 0.250 mole of KH_2PO_4, and enough water to make 0.500 L of solution.

88. How much solid $NaCH_3CO_2{\bullet}3H_2O$ must be added to 0.300 L of a 0.50-*M* acetic acid solution to give a buffer with a pH of 5.00? (Hint: Assume a negligible change in volume as the solid is added.)

89. What mass of NH_4Cl must be added to 0.750 L of a 0.100-*M* solution of NH_3 to give a buffer solution with a pH of 9.26? (Hint: Assume a negligible change in volume as the solid is added.)

90. A buffer solution is prepared from equal volumes of 0.200 *M* acetic acid and 0.600 *M* sodium acetate. Use 1.80×10^{-5} as K_a for acetic acid.

(a) What is the pH of the solution?

(b) Is the solution acidic or basic?

(c) What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to 0.200 L of the original buffer?

91. A 5.36–g sample of NH_4Cl was added to 25.0 mL of 1.00 *M* NaOH and the resulting solution

diluted to 0.100 L.

(a) What is the pH of this buffer solution?

(b) Is the solution acidic or basic?

(c) What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to the solution?

14.7 Acid-Base Titrations

92. Explain how to choose the appropriate acid-base indicator for the titration of a weak base with a strong acid.

93. Explain why an acid-base indicator changes color over a range of pH values rather than at a specific pH.

94. Calculate the pH at the following points in a titration of 40 mL (0.040 L) of 0.100 *M* barbituric acid ($K_a = 9.8 \times 10^{-5}$) with 0.100 *M* KOH.

(a) no KOH added

(b) 20 mL of KOH solution added

(c) 39 mL of KOH solution added

(d) 40 mL of KOH solution added

(e) 41 mL of KOH solution added

95. The indicator dinitrophenol is an acid with a K_a of 1.1×10^{-4}. In a 1.0×10^{-4}-*M* solution, it is colorless in acid and yellow in base. Calculate the pH range over which it goes from 10% ionized (colorless) to 90% ionized (yellow).

Chapter 15

Equilibria of Other Reaction Classes

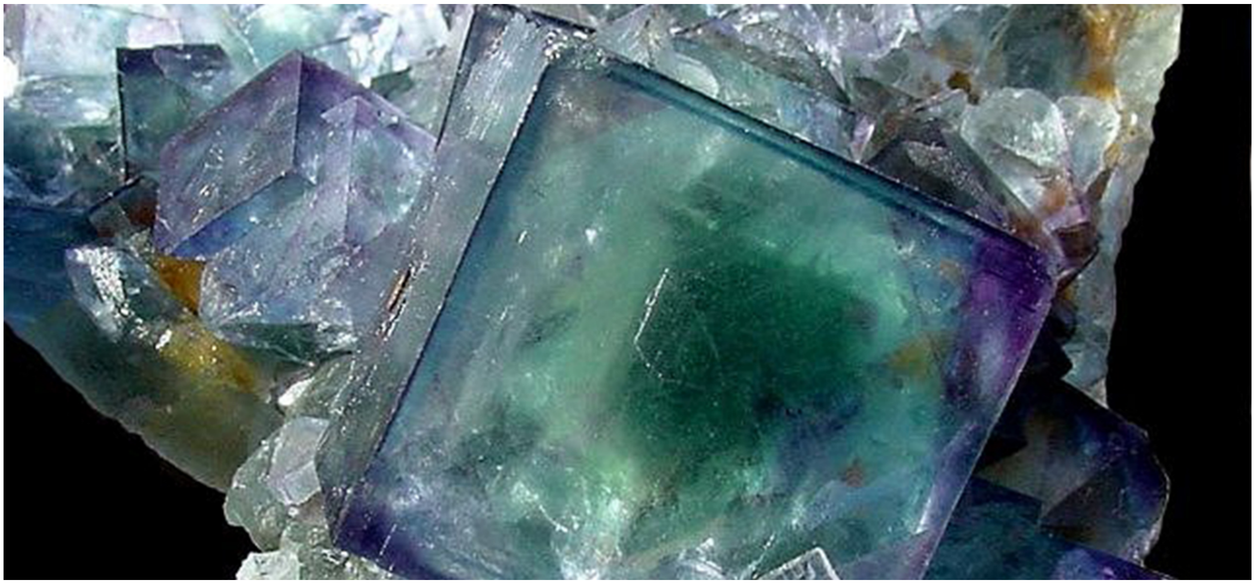


Figure 15.1 The mineral fluorite (CaF_2) is formed when dissolved calcium and fluoride ions precipitate from groundwater within the Earth's crust. Note that pure fluorite is colorless, and that the color in this sample is due to the presence of other metal ions in the crystal.

Chapter Outline

Introduction

The mineral fluorite, CaF_2 **Figure 15.1**, is commonly used as a semiprecious stone in many types of jewelry because of its striking appearance. Deposits of fluorite are formed through a process called hydrothermal precipitation in which calcium and fluoride ions dissolved in groundwater combine to produce insoluble CaF_2 in response to some change in solution conditions. For example, a decrease in temperature may trigger fluorite precipitation if its solubility is exceeded at the lower temperature. Because fluoride ion is a weak base, its solubility is also affected by solution pH, and so geologic or other processes that change groundwater pH will also affect the precipitation of fluorite. This chapter extends the equilibrium discussion of other chapters by addressing some additional reaction classes (including precipitation) and systems involving coupled equilibrium reactions.

15.1 Precipitation and Dissolution

By the end of this section, you will be able to:

- Write chemical equations and equilibrium expressions representing solubility equilibria
- Carry out equilibrium computations involving solubility, equilibrium expressions, and solute concentrations

Solubility equilibria are established when the dissolution and precipitation of a solute species occur at equal rates. These equilibria underlie many natural and technological processes, ranging from tooth decay to water purification. An understanding of the factors affecting compound solubility is, therefore, essential to the effective management of these processes. This section applies previously introduced equilibrium concepts and tools to systems involving dissolution and precipitation.

The Solubility Product

Recall from the chapter on solutions that the solubility of a substance can vary from essentially zero (*insoluble* or *sparingly soluble*) to infinity (*miscible*). A solute with finite solubility can yield a *saturated* solution when it is added to a solvent in an amount exceeding its solubility, resulting in a heterogeneous mixture of the saturated solution and the excess, undissolved solute. For example, a saturated solution of silver chloride is one in which the equilibrium shown below has been established.

$$\text{AgCl}(s) \underset{\text{precipitation}}{\overset{\text{dissolution}}{\rightleftharpoons}} \text{Ag}^{+}(aq) + \text{Cl}^{-}(aq)$$

In this solution, an excess of solid AgCl dissolves and dissociates to produce aqueous Ag^+ and Cl^- ions at the same rate that these aqueous ions combine and precipitate to form solid AgCl (**Figure 15.2**). Because silver chloride is a sparingly soluble salt, the equilibrium concentration of its dissolved ions in the solution is relatively low.

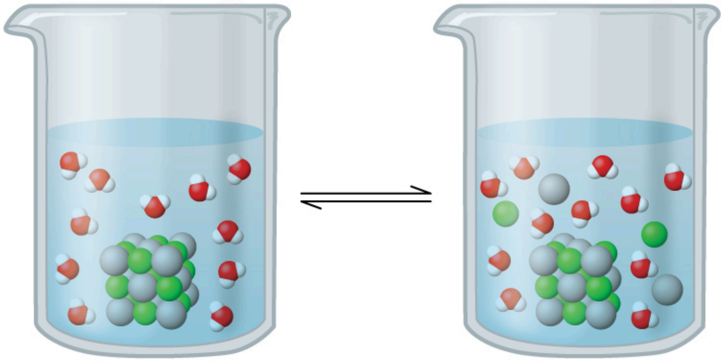


Figure 15.2 Silver chloride is a sparingly soluble ionic solid. When it is added to water, it dissolves slightly and produces a mixture consisting of a very dilute solution of Ag^+ and Cl^- ions in equilibrium with undissolved silver chloride.

The equilibrium constant for solubility equilibria such as this one is called the **solubility product constant, K_{sp}**, in this case

$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^{+}(aq) + \text{Cl}^{-}(aq) \qquad K_{\text{sp}} = [\text{Ag}^{+}(aq)][\text{Cl}^{-}(aq)]$$

Recall that only gases and solutes are represented in equilibrium constant expressions, so the K_{sp} does not include a term for the undissolved AgCl. A listing of solubility product constants for several sparingly soluble compounds is provided in **Appendix J**.

Example 15.1

Writing Equations and Solubility Products

Write the dissolution equation and the solubility product expression for each of the following slightly soluble ionic compounds:

(a) AgI, silver iodide, a solid with antiseptic properties

(b) $CaCO_3$, calcium carbonate, the active ingredient in many over-the-counter chewable antacids

(c) $Mg(OH)_2$, magnesium hydroxide, the active ingredient in Milk of Magnesia

(d) $Mg(NH_4)PO_4$, magnesium ammonium phosphate, an essentially insoluble substance used in tests for magnesium

(e) $Ca_5(PO_4)_3OH$, the mineral apatite, a source of phosphate for fertilizers

Solution

$$\begin{aligned}
&\text{(a) } \mathrm{AgI}(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{I}^{-}(aq) && K_{\mathrm{sp}} = [\mathrm{Ag}^{+}][\mathrm{I}^{-}] \\
&\text{(b) } \mathrm{CaCO}_3(s) \rightleftharpoons \mathrm{Ca}^{2+}(aq) + \mathrm{CO_3}^{2-}(aq) && K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}][\mathrm{CO_3}^{2-}] \\
&\text{(c) } \mathrm{Mg(OH)}_2(s) \rightleftharpoons \mathrm{Mg}^{2+}(aq) + 2\mathrm{OH}^{-}(aq) && K_{\mathrm{sp}} = [\mathrm{Mg}^{2+}][\mathrm{OH}^{-}]^2 \\
&\text{(d) } \mathrm{Mg(NH_4)PO_4}(s) \rightleftharpoons \mathrm{Mg}^{2+}(aq) + \mathrm{NH_4}^{+}(aq) + \mathrm{PO_4}^{3-}(aq) && K_{\mathrm{sp}} = [\mathrm{Mg}^{2+}][\mathrm{NH_4}^{+}][\mathrm{PO_4}^{3-}] \\
&\text{(e) } \mathrm{Ca_5(PO_4)3OH}(s) \rightleftharpoons 5\mathrm{Ca}^{2+}(aq) + 3\mathrm{PO_4}^{3-}(aq) + \mathrm{OH}^{-}(aq) && K_{\mathrm{sp}} = [\mathrm{Ca}^{2+}]^5[\mathrm{PO_4}^{3-}]^3[\mathrm{OH}^{-}]
\end{aligned}$$

Check Your Learning

Write the dissolution equation and the solubility product for each of the following slightly soluble compounds:

(a) $BaSO_4$

(b) Ag_2SO_4

(c) $Al(OH)_3$

(d) Pb(OH)Cl

Answer:

$$\begin{aligned}
&\text{(a) } \mathrm{BaSO_4}(s) \rightleftharpoons \mathrm{Ba}^{2+}(aq) + \mathrm{SO_4}^{2-}(aq) && K_{\mathrm{sp}} = [\mathrm{Ba}^{2+}][\mathrm{SO_4}^{2-}]; \\
&\text{(b) } \mathrm{Ag_2SO_4}(s) \rightleftharpoons 2\mathrm{Ag}^{+}(aq) + \mathrm{SO_4}^{2-}(aq) && K_{\mathrm{sp}} = [\mathrm{Ag}^{+}]^2[\mathrm{SO_4}^{2-}]; \\
&\text{(c) } \mathrm{Al(OH)_3}(s) \rightleftharpoons \mathrm{Al}^{3+}(aq) + 3\mathrm{OH}^{-}(aq) && K_{\mathrm{sp}} = [\mathrm{Al}^{3+}][\mathrm{OH}^{-}]^3; \\
&\text{(d) } \mathrm{Pb(OH)Cl}(s) \rightleftharpoons \mathrm{Pb}^{2+}(aq) + \mathrm{OH}^{-}(aq) + \mathrm{Cl}^{-}(aq) && K_{\mathrm{sp}} = [\mathrm{Pb}^{2+}][\mathrm{OH}^{-}][\mathrm{Cl}^{-}]
\end{aligned}$$

K_{sp} and Solubility

The K_{sp} of a slightly soluble ionic compound may be simply related to its measured solubility provided the dissolution process involves only dissociation and solvation, for example:

$$\mathrm{M}_p\mathrm{X}_q(s) \rightleftharpoons p\mathrm{M}^{\mathrm{m}+}(aq) + q\mathrm{X}^{\mathrm{n}-}(aq)$$

For cases such as these, one may derive K_{sp} values from provided solubilities, or vice-versa. Calculations of this sort are most conveniently performed using a compound's molar solubility, measured as moles of dissolved solute per liter of saturated solution.

Example 15.2

Calculation of K_{sp} from Equilibrium Concentrations

Fluorite, CaF_2, is a slightly soluble solid that dissolves according to the equation:

$$\mathrm{CaF_2}(s) \rightleftharpoons \mathrm{Ca}^{2+}(aq) + 2\mathrm{F}^{-}(aq)$$

The concentration of Ca^{2+} in a saturated solution of CaF_2 is 2.15×10^{-4} *M*. What is the solubility product of fluorite?

Solution

According to the stoichiometry of the dissolution equation, the fluoride ion molarity of a CaF_2 solution is equal to twice its calcium ion molarity:

$$[F^-] = (2 \text{ mol } F^- \;/\; 1 \text{ mol } Ca^{2+}) = (2)(2.15 \times 10^{-4}\ M) = 4.30 \times 10^{-4}\ M$$

Substituting the ion concentrations into the K_{sp} expression gives

$$K_{sp} = [Ca^{2+}][F^-]^2 = (2.15 \times 10^{-4})(4.30 \times 10^{-4})^2 = 3.98 \times 10^{-11}$$

Check Your Learning

In a saturated solution of $Mg(OH)_2$, the concentration of Mg^{2+} is 1.31×10^{-4} *M*. What is the solubility product for $Mg(OH)_2$?

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

Answer: 8.99×10^{-12}

Example 15.3

Determination of Molar Solubility from K_{sp}

The K_{sp} of copper(I) bromide, CuBr, is 6.3×10^{-9}. Calculate the molar solubility of copper bromide.

Solution

The dissolution equation and solubility product expression are

$$CuBr(s) \rightleftharpoons Cu^+(aq) + Br^-(aq)$$
$$K_{sp} = [Cu^+][Br^-]$$

Following the ICE approach to this calculation yields the table

	CuBr (*s*) $\rightleftharpoons$	Cu^+ (*aq*) +	Br^- (*aq*)
Initial concentration (*M*)		0	0
Change (*M*)		+*x*	+*x*
Equilibrium concentration (*M*)		*x*	*x*

Substituting the equilibrium concentration terms into the solubility product expression and solving for *x* yields

$$K_{sp} = [Cu^+][Br^-]$$
$$6.3 \times 10^{-9} = (x)(x) = x^2$$
$$x = \sqrt{(6.3 \times 10^{-9})} = 7.9 \times 10^{-5}\ M$$

Since the dissolution stoichiometry shows one mole of copper(I) ion and one mole of bromide ion are produced for each moles of Br dissolved, the molar solubility of CuBr is 7.9×10^{-5} *M*.

Check Your Learning

The K_{sp} of AgI is 1.5×10^{-16}. Calculate the molar solubility of silver iodide.

Answer: 1.2×10^{-8} *M*

Example 15.4

Determination of Molar Solubility from K_{sp}

The K_{sp} of calcium hydroxide, $Ca(OH)_2$, is 1.3×10^{-6}. Calculate the molar solubility of calcium hydroxide.

Solution

The dissolution equation and solubility product expression are

$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$
$$K_{sp} = [Ca^{2+}][OH^-]^2$$

The ICE table for this system is

	$Ca(OH)_2(s)$ $\rightleftharpoons$	$Ca^{2+}(aq)$ +	$2OH^-(aq)$
Initial concentration (*M*)		0	0
Change (*M*)		$+x$	$+2x$
Equilibrium concentration (*M*)		x	$2x$

Substituting terms for the equilibrium concentrations into the solubility product expression and solving for x gives

$$K_{sp} = [Ca^{2+}][OH^-]^2$$
$$1.3 \times 10^{-6} = (x)(2x)^2 = (x)(4x^2) = 4x^3$$
$$x = \sqrt[3]{\frac{1.3 \times 10^{-6}}{4}} = 7.0 \times 10^{-3}\ M$$

As defined in the ICE table, x is the molarity of calcium ion in the saturated solution. The dissolution stoichiometry shows a 1:1 relation between moles of calcium ion in solution and moles of compound dissolved, and so, the molar solubility of $Ca(OH)_2$ is 6.9×10^{-3} *M*.

Check Your Learning

The K_{sp} of PbI_2 is 1.4×10^{-8}. Calculate the molar solubility of lead(II) iodide.

Answer: 1.5×10^{-3} *M*

Example 15.5

Determination of K_{sp} from Gram Solubility

Many of the pigments used by artists in oil-based paints (**Figure 15.3**) are sparingly soluble in water. For example, the solubility of the artist's pigment chrome yellow, $PbCrO_4$, is 4.6×10^{-6} g/L. Determine the solubility product for $PbCrO_4$.

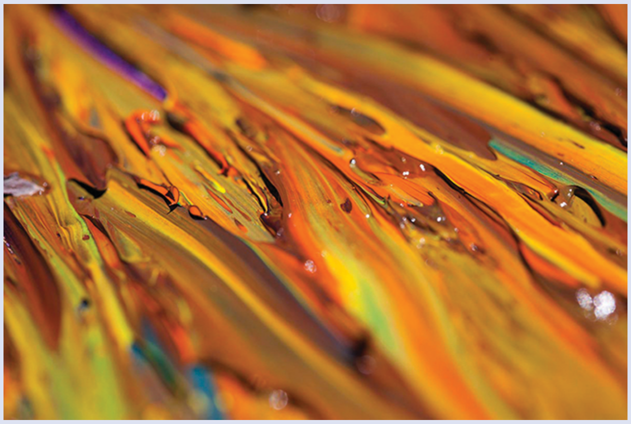


Figure 15.3 Oil paints contain pigments that are very slightly soluble in water. In addition to chrome yellow ($PbCrO_4$), examples include Prussian blue ($Fe_7(CN)_{18}$), the reddish-orange color vermilion (HgS), and green color veridian (Cr_2O_3). (credit: Sonny Abesamis)

Solution

Before calculating the solubility product, the provided solubility must be converted to molarity:

$$\begin{aligned}[\text{PbCrO}_4] &= \frac{4.6\times 10^{-6}\,\text{g PbCrO}_4}{1\text{ L}} \times \frac{1\text{ mol PbCrO}_4}{323.2\text{ g PbCrO}_4} \\ &= \frac{1.4\times 10^{-8}\text{ mol PbCrO}_4}{1\text{ L}} \\ &= 1.4\times 10^{-8}\,M\end{aligned}$$

The dissolution equation for this compound is

$$\text{PbCrO}_4(s) \rightleftharpoons \text{Pb}^{2+}(aq) + \text{CrO}_4{}^{2-}(aq)$$

The dissolution stoichiometry shows a 1:1 relation between the molar amounts of compound and its two ions, and so both $[\text{Pb}^{2+}]$ and $[\text{CrO}_4{}^{2-}]$ are equal to the molar solubility of $PbCrO_4$:

$$[\text{Pb}^{2+}] = [\text{CrO}_4{}^{2-}] = 1.4\times 10^{-8}\,M$$

$K_{sp} = [\text{Pb}^{2+}][\text{CrO}_4{}^{2-}] = (1.4 \times 10^{-8})(1.4 \times 10^{-8}) = 2.0 \times 10^{-16}$

Check Your Learning

The solubility of TlCl [thallium(I) chloride], an intermediate formed when thallium is being isolated from ores, is 3.12 grams per liter at 20 °C. What is its solubility product?

Answer: 2.08×10^{-4}

Example 15.6

Calculating the Solubility of Hg_2Cl_2

Calomel, Hg_2Cl_2, is a compound composed of the diatomic ion of mercury(I), $\text{Hg}_2{}^{2+}$, and chloride ions, $Cl^–$. Although most mercury compounds are now known to be poisonous, eighteenth-century physicians used calomel as a medication. Their patients rarely suffered any mercury poisoning from the treatments because calomel has a very low solubility, as suggested by its very small K_{sp}:

$$Hg_2Cl_2(s) \rightleftharpoons Hg_2{}^{2+}(aq) + 2Cl^-(aq) \qquad K_{sp} = 1.1 \times 10^{-18}$$

Calculate the molar solubility of Hg_2Cl_2.

Solution

The dissolution stoichiometry shows a 1:1 relation between the amount of compound dissolved and the amount of mercury(I) ions, and so the molar solubility of Hg_2Cl_2 is equal to the concentration of $Hg_2{}^{2+}$ ions

Following the ICE approach results in

	$Hg_2Cl_2(s) \rightleftharpoons$	$Hg_2{}^{2+}(aq)$ +	$2Cl^-(aq)$
Initial concentration (*M*)		0	0
Change (*M*)		$+x$	$+2x$
Equilibrium concentration (*M*)		x	$2x$

Substituting the equilibrium concentration terms into the solubility product expression and solving for x gives

$$\begin{aligned} K_{sp} &= [Hg_2{}^{2+}][Cl^-]^2 \\ 1.1 \times 10^{-18} &= (x)(2x)^2 \\ 4x^3 &= 1.1 \times 10^{-18} \\ x &= \sqrt[3]{\left(\frac{1.1 \times 10^{-18}}{4}\right)} = 6.5 \times 10^{-7}\ M \\ [Hg_2{}^{2+}] &= 6.5 \times 10^{-7}\ M = 6.5 \times 10^{-7}\ M \\ [Cl^-] &= 2x = 2(6.5 \times 10^{-7}) = 1.3 \times 10^{-6}\ M \end{aligned}$$

The dissolution stoichiometry shows the molar solubility of Hg_2Cl_2 is equal to $[Hg_2{}^{2+}]$, or 6.5×10^{-7} *M*.

Check Your Learning

Determine the molar solubility of MgF_2 from its solubility product: $K_{sp} = 6.4 \times 10^{-9}$.

Answer: 1.2×10^{-3} *M*

How Sciences Interconnect

Using Barium Sulfate for Medical Imaging

Various types of medical imaging techniques are used to aid diagnoses of illnesses in a noninvasive manner. One such technique utilizes the ingestion of a barium compound before taking an X-ray image. A suspension of barium sulfate, a chalky powder, is ingested by the patient. Since the K_{sp} of barium sulfate is 2.3×10^{-8}, very little of it dissolves as it coats the lining of the patient's intestinal tract. Barium-coated areas of the digestive tract then appear on an X-ray as white, allowing for greater visual detail than a traditional X-ray (**Figure 15.4**).

Figure 15.4 A suspension of barium sulfate coats the intestinal tract, permitting greater visual detail than a traditional X-ray. (credit modification of work by “glitzy queen00”/Wikimedia Commons)

Medical imaging using barium sulfate can be used to diagnose acid reflux disease, Crohn’s disease, and ulcers in addition to other conditions.

Visit this **website (http://openstaxcollege.org/l/16barium)** for more information on how barium is used in medical diagnoses and which conditions it is used to diagnose.

Predicting Precipitation

The equation that describes the equilibrium between solid calcium carbonate and its solvated ions is:

$$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + \mathrm{CO_3}\,2{-}(aq) \qquad K_{sp} = [\mathrm{Ca}^{2+}][\mathrm{CO_3}^{2-}] = 8.7 \times 10^{-9}$$

It is important to realize that this equilibrium is established in any aqueous solution containing Ca^{2+} and CO_3^{2-} ions, not just in a solution formed by saturating water with calcium carbonate. Consider, for example, mixing aqueous solutions of the soluble compounds sodium carbonate and calcium nitrate. If the concentrations of calcium and carbonate ions in the mixture do not yield a reaction quotient, Q_{sp}, that exceeds the solubility product, K_{sp}, then no precipitation will occur. If the ion concentrations yield a reaction quotient greater than the solubility product, then precipitation will occur, lowering those concentrations until equilibrium is established ($Q_{sp} = K_{\mathrm{sp}}$). The comparison of Q_{sp} to K_{sp} to predict precipitation is an example of the general approach to predicting the direction of a reaction first introduced in the chapter on equilibrium. For the specific case of solubility equilibria:

$Q_{sp} < K_{sp}$: the reaction proceeds in the forward direction (solution is not saturated; no precipitation observed)

$Q_{sp} > K_{sp}$: the reaction proceeds in the reverse direction (solution is supersaturated; precipitation will occur)

This predictive strategy and related calculations are demonstrated in the next few example exercises.

Example 15.7

Precipitation of $Mg(OH)_2$

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of lime, $Ca(OH)_2$, a readily available inexpensive source of OH^- ion:

$$\text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^-(aq) \qquad K_{sp} = 8.9 \times 10^{-12}$$

The concentration of $Mg^{2+}(aq)$ in sea water is 0.0537 *M*. Will $Mg(OH)_2$ precipitate when enough $Ca(OH)_2$ is added to give a $[OH^-]$ of 0.0010 *M*?

Solution

Calculation of the reaction quotient under these conditions is shown here:

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.0537)(0.0010)^2 = 5.4 \times 10^{-8}$$

Because Q is greater than K_{sp} ($Q = 5.4 \times 10^{-8}$ is larger than $K_{sp} = 8.9 \times 10^{-12}$), the reverse reaction will proceed, precipitating magnesium hydroxide until the dissolved ion concentrations have been sufficiently lowered, so that $Q_{sp} = K_{sp}$.

Check Your Learning

Predict whether $CaHPO_4$ will precipitate from a solution with $[Ca^{2+}] = 0.0001$ *M* and $[HPO_4{}^{2-}] = 0.001$ *M*.

Answer: No precipitation of $CaHPO_4$; $Q = 1 \times 10^{-7}$, which is less than K_{sp} (7×10^{-7})

Example 15.8

Precipitation of AgCl

Does silver chloride precipitate when equal volumes of a 2.0×10^{-4}-*M* solution of $AgNO_3$ and a 2.0×10^{-4}-*M* solution of NaCl are mixed?

Solution

The equation for the equilibrium between solid silver chloride, silver ion, and chloride ion is:

$$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$$

The solubility product is 1.6×10^{-10} (see **Appendix J**).

AgCl will precipitate if the reaction quotient calculated from the concentrations in the mixture of $AgNO_3$ and NaCl is greater than K_{sp}. Because the volume doubles when equal volumes of $AgNO_3$ and NaCl solutions are mixed, each concentration is reduced to half its initial value

$$\frac{1}{2}(2.0 \times 10^{-4})\,M = 1.0 \times 10^{-4}\ M$$

The reaction quotient, Q, is greater than K_{sp} for AgCl, so a supersaturated solution is formed:

$$Q = [\text{Ag}^+][\text{Cl}^-] = (1.0 \times 10^{-4})(1.0 \times 10^{-4}) = 1.0 \times 10^{-8} > K_{sp}$$

AgCl will precipitate from the mixture until the dissolution equilibrium is established, with Q equal to K_{sp}.

Check Your Learning

Will $KClO_4$ precipitate when 20 mL of a 0.050-M solution of K^+ is added to 80 mL of a 0.50-M solution of $ClO_4{}^-$? (Hint: Use the dilution equation to calculate the concentrations of potassium and perchlorate ions in the mixture.)

Answer: No, $Q = 4.0 \times 10^{-3}$, which is less than $K_{sp} = 1.05 \times 10^{-2}$

Example 15.9

Precipitation of Calcium Oxalate

Blood will not clot if calcium ions are removed from its plasma. Some blood collection tubes contain salts of the oxalate ion, $C_2O_4{}^{2-}$, for this purpose (Figure 15.5). At sufficiently high concentrations, the calcium and oxalate ions form solid, $CaC_2O_4{\cdot}H_2O$ (calcium oxalate monohydrate). The concentration of Ca^{2+} in a sample of blood serum is 2.2×10^{-3} M. What concentration of $C_2O_4{}^{2-}$ ion must be established before $CaC_2O_4{\cdot}H_2O$ begins to precipitate?

Figure 15.5 Anticoagulants can be added to blood that will combine with the Ca^{2+} ions in blood serum and prevent the blood from clotting. (credit: modification of work by Neeta Lind)

Solution

The equilibrium expression is:

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4{}^{2-}(aq)$$

For this reaction:

$$K_{sp} = [Ca^{2+}][C_2O_4{}^{2-}] = 1.96 \times 10^{-8}$$

(see Appendix J)

Substitute the provided calcium ion concentration into the solubility product expression and solve for oxalate concentration:

$$Q = K_{\text{sp}} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4{}^{2-}] = 1.96 \times 10^{-8}$$
$$(2.2 \times 10^{-3})[\text{C}_2\text{O}_4{}^{2-}] = 1.96 \times 10^{-8}$$
$$[\text{C}_2\text{O}_4{}^{2-}] = \frac{1.96 \times 10^{-8}}{2.2 \times 10^{-3}} = 8.9 \times 10^{-6}\ M$$

A concentration of $[\text{C}_2\text{O}_4{}^{2-}] = 8.9 \times 10^{-6}$ *M* is necessary to initiate the precipitation of CaC_2O_4 under these conditions.

Check Your Learning

If a solution contains 0.0020 mol of $\text{CrO}_4{}^{2-}$ per liter, what concentration of Ag^+ ion must be reached by adding solid $AgNO_3$ before Ag_2CrO_4 begins to precipitate? Neglect any increase in volume upon adding the solid silver nitrate.

Answer: 6.7×10^{-5} *M*

Example 15.10

Concentrations Following Precipitation

Clothing washed in water that has a manganese $[\text{Mn}^{2+}(aq)]$ concentration exceeding 0.1 mg/L (1.8×10^{-6} *M*) may be stained by the manganese upon oxidation, but the amount of Mn^{2+} in the water can be decreased by adding a base to precipitate $Mn(OH)_2$. What pH is required to keep $[Mn^{2+}]$ equal to 1.8×10^{-6} *M*?

Solution

The dissolution of $Mn(OH)_2$ is described by the equation:

$$\text{Mn(OH)}_2(s) \rightleftharpoons \text{Mn}^{2+}(aq) + 2\text{OH}^-(aq) \qquad K_{\text{sp}} = 2 \times 10^{-13}$$

At equilibrium:

$$K_{\text{sp}} = [\text{Mn}^{2+}][\text{OH}^-]^2$$

or

$$(1.8 \times 10^{-6})[\text{OH}^-]^2 = 2 \times 10^{-13}$$

so

$$[\text{OH}^-] = 3.3 \times 10^{-4}\ M$$

Calculate the pH from the pOH:

$$\text{pOH} = -\log[\text{OH}^-] = -\log(3.3 \times 10 - 4) = 3.48$$
$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.80 = 10.5$$

(final result rounded to one significant digit, limited by the certainty of the K_{sp})

Check Your Learning

The first step in the preparation of magnesium metal is the precipitation of $Mg(OH)_2$ from sea water by the addition of $Ca(OH)_2$. The concentration of $Mg^{2+}(aq)$ in sea water is 5.37×10^{-2} *M*. Calculate the pH at which $[Mg^{2+}]$ is decreased to 1.0×10^{-5} *M*

Answer: 10.97

In solutions containing two or more ions that may form insoluble compounds with the same counter ion, an experimental strategy called **selective precipitation** may be used to remove individual ions from solution. By increasing the counter ion concentration in a controlled manner, ions in solution may be precipitated individually, assuming their compound solubilities are adequately different. In solutions with equal concentrations of target ions, the ion forming the least soluble compound will precipitate first (at the lowest concentration of counter ion), with the other ions subsequently precipitating as their compound's solubilities are reached. As an illustration of this technique, the next example exercise describes separation of a two halide ions via precipitation of one as a silver salt.

Chemistry in Everyday Life

The Role of Precipitation in Wastewater Treatment

Solubility equilibria are useful tools in the treatment of wastewater carried out in facilities that may treat the municipal water in your city or town (**Figure 15.6**). Specifically, selective precipitation is used to remove contaminants from wastewater before it is released back into natural bodies of water. For example, phosphate ions $(PO_4{}^{3-})$ are often present in the water discharged from manufacturing facilities. An abundance of phosphate causes excess algae to grow, which impacts the amount of oxygen available for marine life as well as making water unsuitable for human consumption.

Figure 15.6 Wastewater treatment facilities, such as this one, remove contaminants from wastewater before the water is released back into the natural environment. (credit: "eutrophication&hypoxia"/Wikimedia Commons)

One common way to remove phosphates from water is by the addition of calcium hydroxide, or lime, $Ca(OH)_2$. As the water is made more basic, the calcium ions react with phosphate ions to produce hydroxylapatite, $Ca_5(PO4)_3OH$, which then precipitates out of the solution:

$$5Ca^{2+} + 3PO_4{}^{3-} + OH^- \rightleftharpoons Ca_5(PO_4)_3 \cdot OH(s)$$

Because the amount of calcium ion added does not result in exceeding the solubility products for other calcium salts, the anions of those salts remain behind in the wastewater. The precipitate is then removed by filtration and the water is brought back to a neutral pH by the addition of CO_2 in a recarbonation process. Other chemicals can also be used for the removal of phosphates by precipitation, including iron(III) chloride and aluminum sulfate.

View this **site (http://openstaxcollege.org/l/16Wastewater)** for more information on how phosphorus is removed from wastewater.

Example 15.11

Precipitation of Silver Halides

A solution contains 0.00010 mol of KBr and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgBr or solid AgCl?

Solution

The two equilibria involved are:

$$\begin{aligned} \text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \qquad K_{\text{sp}} &= 1.6 \times 10^{-10} \\ \text{AgBr}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Br}^-(aq) \qquad K_{\text{sp}} &= 5.0 \times 10^{-13} \end{aligned}$$

If the solution contained about *equal* concentrations of Cl^- and Br^-, then the silver salt with the smaller K_{sp} (AgBr) would precipitate first. The concentrations are not equal, however, so the $[\text{Ag}^+]$ at which AgCl begins to precipitate and the $[\text{Ag}^+]$ at which AgBr begins to precipitate must be calculated. The salt that forms at the lower $[\text{Ag}^+]$ precipitates first.

AgBr precipitates when Q equals K_{sp} for AgBr

$$Q = [\text{Ag}^+][\text{Br}^-] = [\text{Ag}^+](0.00010) = 5.0 \times 10^{-13}$$

$$[\text{Ag}^+] = \frac{5.0 \times 10^{-13}}{0.00010} = 5.0 \times 10^{-9}\ M$$

AgI begins to precipitate when $[\text{Ag}^+]$ is $5.0 \times 10^{-9}\ M$.

For AgCl: AgCl precipitates when Q equals K_{sp} for AgCl (1.6×10^{-10}). When $[\text{Cl}^-] = 0.10\ M$:

$$Q_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = [\text{Ag}^+](0.10) = 1.6 \times 10^{-10}$$

$$[\text{Ag}^+] = \frac{1.6 \times 10^{-10}}{0.10} = 1.6 \times 10^{-9}\ M$$

AgCl begins to precipitate when $[\text{Ag}^+]$ is $1.6 \times 10^{-9}\ M$.

AgCl begins to precipitate at a lower $[\text{Ag}^+]$ than AgBr, so AgCl begins to precipitate first. Note the chloride ion concentration of the initial mixture was significantly greater than the bromide ion concentration, and so silver chloride precipitated first despite having a K_{sp} greater than that of silver bromide.

Check Your Learning

If silver nitrate solution is added to a solution which is 0.050 M in both Cl^- and Br^- ions, at what $[\text{Ag}^+]$ would precipitation begin, and what would be the formula of the precipitate?

Answer: $[\text{Ag}^+] = 1.0 \times 10^{-11}\ M$; AgBr precipitates first

Common Ion Effect

Compared with pure water, the solubility of an ionic compound is less in aqueous solutions containing a *common ion* (one also produced by dissolution of the ionic compound). This is an example of a phenomenon known as the **common ion effect**, which is a consequence of the law of mass action that may be explained using Le ChÂtelier's principle. Consider the dissolution of silver iodide:

$$\text{AgI}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{I}^-(aq)$$

This solubility equilibrium may be shifted left by the addition of either silver(I) or iodide ions, resulting in the precipitation of AgI and lowered concentrations of dissolved Ag^+ and I^-. In solutions that already contain either of these ions, less AgI may be dissolved than in solutions without these ions.

This effect may also be explained in terms of mass action as represented in the solubility product expression:

$$K_{\text{sp}} = [\text{Ag}^+][\text{I}^-]$$

The mathematical product of silver(I) and iodide ion molarities is constant in an equilibrium mixture *regardless of the source of the ions*, and so an increase in one ion's concentration must be balanced by a proportional decrease in the other.

Link to Learning

View this **simulation (http://openstaxcollege.org/l/16solublesalts)** to explore various aspects of the common ion effect.

Link to Learning

View this **simulation (http://openstax.org/l/16commonion)** to see how the common ion effect works with different concentrations of salts.

Example 15.12

Common Ion Effect on Solubility

What is the effect on the amount of solid $Mg(OH)_2$ and the concentrations of Mg^{2+} and OH^- when each of the following are added to a saturated solution of $Mg(OH)_2$?

(a) $MgCl_2$

(b) KOH

(c) $NaNO_3$

(d) $Mg(OH)_2$

Solution

The solubility equilibrium is

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

(a) The reaction shifts to the left to relieve the stress produced by the additional Mg^{2+} ion, in accordance with Le Châtelier's principle. In quantitative terms, the added Mg^{2+} causes the reaction quotient to be larger than the solubility product ($Q > K_{sp}$), and $Mg(OH)_2$ forms until the reaction quotient again equals K_{sp}. At the new equilibrium, $[OH^-]$ is less and $[Mg^{2+}]$ is greater than in the solution of $Mg(OH)_2$ in pure water. More solid $Mg(OH)_2$ is present.

(b) The reaction shifts to the left to relieve the stress of the additional OH^- ion. $Mg(OH)_2$ forms until the reaction quotient again equals K_{sp}. At the new equilibrium, $[OH^-]$ is greater and $[Mg^{2+}]$ is less than in the solution of $Mg(OH)_2$ in pure water. More solid $Mg(OH)_2$ is present.

(c) The concentration of OH^- is reduced as the OH^- reacts with the acid. The reaction shifts to the right to

(a) Adding a common ion, Mg^{2+}, will increase the concentration of this ion and shift the solubility equilibrium to the left, decreasing the concentration of hydroxide ion and increasing the amount of undissolved magnesium hydroxide.

(b) Adding a common ion, OH^-, will increase the concentration of this ion and shift the solubility equilibrium to the left, decreasing the concentration of magnesium ion and increasing the amount of undissolved magnesium hydroxide.

(c) The added compound does not contain a common ion, and no effect on the magnesium hydroxide solubility equilibrium is expected.

(d) Adding more solid magnesium hydroxide will increase the amount of undissolved compound in the mixture. The solution is already saturated, though, so the concentrations of dissolved magnesium and hydroxide ions will remain the same.

$$Q = [\text{Mg}^{2+}][\text{OH}^-]^2$$

Thus, changing the amount of solid magnesium hydroxide in the mixture has no effect on the value of Q, and no shift is required to restore Q to the value of the equilibrium constant.

Check Your Learning

What is the effect on the amount of solid $NiCO_3$ and the concentrations of Ni^{2+} and $CO_3{}^{2-}$ when each of the following are added to a saturated solution of $NiCO_3$

(a) $Ni(NO_3)_2$

(b) $KClO_4$

(c) $NiCO_3$

(d) K_2CO_3

Answer: (a) mass of $NiCO_3(s)$ increases, $[Ni^{2+}]$ increases, $[CO_3{}^{2-}]$ decreases; (b) no appreciable effect; (c) no effect except to increase the amount of solid $NiCO_3$; (d) mass of $NiCO_3(s)$ increases, $[Ni^{2+}]$ decreases, $[CO_3{}^{2-}]$ increases;

Example 15.13

Common Ion Effect

Calculate the molar solubility of cadmium sulfide (CdS) in a 0.010-*M* solution of cadmium bromide ($CdBr_2$). The K_{sp} of CdS is 1.0×10^{-28}.

Solution

This calculation can be performed using the ICE approach:

$$\text{CdS}(s) \rightleftharpoons \text{Cd}^{2+}(aq) + \text{S}^{2-}(aq)$$

	CdS (s) ⇌	Cd^{2+} (aq) +	S^{2-} (aq)
Initial concentration (*M*)		0.010	0
Change (*M*)		$+x$	$+x$
Equilibrium concentration (*M*)		$0.010 + x$	x

$$K_{sp} = [\text{Cd}^{2+}][\text{S}^{2-}] = 1.0 \times 10^{-28}$$
$$(0.010 + x)(x) = 1.0 \times 10^{-28}$$

Because K_{sp} is very small, assume $x << 0.010$ and solve the simplified equation for x:

$$(0.010)(x) = 1.0 \times 10^{-28}$$
$$x = 1.0 \times 10^{-26}\ M$$

The molar solubility of CdS in this solution is 1.0×10^{-26} *M*.

Check Your Learning

Calculate the molar solubility of aluminum hydroxide, $Al(OH)_3$, in a 0.015-*M* solution of aluminum nitrate,

$Al(NO_3)_3$. The K_{sp} of $Al(OH)_3$ is 2×10^{-32}.

Answer: $4 \times 10^{-11}\ M$

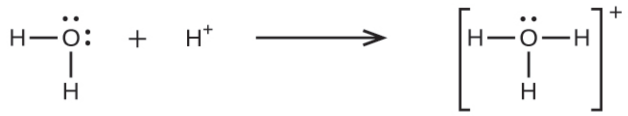
15.2 Lewis Acids and Bases

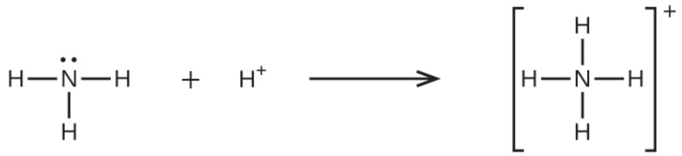
By the end of this section, you will be able to:

- Explain the Lewis model of acid-base chemistry
- Write equations for the formation of adducts and complex ions
- Perform equilibrium calculations involving formation constants

In 1923, G. N. Lewis proposed a generalized definition of acid-base behavior in which acids and bases are identified by their ability to accept or to donate a pair of electrons and form a coordinate covalent bond.

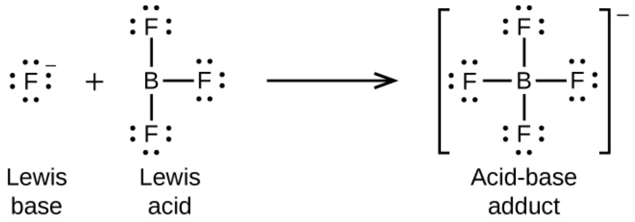
A **coordinate covalent bond** (or dative bond) occurs when one of the atoms in the bond provides both bonding electrons. For example, a coordinate covalent bond occurs when a water molecule combines with a hydrogen ion to form a hydronium ion. A coordinate covalent bond also results when an ammonia molecule combines with a hydrogen ion to form an ammonium ion. Both of these equations are shown here.



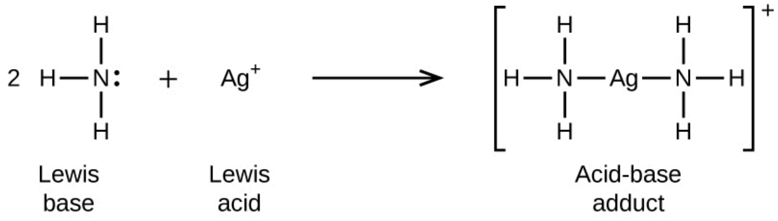


Reactions involving the formation of coordinate covalent bonds are classified as **Lewis acid-base chemistry**. The species donating the electron pair that compose the bond is a **Lewis base**, the species accepting the electron pair is a **Lewis acid**, and the product of the reaction is a **Lewis acid-base adduct**. As the two examples above illustrate, Brønsted-Lowry acid-base reactions represent a subcategory of Lewis acid reactions, specifically, those in which the acid species is H^+. A few examples involving other Lewis acids and bases are described below.

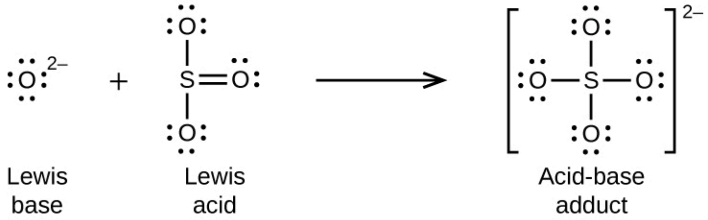
The boron atom in boron trifluoride, BF_3, has only six electrons in its valence shell. Being short of the preferred octet, BF_3 is a very good Lewis acid and reacts with many Lewis bases; a fluoride ion is the Lewis base in this reaction, donating one of its lone pairs:



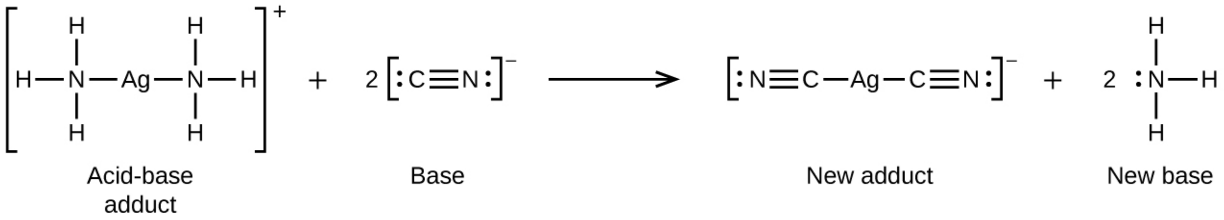
In the following reaction, each of two ammonia molecules, Lewis bases, donates a pair of electrons to a silver ion, the Lewis acid:

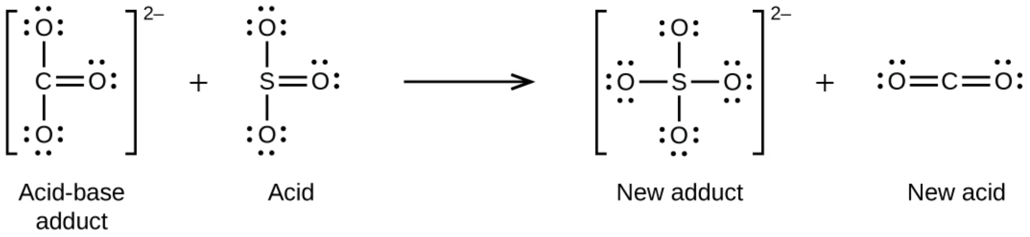


Nonmetal oxides act as Lewis acids and react with oxide ions, Lewis bases, to form oxyanions:



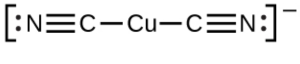
Many Lewis acid-base reactions are displacement reactions in which one Lewis base displaces another Lewis base from an acid-base adduct, or in which one Lewis acid displaces another Lewis acid:





Another type of Lewis acid-base chemistry involves the formation of a complex ion (or a coordination complex) comprising a central atom, typically a transition metal cation, surrounded by ions or molecules called **ligands**. These ligands can be neutral molecules like H_2O or NH_3, or ions such as $CN^–$ or $OH^–$. Often, the ligands act as Lewis bases, donating a pair of electrons to the central atom. These types of Lewis acid-base reactions are examples of a broad subdiscipline called *coordination chemistry*—the topic of another chapter in this text.

The equilibrium constant for the reaction of a metal ion with one or more ligands to form a coordination complex is called a **formation constant (K_f)** (sometimes called a stability constant). For example, the complex ion $\text{Cu(CN)}_2{}^-$



is produced by the reaction

$$\text{Cu}^+(aq) + 2\text{CN}^-(aq) \rightleftharpoons \text{Cu(CN)}_2{}^-(aq)$$

The formation constant for this reaction is

$$K_\text{f} = \frac{[\text{Cu(CN)}_2{}^-]}{[\text{Cu}^+][\text{CN}^-]^2}$$

Alternatively, the reverse reaction (decomposition of the complex ion) can be considered, in which case the equilibrium constant is a **dissociation constant (K_d)**. Per the relation between equilibrium constants for reciprocal reactions described, the dissociation constant is the mathematical inverse of the formation constant, $K_d = K_f^{-1}$. A tabulation of formation constants is provided in **Appendix K**.

As an example of dissolution by complex ion formation, let us consider what happens when we add aqueous ammonia to a mixture of silver chloride and water. Silver chloride dissolves slightly in water, giving a small concentration of Ag^+ ($[Ag^+] = 1.3 \times 10^{-5}$ *M*):

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

However, if NH_3 is present in the water, the complex ion, $Ag(NH_3)_2{}^+$, can form according to the equation:

Example 15.14

Dissociation of a Complex Ion

Calculate the concentration of the silver ion in a solution that initially is 0.10 *M* with respect to $Ag(NH_3)_2{}^+$.

Solution

Applying the standard ICE approach to this reaction yields the following:

	Ag^+ +	$2NH_3 \rightleftharpoons$	$Ag(NH_3)_2{}^+$
Initial concentration (*M*)	0	0	0.10
Change (*M*)	$+x$	$+2x$	$-x$
Equilibrium concentration (*M*)	x	$2x$	$0.10 - x$

Substituting these equilibrium concentration terms into the K_f expression gives

$$K_f = \frac{[Ag(NH_3)_2{}^+]}{[Ag^+][NH_3]^2}$$
$$1.7 \times 10^7 = \frac{0.10 - x}{(x)(2x)^2}$$

The very large equilibrium constant means the amount of the complex ion that will dissociate, x, will be very small. Assuming $x << 0.1$ permits simplifying the above equation:

$$1.7 \times 10^7 = \frac{0.10}{(x)(2x)^2}$$
$$x^3 = \frac{0.10}{4(1.7 \times 10^7)} = 1.5 \times 10^{-9}$$
$$x = \sqrt[3]{1.5 \times 10^{-9}} = 1.1 \times 10^{-3}$$

Because only 1.1% of the $Ag(NH_3)_2{}^+$ dissociates into Ag^+ and NH_3, the assumption that x is small is justified.

Using this value of x and the relations in the above ICE table allows calculation of all species' equilibrium concentrations:

$$[Ag^+] = 0 + x = 1.1 \times 10^{-3}\ M$$
$$[NH_3] = 0 + 2x = 2.2 \times 10^{-3}\ M$$
$$[Ag(NH_3)_2{}^+] = 0.10 - x = 0.10 - 0.0011 = 0.099$$

The concentration of free silver ion in the solution is 0.0011 *M*.

Check Your Learning

Calculate the silver ion concentration, $[Ag^+]$, of a solution prepared by dissolving 1.00 g of $AgNO_3$ and 10.0 g of KCN in sufficient water to make 1.00 L of solution. (Hint: Because K_f is very large, assume the reaction goes to completion then calculate the $[Ag^+]$ produced by dissociation of the complex.)

Answer: $2.5 \times 10^{-22}\ M$

15.3 Coupled Equilibria

By the end of this section, you will be able to:

- Describe examples of systems involving two (or more) coupled chemical equilibria
- Calculate reactant and product concentrations for coupled equilibrium systems

As discussed in preceding chapters on equilibrium, *coupled equilibria* involve two or more separate chemical reactions that share one or more reactants or products. This section of this chapter will address solubility equilibria coupled with acid-base and complex-formation reactions.

An environmentally relevant example illustrating the coupling of solubility and acid-base equilibria is the impact of ocean acidification on the health of the ocean’s coral reefs. These reefs are built upon skeletons of sparingly soluble calcium carbonate excreted by colonies of corals (small marine invertebrates). The relevant dissolution equilibrium is

$$\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3{}^{-2}(aq) \qquad K_{\text{sp}} = 8.7 \times 10^{-9}$$

Rising concentrations of atmospheric carbon dioxide contribute to an increased acidity of ocean waters due to the dissolution, hydrolysis, and acid ionization of carbon dioxide:

$$\text{CO}_2(g) \rightleftharpoons \text{CO}_2(aq)$$
$$\text{CO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq)$$
$$\text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3{}^-(aq) + \text{H}_3\text{O}^+(aq) \qquad K_{\text{a1}} = 4.3 \times 10^{-7}$$
$$\text{HCO}_3{}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CO}_3{}^{2-}(aq) + \text{H}_3\text{O}^+(aq) \qquad K_{\text{a2}} = 4.7 \times 10^{-11}$$

Inspection of these equilibria shows the carbonate ion is involved in the calcium carbonate dissolution and the acid hydrolysis of bicarbonate ion. Combining the dissolution equation with the reverse of the acid hydrolysis equation yields

$$\text{CaCO}_3(s) + \text{H}_3\text{O}^+(aq) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{HCO}_3{}^-(aq) + \text{H}_2\text{O}(l) \qquad K = K_{\text{sp}} / K_{\text{a2}} = 180$$

The equilibrium constant for this net reaction is much greater than the K_{sp} for calcium carbonate, indicating its solubility is markedly increased in acidic solutions. As rising carbon dioxide levels in the atmosphere increase the acidity of ocean waters, the calcium carbonate skeletons of coral reefs become more prone to dissolution and subsequently less healthy (**Figure 15.7**).

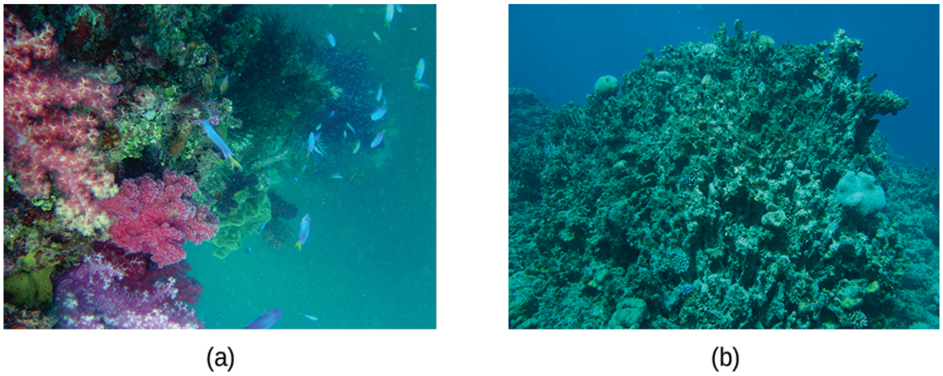


Figure 15.7 Healthy coral reefs (a) support a dense and diverse array of sea life across the ocean food chain. But when coral are unable to adequately build and maintain their calcium carbonate skeletons because of excess ocean acidification, the unhealthy reef (b) is only capable of hosting a small fraction of the species as before, and the local food chain starts to collapse. (credit a: modification of work by NOAA Photo Library; credit b: modification of work by "prilfish"/Flickr)

Link to Learning

Learn more about ocean **acidification (http://openstaxcollege.org/l/16acidicocean)** and how it affects other marine creatures.

This **site (http://openstaxcollege.org/l/16coralreef)** has detailed information about how ocean acidification specifically affects coral reefs.

The dramatic increase in solubility with increasing acidity described above for calcium carbonate is typical of salts containing basic anions (e.g., carbonate, fluoride, hydroxide, sulfide). Another familiar example is the formation of dental cavities in tooth enamel. The major mineral component of enamel is calcium hydroxyapatite (**Figure 15.8**), a sparingly soluble ionic compound whose dissolution equilibrium is

$$\text{Ca}_5(\text{PO}_4)_3\text{OH}(s) \rightleftharpoons 5\text{Ca}^{2+}(aq) + 3\text{PO}_4{}^{3-}(aq) + \text{OH}^-(aq)$$

Figure 15.8 Crystal of the mineral hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, is shown here. The pure compound is white, but like many other minerals, this sample is colored because of the presence of impurities.

This compound dissolved to yield two different basic ions: triprotic phosphate ions

$$\mathrm{PO_4{}^{3-}}(aq) + \mathrm{H_3O^+}(aq) \longrightarrow \mathrm{H_2PO_4{}^{2-}}(aq) + \mathrm{H_2O}(l)$$
$$\mathrm{H_2PO_4{}^{2-}}(aq) + \mathrm{H_3O^+}(aq) \longrightarrow \mathrm{H_2PO_4{}^{-}}(aq) + \mathrm{H_2O}(l)$$
$$\mathrm{H_2PO_4{}^{-}}(aq) + \mathrm{H_3O^+}(aq) \longrightarrow \mathrm{H_3PO_4}(aq) + \mathrm{H_2O}(l)$$

and monoprotic hydroxide ions:

$$\mathrm{OH^-}(aq) + \mathrm{H_3O^+} \longrightarrow \mathrm{2H_2O}$$

Of the two basic productions, the hydroxide is, of course, by far the stronger base (it's the strongest base that can exist in aqueous solution), and so it is the dominant factor providing the compound an acid-dependent solubility. Dental cavities form when the acid waste of bacteria growing on the surface of teeth hastens the dissolution of tooth enamel by reacting completely with the strong base hydroxide, shifting the hydroxyapatite solubility equilibrium to the right. Some toothpastes and mouth rinses contain added NaF or SnF_2 that make enamel more acid resistant by replacing the strong base hydroxide with the weak base fluoride:

$$\mathrm{NaF} + \mathrm{Ca_5(PO_4)_3OH} \rightleftharpoons \mathrm{Ca_5(PO_4)_3F} + \mathrm{Na^+} + \mathrm{OH^-}$$

The weak base fluoride ion reacts only partially with the bacterial acid waste, resulting in a less extensive shift in the solubility equilibrium and an increased resistance to acid dissolution. See the Chemistry in Everyday Life feature on the role of fluoride in preventing tooth decay for more information.

Chemistry in Everyday Life

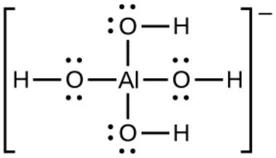
Role of Fluoride in Preventing Tooth Decay

As we saw previously, fluoride ions help protect our teeth by reacting with hydroxylapatite to form fluorapatite, $Ca_5(PO_4)_3F$. Since it lacks a hydroxide ion, fluorapatite is more resistant to attacks by acids in our mouths and is thus less soluble, protecting our teeth. Scientists discovered that naturally fluorinated water could be beneficial to your teeth, and so it became common practice to add fluoride to drinking water. Toothpastes and mouthwashes also contain amounts of fluoride (**Figure 15.9**).

Figure 15.9 Fluoride, found in many toothpastes, helps prevent tooth decay (credit: Kerry Ceszyk).

Unfortunately, excess fluoride can negate its advantages. Natural sources of drinking water in various parts of the world have varying concentrations of fluoride, and places where that concentration is high are prone to certain health risks when there is no other source of drinking water. The most serious side effect of excess fluoride is the bone disease, skeletal fluorosis. When excess fluoride is in the body, it can cause the joints to stiffen and the bones to thicken. It can severely impact mobility and can negatively affect the thyroid gland. Skeletal fluorosis is a condition that over 2.7 million people suffer from across the world. So while fluoride can protect our teeth from decay, the US Environmental Protection Agency sets a maximum level of 4 ppm (4 mg/L) of fluoride in drinking water in the US. Fluoride levels in water are not regulated in all countries, so fluorosis is a problem in areas with high levels of fluoride in the groundwater.

The solubility of ionic compounds may also be increased when dissolution is coupled to the formation of a complex ion. For example, aluminum hydroxide dissolves in a solution of sodium hydroxide or another strong base because of the formation of the complex ion $Al(OH)_4{}^-$.



The equations for the dissolution of aluminum hydroxide, the formation of the complex ion, and the combined (net) equation are shown below. As indicated by the relatively large value of K for the net reaction, coupling complex formation with dissolution drastically increases the solubility of $Al(OH)_3$.

$$\begin{array}{ll} \text{Al(OH)}_3(s) \rightleftharpoons \text{Al}^{3+}(aq) + 3\text{OH}^-(aq) & K_{\text{sp}} = 2 \times 10^{-32} \\ \text{Al}^{3+}(aq) + 4\text{OH}^-(aq) \rightleftharpoons \text{Al(OH)}_4{}^-(aq) & K_{\text{f}} = 1.1 \times 10^{33} \\ \text{Net: Al(OH)}_3(s) + \text{OH}^-(aq) \rightleftharpoons \text{Al(OH)}_4{}^-(aq) & K = K_{\text{sp}}\,K_{\text{f}} = 22 \end{array}$$

Example 15.15

Increased Solubility in Acidic Solutions

Compute and compare the molar solublities for aluminum hydroxide, Ca(OH)_2, dissolved in (a) pure water and (b) a buffer containing 0.100 *M* acetic acid and 0.100 *M* sodium acetate.

Solution

(a) The molar solubility of calcium fluoride in water is computed considering the dissolution equilibrium only as demonstrated in several previous examples:

$$\text{Al(OH)}_3(s) \rightleftharpoons \text{Al}^{3+}(aq) + 3\text{OH}^-(aq) \qquad K_{\text{sp}} = 2 \times 10^{-32}$$

$$\text{molar solubility in water} = [\text{Al}^{3+}] = (2 \times 10^{-32}/27)^{1/3} = 9 \times 10^{-12}\ M$$

(b) The concentration of hydroxide ion of the buffered solution is conveniently calculated by the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_\text{a} + \log\,[\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}]$$

$$\text{pH} = 4.74 + \log\,(0.100/0.100) = 4.74$$

At this pH, the concentration of hydroxide ion is

$$\text{pOH} = 14.00 - 4.74 = 9.26$$

$$[\text{OH}^-] = 10^{-9.26} = 5.5 \times 10^{-10}$$

The solubility of Al(OH)_3 in this buffer is then calculated from its solubility product expressions:

$$K_{\text{sp}} = [\text{Al}^{3+}][\text{OH}^-]^3$$

$$\text{molar solubility in buffer} = \left[\text{Al}^{2+}\right] = K_{\text{sp}}/[\text{OH}^-]^3 = (2 \times 10^{-32})/(5.5 \times 10^{-10})^3 = 1.2 \times 10^{-4}\ M$$

Compared to pure water, the solubility of aluminum hydroxide in this mildly acidic buffer is approximately ten million times greater (though still relatively low).

Check Your Learning

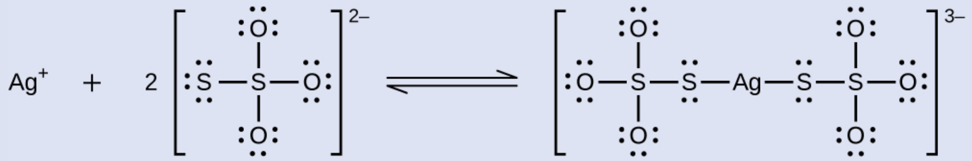
What is the solubility of aluminum hydroxide in a buffer comprised of 0.100 *M* formic acid and 0.100 *M* sodium formate?

Answer: 0.1 *M*

Example 15.16

Multiple Equilibria

Unexposed silver halides are removed from photographic film when they react with sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$, called hypo) to form the complex ion $\text{Ag(S}_2\text{O}_3)_2{}^{3-}$ ($K_\text{f} = 4.7 \times 10^{13}$).



What mass of $Na_2S_2O_3$ is required to prepare 1.00 L of a solution that will dissolve 1.00 g of AgBr by the formation of $Ag(S_2O_3)_2{}^{3-}$?

Solution

Two equilibria are involved when AgBr dissolves in a solution containing the $S_2O_3{}^{2-}$ ion:

dissolution: $AgBr(s) \rightleftharpoons Ag^{+}(aq) + Br^{-}(aq) \qquad K_{sp} = 5.0 \times 10^{-13}$

complexation: $Ag^{+}(aq) + 2S_2O_3{}^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2{}^{3-}(aq) \qquad K_f = 4.7 \times 10^{13}$

First, calculate the concentration of bromide that will result when the 1.00 g of AgBr is completely dissolved via the cited complexation reaction:

$$1.00\text{ g AgBr} / (187.77\text{ g/mol})(1\text{ mol Br}^{-} \ / \ 1\text{ mol AgBr}) = 0.00532\text{ mol Br}_{-}$$
$$0.00521\text{ mol Br}^{-} \ / \ 1.00\text{ L} = 0.00521\ M\text{ Br}^{-}$$

Next, use this bromide molarity and the solubility product for silver bromide to calculate the silver ion molarity in the solution:

$$[Ag^{+}] = K_{sp} / [Br^{-}] = 5.0 \times 10^{-13} / 0.00521 = 9.6 \times 10^{-11}\ M$$

Based on the stoichiometry of the complex ion formation, the concentration of complex ion produced is

$$0.00521 - 9.6 \times 10^{-11} = 0.00521\ M$$

Use the silver ion and complex ion concentrations and the formation constant for the complex ion to compute the concentration of thiosulfate ion.

$$[S_2O_{32}{}^{-}]^2 = [Ag(S_2O_3)^2]/[Ag^{+}]K_f = 0.00521/(9.6 \times 10^{-11})(4.7 \times 10^{13}) = 1.15 \times 10^{-6}$$
$$[S_2O_{32}{}^{-}] = 1.1 \times 10^{-3}\ M$$

Finally, use this molar concentration to derive the required mass of sodium thiosulfate:

$$(1.1 \times 10^{-3}\text{ mol } S_2O_{32}{}^{-} \ / \text{L})(1\text{ mol } NaS_2O_3 \ / \ 1\text{ mol } S_2O_{32}{}^{-})(158.1\text{ g } NaS_2O_3 \ / \text{mol}) = 1.7\text{ g}$$

Thus, 1.00 L of a solution prepared from 1.7 g $Na_2S_2O_3$ dissolves 1.0 g of AgBr.

Check Your Learning

AgCl(s), silver chloride, has a very low solubility: $AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$, $K_{sp} = 1.6 \times 10^{-10}$. Adding ammonia significantly increases the solubility of AgCl because a complex ion is formed: $Ag^{+}(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^{+}(aq)$, $K_f = 1.7 \times 10^{7}$. What mass of NH_3 is required to prepare 1.00 L of solution that will dissolve 2.00 g of AgCl by formation of $Ag(NH_3)_2{}^{+}$?

Answer: 1.00 L of a solution prepared with 4.81 g NH_3 dissolves 2.0 g of AgCl.

Key Terms

common ion effect effect on equilibrium when a substance with an ion in common with the dissolved species is added to the solution; causes a decrease in the solubility of an ionic species, or a decrease in the ionization of a weak acid or base

complex ion ion consisting of a central atom surrounding molecules or ions called ligands via coordinate covalent bonds

coordinate covalent bond (also, dative bond) covalent bond in which both electrons originated from the same atom

coupled equilibria system characterized the simultaneous establishment of two or more equilibrium reactions sharing one or more reactant or product

dissociation constant (K_d) equilibrium constant for the decomposition of a complex ion into its components

formation constant (K_f) (also, stability constant) equilibrium constant for the formation of a complex ion from its components

Lewis acid any species that can accept a pair of electrons and form a coordinate covalent bond

Lewis acid-base adduct compound or ion that contains a coordinate covalent bond between a Lewis acid and a Lewis base

Lewis acid-base chemistry reactions involving the formation of coordinate covalent bonds

Lewis base any species that can donate a pair of electrons and form a coordinate covalent bond

ligand molecule or ion acting as a Lewis base in complex ion formation; bonds to the central atom of the complex

molar solubility solubility of a compound expressed in units of moles per liter (mol/L)

selective precipitation process in which ions are separated using differences in their solubility with a given precipitating reagent

solubility product constant (K_{sp}) equilibrium constant for the dissolution of an ionic compound

Key Equations

- $\mathrm{M}_p\mathrm{X}_q(s) \rightleftharpoons p\mathrm{M}^{m+}(aq) + q\mathrm{X}^{n-}(aq)$ $\quad K_{sp} = [\mathrm{M}^{m+}]^p[\mathrm{X}^{n-}]^q$

Summary

15.1 Precipitation and Dissolution

The equilibrium constant for an equilibrium involving the precipitation or dissolution of a slightly soluble ionic solid is called the solubility product, K_{sp}, of the solid. For a heterogeneous equilibrium involving the slightly soluble solid $\mathrm{M}_p\mathrm{X}_q$ and its ions M^{m+} and X^{n-}:

$$\mathrm{M}_p\mathrm{X}_q(s) \rightleftharpoons p\mathrm{M}^{m+}(aq) + q\mathrm{X}^{n-}(aq)$$

the solubility product expression is:

$$K_{sp} = [\mathrm{M}^{m+}]^p\,[\mathrm{X}^{n-}]^q$$

The solubility product of a slightly soluble electrolyte can be calculated from its solubility; conversely, its solubility can be calculated from its K_{sp}, provided the only significant reaction that occurs when the solid dissolves is the formation of its ions.

A slightly soluble electrolyte begins to precipitate when the magnitude of the reaction quotient for the dissolution reaction exceeds the magnitude of the solubility product. Precipitation continues until the reaction quotient equals the solubility product.

15.2 Lewis Acids and Bases

A Lewis acid is a species that can accept an electron pair, whereas a Lewis base has an electron pair available for donation to a Lewis acid. Complex ions are examples of Lewis acid-base adducts and comprise central metal atoms or ions acting as Lewis acids bonded to molecules or ions called ligands that act as Lewis bases. The equilibrium constant for the reaction between a metal ion and ligands produces a complex ion called a formation constant; for the reverse reaction, it is called a dissociation constant.

15.3 Coupled Equilibria

Systems involving two or more chemical equilibria that share one or more reactant or product are called coupled equilibria. Common examples of coupled equilibria include the increased solubility of some compounds in acidic solutions (coupled dissolution and neutralization equilibria) and in solutions containing ligands (coupled dissolution and complex formation). The equilibrium tools from other chapters may be applied to describe and perform calculations on these systems.

Exercises

15.1 Precipitation and Dissolution

1. Complete the changes in concentrations for each of the following reactions:

(a) $\mathrm{AgI}(s) \longrightarrow \underset{x}{\mathrm{Ag}^{+}(aq)} + \underset{\_\_\_\_\_}{\mathrm{I}^{-}(aq)}$

(b) $\mathrm{CaCO_3}(s) \longrightarrow \underset{\_\_\_\_\_}{\mathrm{Ca}^{2+}(aq)} + \underset{x}{\mathrm{CO_3}^{2-}(aq)}$

(c) $\mathrm{Mg(OH)_2}(s) \longrightarrow \underset{x}{\mathrm{Mg}^{2+}(aq)} + \underset{\_\_\_\_\_}{\mathrm{2OH}^{-}(aq)}$

(d) $\mathrm{Mg_3(PO_4)_2}(s) \longrightarrow \mathrm{3Mg}^{2+}(aq) + \underset{x\_\_\_\_\_}{\mathrm{2PO_4}^{3-}(aq)}$

(e) $\mathrm{Ca_5(PO_4)_3OH}(s) \longrightarrow \underset{\_\_\_\_\_}{\mathrm{5Ca}^{2+}(aq)} + \underset{\_\_\_\_\_}{\mathrm{3PO_4}^{3-}(aq)} + \underset{x}{\mathrm{OH}^{-}(aq)}$

2. Complete the changes in concentrations for each of the following reactions:

(a) $$\begin{array}{lcc} \mathrm{BaSO_4}(s) \longrightarrow & \mathrm{Ba^{2+}}(aq) + & \mathrm{SO_4{}^{2-}}(aq) \\ & x & \underline{\hspace{2em}} \end{array}$$

(b) $$\begin{array}{lcc} \mathrm{Ag_2SO_4}(s) \longrightarrow & \mathrm{2Ag^{+}}(aq) + & \mathrm{SO_4{}^{2-}}(aq) \\ & \underline{\hspace{2em}} & x \end{array}$$

(c) $$\begin{array}{lcc} \mathrm{Al(OH)_3}(s) \longrightarrow & \mathrm{Al^{3+}}(aq) + & \mathrm{3OH^{-}}(aq) \\ & x & \underline{\hspace{2em}} \end{array}$$

(d) $$\begin{array}{lccc} \mathrm{Pb(OH)Cl}(s) \longrightarrow & \mathrm{Pb^{2+}}(aq) + & \mathrm{OH^{-}}(aq) + & \mathrm{Cl^{-}}(aq) \\ & \underline{\hspace{2em}} & x & \underline{\hspace{2em}} \end{array}$$

(e) $$\begin{array}{lcc} \mathrm{Ca_3(AsO_4)_2}(s) \longrightarrow & \mathrm{3Ca^{2+}}(aq) + & \mathrm{2AsO_4{}^{3-}}(aq) \\ & 3x & \underline{\hspace{2em}} \end{array}$$

3. How do the concentrations of Ag^+ and $CrO_4{}^{2-}$ in a saturated solution above 1.0 g of solid Ag_2CrO_4 change when 100 g of solid Ag_2CrO_4 is added to the system? Explain.

4. How do the concentrations of Pb^{2+} and S^{2-} change when K_2S is added to a saturated solution of PbS?

5. What additional information do we need to answer the following question: How is the equilibrium of solid silver bromide with a saturated solution of its ions affected when the temperature is raised?

6. Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: $CoSO_3$, CuI, $PbCO_3$, $PbCl_2$, Tl_2S, $KClO_4$?

7. Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present: AgCl, $BaSO_4$, CaF_2, Hg_2I_2, $MnCO_3$, ZnS, PbS?

8. Write the ionic equation for dissolution and the solubility product (K_{sp}) expression for each of the following slightly soluble ionic compounds:

(a) $PbCl_2$

(b) Ag_2S

(c) $Sr_3(PO_4)_2$

(d) $SrSO_4$

9. Write the ionic equation for the dissolution and the K_{sp} expression for each of the following slightly soluble ionic compounds:

(a) LaF_3

(b) $CaCO_3$

(c) Ag_2SO_4

(d) $Pb(OH)_2$

10. The ***Handbook of Chemistry and Physics (http://openstaxcollege.org/l/16Handbook)*** gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.

(a) $BaSiF_6$, 0.026 g/100 mL (contains $SiF_6{}^{2-}$ ions)

(b) $Ce(IO_3)_4$, 1.5×10^{-2} g/100 mL

(c) $Gd_2(SO_4)_3$, 3.98 g/100 mL

(d) $(NH_4)_2PtBr_6$, 0.59 g/100 mL (contains $PtBr_6{}^{2-}$ ions)

11. The ***Handbook of Chemistry and Physics (http://openstaxcollege.org/l/16Handbook)*** gives solubilities of the following compounds in grams per 100 mL of water. Because these compounds are only slightly soluble, assume that the volume does not change on dissolution and calculate the solubility product for each.

(a) $BaSeO_4$, 0.0118 g/100 mL

(b) $Ba(BrO_3)_2{\cdot}H_2O$, 0.30 g/100 mL

(c) $NH_4MgAsO_4{\cdot}6H_2O$, 0.038 g/100 mL

(d) $La_2(MoO_4)_3$, 0.00179 g/100 mL

12. Use solubility products and predict which of the following salts is the most soluble, in terms of moles per liter, in pure water: CaF_2, Hg_2Cl_2, PbI_2, or $Sn(OH)_2$.

13. Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:

(a) $KHC_4H_4O_6$

(b) PbI_2

(c) $Ag_4[Fe(CN)_6]$, a salt containing the $\text{Fe(CN)}_4{}^{-}$ ion

(d) Hg_2I_2

14. Assuming that no equilibria other than dissolution are involved, calculate the molar solubility of each of the following from its solubility product:

(a) Ag_2SO_4

(b) $PbBr_2$

(c) AgI

(d) $CaC_2O_4{\cdot}H_2O$

15. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.

(a) AgCl(*s*) in 0.025 *M* NaCl

(b) CaF_2(*s*) in 0.00133 *M* KF

(c) Ag_2SO_4(*s*) in 0.500 L of a solution containing 19.50 g of K_2SO_4

(d) $Zn(OH)_2$(*s*) in a solution buffered at a pH of 11.45

16. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that changes in the initial concentrations of the common ions can be neglected.

(a) TlCl(*s*) in 1.250 *M* HCl

(b) PbI_2(*s*) in 0.0355 *M* CaI_2

(c) Ag_2CrO_4(*s*) in 0.225 L of a solution containing 0.856 g of K_2CrO_4

(d) $Cd(OH)_2$(*s*) in a solution buffered at a pH of 10.995

17. Assuming that no equilibria other than dissolution are involved, calculate the concentration of all solute species in each of the following solutions of salts in contact with a solution containing a common ion. Show that it is not appropriate to neglect the changes in the initial concentrations of the common ions.

(a) $TlCl(s)$ in 0.025 M $TlNO_3$

(b) $BaF_2(s)$ in 0.0313 M KF

(c) MgC_2O_4 in 2.250 L of a solution containing 8.156 g of $Mg(NO_3)_2$

(d) $Ca(OH)_2(s)$ in an unbuffered solution initially with a pH of 12.700

18. Explain why the changes in concentrations of the common ions in **Exercise 15.17** can be neglected.

19. Explain why the changes in concentrations of the common ions in **Exercise 15.18** cannot be neglected.

20. Calculate the solubility of aluminum hydroxide, $Al(OH)_3$, in a solution buffered at pH 11.00.

21. Refer to **Appendix J** for solubility products for calcium salts. Determine which of the calcium salts listed is most soluble in moles per liter and which is most soluble in grams per liter.

22. Most barium compounds are very poisonous; however, barium sulfate is often administered internally as an aid in the X-ray examination of the lower intestinal tract (**Figure 15.4**). This use of $BaSO_4$ is possible because of its low solubility. Calculate the molar solubility of $BaSO_4$ and the mass of barium present in 1.00 L of water saturated with $BaSO_4$.

23. Public Health Service standards for drinking water set a maximum of 250 mg/L (2.60×10^{-3} M) of $SO_4{}^{2-}$ because of its cathartic action (it is a laxative). Does natural water that is saturated with $CaSO_4$ (“gyp” water) as a result or passing through soil containing gypsum, $CaSO_4{\cdot}2H_2O$, meet these standards? What is the concentration of $SO_4{}^{2-}$ in such water?

24. Perform the following calculations:

(a) Calculate $[Ag^+]$ in a saturated aqueous solution of AgBr.

(b) What will $[Ag^+]$ be when enough KBr has been added to make $[Br^-] = 0.050$ M?

(c) What will $[Br^-]$ be when enough $AgNO_3$ has been added to make $[Ag^+] = 0.020$ M?

25. The solubility product of $CaSO_4{\cdot}2H_2O$ is 2.4×10^{-5}. What mass of this salt will dissolve in 1.0 L of 0.010 M $SO4^{2-}$?

26. Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a saturated solution of each of the following (see **Appendix J** for solubility products).

(a) TlCl

(b) BaF_2

(c) Ag_2CrO_4

(d) $CaC_2O_4{\cdot}H_2O$

(e) the mineral anglesite, $PbSO_4$

27. Assuming that no equilibria other than dissolution are involved, calculate the concentrations of ions in a saturated solution of each of the following (see **Appendix J** for solubility products):

(a) AgI

(b) Ag_2SO_4

(c) $Mn(OH)_2$

(d) $Sr(OH)_2{\cdot}8H_2O$

(e) the mineral brucite, $Mg(OH)_2$

28. The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:

(a) AgBr: $[Ag^+] = 5.7 \times 10^{-7}\ M$, $[Br^-] = 5.7 \times 10^{-7}\ M$

(b) $CaCO_3$: $[Ca^{2+}] = 5.3 \times 10^{-3}\ M$, $[CO_3{}^{2-}] = 9.0 \times 10^{-7}\ M$

(c) PbF_2: $[Pb^{2+}] = 2.1 \times 10^{-3}\ M$, $[F^-] = 4.2 \times 10^{-3}\ M$

(d) Ag_2CrO_4: $[Ag^+] = 5.3 \times 10^{-5}\ M$, $3.2 \times 10^{-3}\ M$

(e) InF_3: $[In^{3+}] = 2.3 \times 10^{-3}\ M$, $[F^-] = 7.0 \times 10^{-3}\ M$

29. The following concentrations are found in mixtures of ions in equilibrium with slightly soluble solids. From the concentrations given, calculate K_{sp} for each of the slightly soluble solids indicated:

(a) TlCl: $[Tl^+] = 1.21 \times 10^{-2}\ M$, $[Cl^-] = 1.2 \times 10^{-2}\ M$

(b) $Ce(IO_3)_4$: $[Ce^{4+}] = 1.8 \times 10^{-4}\ M$, $[IO_3{}^-] = 2.6 \times 10^{-13}\ M$

(c) $Gd_2(SO_4)_3$: $[Gd^{3+}] = 0.132\ M$, $[SO_4{}^{2-}] = 0.198\ M$

(d) Ag_2SO_4: $[Ag^+] = 2.40 \times 10^{-2}\ M$, $[SO_4{}^{2-}] = 2.05 \times 10^{-2}\ M$

(e) $BaSO_4$: $[Ba^{2+}] = 0.500\ M$, $[SO_4{}^{2-}] = 4.6 \times 10^{-8}\ M$

30. Which of the following compounds precipitates from a solution that has the concentrations indicated? (See **Appendix J** for K_{sp} values.)

(a) $KClO_4$: $[K^+] = 0.01\ M$, $[ClO_4{}^-] = 0.01\ M$

(b) K_2PtCl_6: $[K^+] = 0.01\ M$, $[PtCl_6{}^{2-}] = 0.01\ M$

(c) PbI_2: $[Pb^{2+}] = 0.003\ M$, $[I^-] = 1.3 \times 10^{-3}\ M$

(d) Ag_2S: $[Ag^+] = 1 \times 10^{-10}\ M$, $[S^{2-}] = 1 \times 10^{-13}\ M$

31. Which of the following compounds precipitates from a solution that has the concentrations indicated? (See **Appendix J** for K_{sp} values.)

(a) $CaCO_3$: $[Ca^{2+}] = 0.003\ M$, $[CO_3{}^{2-}] = 0.003\ M$

(b) $Co(OH)_2$: $[Co^{2+}] = 0.01\ M$, $[OH^-] = 1 \times 10^{-7}\ M$

(c) $CaHPO_4$: $[Ca^{2+}] = 0.01\ M$, $[HPO_4{}^{2-}] = 2 \times 10^{-6}\ M$

(d) $Pb_3(PO_4)_2$: $[Pb^{2+}] = 0.01\ M$, $[PO_4{}^{3-}] = 1 \times 10^{-13}\ M$

32. Calculate the concentration of Tl^+ when TlCl just begins to precipitate from a solution that is 0.0250 M in Cl^-.

33. Calculate the concentration of sulfate ion when $BaSO_4$ just begins to precipitate from a solution that is 0.0758 M in Ba^{2+}.

34. Calculate the concentration of Sr^{2+} when SrF_2 starts to precipitate from a solution that is 0.0025 M in F^-.

35. Calculate the concentration of $PO_4{}^{3-}$ when Ag_3PO_4 starts to precipitate from a solution that is 0.0125 M in Ag^+.

36. Calculate the concentration of F^- required to begin precipitation of CaF_2 in a solution that is 0.010 M in Ca^{2+}.

37. Calculate the concentration of Ag^+ required to begin precipitation of Ag_2CO_3 in a solution that is 2.50×10^{-6} M in $CO_3{}^{2-}$.

38. What $[Ag^+]$ is required to reduce $[CO_3{}^{2-}]$ to $8.2 \times 10^{-4}\ M$ by precipitation of Ag_2CO_3?

39. What $[F^-]$ is required to reduce $[Ca^{2+}]$ to $1.0 \times 10^{-4}\ M$ by precipitation of CaF_2?

40. A volume of 0.800 L of a 2×10^{-4}-M $Ba(NO_3)_2$ solution is added to 0.200 L of $5 \times 10^{-4}\ M$ Li_2SO_4. Does $BaSO_4$ precipitate? Explain your answer.

41. Perform these calculations for nickel(II) carbonate. (a) With what volume of water must a precipitate containing $NiCO_3$ be washed to dissolve 0.100 g of this compound? Assume that the wash water becomes saturated with $NiCO_3$ ($K_{sp} = 1.36 \times 10^{-7}$).

(b) If the $NiCO_3$ were a contaminant in a sample of $CoCO_3$ ($K_{sp} = 1.0 \times 10^{-12}$), what mass of $CoCO_3$ would have been lost? Keep in mind that both $NiCO_3$ and $CoCO_3$ dissolve in the same solution.

42. Iron concentrations greater than 5.4×10^{-6} *M* in water used for laundry purposes can cause staining. What $[OH^-]$ is required to reduce $[Fe^{2+}]$ to this level by precipitation of $Fe(OH)_2$?

43. A solution is 0.010 *M* in both Cu^{2+} and Cd^{2+}. What percentage of Cd^{2+} remains in the solution when 99.9% of the Cu^{2+} has been precipitated as CuS by adding sulfide?

44. A solution is 0.15 *M* in both Pb^{2+} and Ag^+. If Cl^- is added to this solution, what is $[Ag^+]$ when $PbCl_2$ begins to precipitate?

45. What reagent might be used to separate the ions in each of the following mixtures, which are 0.1 *M* with respect to each ion? In some cases it may be necessary to control the pH. (Hint: Consider the K_{sp} values given in **Appendix J**.)

(a) ${Hg_2}^{2+}$ and Cu^{2+}

(b) ${SO_4}^{2-}$ and Cl^-

(c) Hg^{2+} and Co^{2+}

(d) Zn^{2+} and Sr^{2+}

(e) Ba^{2+} and Mg^{2+}

(f) ${CO_3}^{2-}$ and OH^-

46. A solution contains 1.0×10^{-5} mol of KBr and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgBr or solid AgCl?

47. A solution contains 1.0×10^{-2} mol of KI and 0.10 mol of KCl per liter. $AgNO_3$ is gradually added to this solution. Which forms first, solid AgI or solid AgCl?

48. The calcium ions in human blood serum are necessary for coagulation (**Figure 15.5**). Potassium oxalate, $K_2C_2O_4$, is used as an anticoagulant when a blood sample is drawn for laboratory tests because it removes the calcium as a precipitate of $CaC_2O_4{\cdot}H_2O$. It is necessary to remove all but 1.0% of the Ca^{2+} in serum in order to prevent coagulation. If normal blood serum with a buffered pH of 7.40 contains 9.5 mg of Ca^{2+} per 100 mL of serum, what mass of $K_2C_2O_4$ is required to prevent the coagulation of a 10 mL blood sample that is 55% serum by volume? (All volumes are accurate to two significant figures. Note that the volume of serum in a 10-mL blood sample is 5.5 mL. Assume that the K_{sp} value for CaC_2O_4 in serum is the same as in water.)

49. About 50% of urinary calculi (kidney stones) consist of calcium phosphate, $Ca_3(PO_4)_2$. The normal mid range calcium content excreted in the urine is 0.10 g of Ca^{2+} per day. The normal mid range amount of urine passed may be taken as 1.4 L per day. What is the maximum concentration of phosphate ion that urine can contain before a calculus begins to form?

50. The pH of normal urine is 6.30, and the total phosphate concentration $([{PO_4}^{3-}] + [{HPO_4}^{2-}] + [H_2{PO_4}^{-}]$ $+ [H_3PO_4])$ is 0.020 *M*. What is the minimum concentration of Ca^{2+} necessary to induce kidney stone formation? (See **Exercise 15.49** for additional information.)

51. Magnesium metal (a component of alloys used in aircraft and a reducing agent used in the production of uranium, titanium, and other active metals) is isolated from sea water by the following sequence of reactions:

$$Mg^{2+}(aq) + Ca(OH)_2(aq) \longrightarrow Mg(OH)_2(s) + Ca^{2+}(aq)$$

$$Mg(OH)_2(s) + 2HCl(aq) \longrightarrow MgCl_2(s) + 2H_2O(l)$$

$$MgCl_2(l) \xrightarrow{\text{electrolysis}} Mg(s) + Cl_2(g)$$

Sea water has a density of 1.026 g/cm^3 and contains 1272 parts per million of magnesium as $Mg^{2+}(aq)$ by mass. What mass, in kilograms, of $Ca(OH)_2$ is required to precipitate 99.9% of the magnesium in 1.00×10^3 L of sea water?

52. Hydrogen sulfide is bubbled into a solution that is 0.10 *M* in both Pb^{2+} and Fe^{2+} and 0.30 *M* in HCl. After the solution has come to equilibrium it is saturated with H_2S ($[H_2S] = 0.10$ *M*). What concentrations of Pb^{2+} and Fe^{2+} remain in the solution? For a saturated solution of H_2S we can use the equilibrium:

$$H_2S(aq) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-}(aq) \qquad K = 1.0 \times 10^{-26}$$

(Hint: The $[H_3O^+]$ changes as metal sulfides precipitate.)

53. Perform the following calculations involving concentrations of iodate ions:

(a) The iodate ion concentration of a saturated solution of $La(IO_3)_3$ was found to be 3.1×10^{-3} mol/L. Find the K_{sp}.

(b) Find the concentration of iodate ions in a saturated solution of $Cu(IO_3)_2$ ($K_{sp} = 7.4 \times 10^{-8}$).

54. Calculate the molar solubility of AgBr in 0.035 *M* NaBr ($K_{sp} = 5 \times 10^{-13}$).

55. How many grams of $Pb(OH)_2$ will dissolve in 500 mL of a 0.050-*M* $PbCl_2$ solution ($K_{sp} = 1.2 \times 10^{-15}$)?

56. Use the **simulation (http://openstaxcollege.org/l/16solublesalts)** from the earlier Link to Learning to complete the following exercise. Using 0.01 g CaF_2, give the K_{sp} values found in a 0.2-*M* solution of each of the salts. Discuss why the values change as you change soluble salts.

57. How many grams of Milk of Magnesia, $Mg(OH)_2$ (*s*) (58.3 g/mol), would be soluble in 200 mL of water. $K_{sp} = 7.1 \times 10^{-12}$. Include the ionic reaction and the expression for K_{sp} in your answer. ($K_w = 1 \times 10^{-14} = [H_3O^+][OH^-]$)

58. Two hypothetical salts, LM_2 and LQ, have the same molar solubility in H_2O. If K_{sp} for LM_2 is 3.20×10^{-5}, what is the K_{sp} value for LQ?

59. The carbonate ion concentration is gradually increased in a solution containing divalent cations of magnesium, calcium, strontium, barium, and manganese. Which of the following carbonates will form first? Which of the following will form last? Explain.

(a) $MgCO_3 \qquad K_{sp} = 3.5 \times 10^{-8}$

(b) $CaCO_3 \qquad K_{sp} = 4.2 \times 10^{-7}$

(c) $SrCO_3 \qquad K_{sp} = 3.9 \times 10^{-9}$

(d) $BaCO_3 \qquad K_{sp} = 4.4 \times 10^{-5}$

(e) $MnCO_3 \qquad K_{sp} = 5.1 \times 10^{-9}$

60. How many grams of $Zn(CN)_2(s)$ (117.44 g/mol) would be soluble in 100 mL of H_2O? Include the balanced reaction and the expression for K_{sp} in your answer. The K_{sp} value for $Zn(CN)_2(s)$ is 3.0×10^{-16}.

15.2 Lewis Acids and Bases

61. Even though $Ca(OH)_2$ is an inexpensive base, its limited solubility restricts its use. What is the pH of a saturated solution of $Ca(OH)_2$?

62. Under what circumstances, if any, does a sample of solid AgCl completely dissolve in pure water?

63. Explain why the addition of NH_3 or HNO_3 to a saturated solution of Ag_2CO_3 in contact with solid Ag_2CO_3 increases the solubility of the solid.

64. Calculate the cadmium ion concentration, $[Cd^{2+}]$, in a solution prepared by mixing 0.100 L of 0.0100 *M* $Cd(NO_3)_2$ with 1.150 L of 0.100 $NH_3(aq)$.

65. Explain why addition of NH_3 or HNO_3 to a saturated solution of $Cu(OH)_2$ in contact with solid $Cu(OH)_2$ increases the solubility of the solid.

66. Sometimes equilibria for complex ions are described in terms of dissociation constants, K_d. For the complex ion $AlF_6{}^{3-}$ the dissociation reaction is:

$$AlF_6{}^{3-} \rightleftharpoons Al^{3+} + 6F^- \text{ and } K_d = \frac{[Al^{3+}][F^-]^6}{[AlF_6{}^{3-}]} = 2 \times 10^{-24}$$

Calculate the value of the formation constant, K_f, for $AlF_6{}^{3-}$.

67. Using the value of the formation constant for the complex ion $Co(NH_3)_6{}^{2+}$, calculate the dissociation constant.

68. Using the dissociation constant, $K_d = 7.8 \times 10^{-18}$, calculate the equilibrium concentrations of Cd^{2+} and CN^- in a 0.250-*M* solution of $Cd(CN)_4{}^{2-}$.

69. Using the dissociation constant, $K_d = 3.4 \times 10^{-15}$, calculate the equilibrium concentrations of Zn^{2+} and OH^- in a 0.0465-*M* solution of $Zn(OH)_4{}^{2-}$.

70. Using the dissociation constant, $K_d = 2.2 \times 10^{-34}$, calculate the equilibrium concentrations of Co^{3+} and NH_3 in a 0.500-*M* solution of $Co(NH_3)_6{}^{3+}$.

71. Using the dissociation constant, $K_d = 1 \times 10^{-44}$, calculate the equilibrium concentrations of Fe^{3+} and CN^- in a 0.333 M solution of $Fe(CN)_6{}^{3-}$.

72. Calculate the mass of potassium cyanide ion that must be added to 100 mL of solution to dissolve 2.0×10^{-2} mol of silver cyanide, AgCN.

73. Calculate the minimum concentration of ammonia needed in 1.0 L of solution to dissolve 3.0×10^{-3} mol of silver bromide.

74. A roll of 35-mm black and white photographic film contains about 0.27 g of unexposed AgBr before developing. What mass of $Na_2S_2O_3{\cdot}5H_2O$ (sodium thiosulfate pentahydrate or hypo) in 1.0 L of developer is required to dissolve the AgBr as $Ag(S_2O_3)_2{}^{3-}$ ($K_f = 4.7 \times 10^{13}$)?

75. We have seen an introductory definition of an acid: An acid is a compound that reacts with water and increases the amount of hydronium ion present. In the chapter on acids and bases, we saw two more definitions of acids: a compound that donates a proton (a hydrogen ion, H^+) to another compound is called a Brønsted-Lowry acid, and a Lewis acid is any species that can accept a pair of electrons. Explain why the introductory definition is a macroscopic definition, while the Brønsted-Lowry definition and the Lewis definition are microscopic definitions.

76. Write the Lewis structures of the reactants and product of each of the following equations, and identify the Lewis acid and the Lewis base in each:

(a) $CO_2 + OH^- \longrightarrow HCO_3{}^-$

(b) $B(OH)_3 + OH^- \longrightarrow B(OH)_4{}^-$

(c) $I^- + I_2 \longrightarrow I_3{}^-$

(d) $AlCl_3 + Cl^- \longrightarrow AlCl_4{}^-$ (use Al-Cl single bonds)

(e) $O^{2-} + SO_3 \longrightarrow SO_4{}^{2-}$

77. Write the Lewis structures of the reactants and product of each of the following equations, and identify the Lewis acid and the Lewis base in each:

(a) $CS_2 + SH^- \longrightarrow HCS_3{}^-$

(b) $BF_3 + F^- \longrightarrow BF_4{}^-$

(c) $I^- + SnI_2 \longrightarrow SnI_3{}^-$

(d) $Al(OH)_3 + OH^- \longrightarrow Al(OH)_4{}^-$

(e) $F^- + SO_3 \longrightarrow SFO_3{}^-$

78. Using Lewis structures, write balanced equations for the following reactions:

(a) $HCl(g) + PH_3(g) \longrightarrow$

(b) $H_3O^+ + CH_3{}^- \longrightarrow$

(c) $CaO + SO_3 \longrightarrow$

(d) $NH_4{}^+ + C_2H_5O^- \longrightarrow$

79. Calculate $[HgCl_4{}^{2-}]$ in a solution prepared by adding 0.0200 mol of NaCl to 0.250 L of a 0.100-*M* $HgCl_2$ solution.

80. In a titration of cyanide ion, 28.72 mL of 0.0100 *M* $AgNO_3$ is added before precipitation begins. [The reaction of Ag^+ with CN^- goes to completion, producing the $Ag(CN)_2{}^-$ complex.] Precipitation of solid AgCN takes place when excess Ag^+ is added to the solution, above the amount needed to complete the formation of $Ag(CN)_2{}^-$. How many grams of NaCN were in the original sample?

81. What are the concentrations of Ag^+, CN^-, and $Ag(CN)_2{}^-$ in a saturated solution of AgCN?

82. In dilute aqueous solution HF acts as a weak acid. However, pure liquid HF (boiling point = 19.5 °C) is a strong acid. In liquid HF, HNO_3 acts like a base and accepts protons. The acidity of liquid HF can be increased by adding one of several inorganic fluorides that are Lewis acids and accept F^- ion (for example, BF_3 or SbF_5). Write balanced chemical equations for the reaction of pure HNO_3 with pure HF and of pure HF with BF_3.

83. The simplest amino acid is glycine, $H_2NCH_2CO_2H$. The common feature of amino acids is that they contain the functional groups: an amine group, $–NH_2$, and a carboxylic acid group, $–CO_2H$. An amino acid can function as either an acid or a base. For glycine, the acid strength of the carboxyl group is about the same as that of acetic acid, CH_3CO_2H, and the base strength of the amino group is slightly greater than that of ammonia, NH_3.

(a) Write the Lewis structures of the ions that form when glycine is dissolved in 1 *M* HCl and in 1 *M* KOH.

(b) Write the Lewis structure of glycine when this amino acid is dissolved in water. (Hint: Consider the relative base strengths of the $–NH_2$ and $-CO_2{}^-$ groups.)

84. Boric acid, H_3BO_3, is not a Brønsted-Lowry acid but a Lewis acid.

(a) Write an equation for its reaction with water.

(b) Predict the shape of the anion thus formed.

(c) What is the hybridization on the boron consistent with the shape you have predicted?

15.3 Coupled Equilibria

85. A saturated solution of a slightly soluble electrolyte in contact with some of the solid electrolyte is said to be a system in equilibrium. Explain. Why is such a system called a heterogeneous equilibrium?

86. Calculate the equilibrium concentration of Ni^{2+} in a 1.0-*M* solution $[Ni(NH_3)_6](NO_3)_2$.

87. Calculate the equilibrium concentration of Zn^{2+} in a 0.30-*M* solution of $Zn(CN)_4{}^{2-}$.

88. Calculate the equilibrium concentration of Cu^{2+} in a solution initially with 0.050 *M* Cu^{2+} and 1.00 *M* NH_3.

89. Calculate the equilibrium concentration of Zn^{2+} in a solution initially with 0.150 *M* Zn^{2+} and 2.50 *M* CN^-.

90. Calculate the Fe^{3+} equilibrium concentration when 0.0888 mole of $K_3[Fe(CN)_6]$ is added to a solution with 0.0.00010 *M* $CN^–$.

91. Calculate the Co^{2+} equilibrium concentration when 0.100 mole of $[Co(NH_3)_6](NO_3)_2$ is added to a solution with 0.025 *M* NH_3. Assume the volume is 1.00 L.

92. Calculate the molar solubility of $Sn(OH)_2$ in a buffer solution containing equal concentrations of NH_3 and $NH_4{}^+$.

93. Calculate the molar solubility of $Al(OH)_3$ in a buffer solution with 0.100 *M* NH_3 and 0.400 *M* $NH_4{}^+$.

94. What is the molar solubility of CaF_2 in a 0.100-*M* solution of HF? K_a for HF = 6.4 × $10^{–4}$.

95. What is the molar solubility of $BaSO_4$ in a 0.250-*M* solution of $NaHSO_4$? K_a for $HSO_4{}^-$ = 1.2 × $10^{–2}$.

96. What is the molar solubility of $Tl(OH)_3$ in a 0.10-*M* solution of NH_3?

97. What is the molar solubility of $Pb(OH)_2$ in a 0.138-*M* solution of CH_3NH_2?

98. A solution of 0.075 *M* $CoBr_2$ is saturated with H_2S ($[H_2S]$ = 0.10 *M*). What is the minimum pH at which CoS begins to precipitate?

$$CoS(s) \rightleftharpoons Co^{2+}(aq) + S^{2-}(aq) \qquad K_{sp} = 4.5 \times 10^{-27}$$

$$H_2S(aq) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-}(aq) \qquad K = 1.0 \times 10^{-26}$$

99. A 0.125-*M* solution of $Mn(NO_3)_2$ is saturated with H_2S ($[H_2S]$ = 0.10 *M*). At what pH does MnS begin to precipitate?

$$MnS(s) \rightleftharpoons Mn^{2+}(aq) + S^{2-}(aq) \qquad K_{sp} = 4.3 \times 10^{-22}$$

$$H_2S(aq) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-}(aq) \qquad K = 1.0 \times 10^{-26}$$

100. Both AgCl and AgI dissolve in NH_3.

(a) What mass of AgI dissolves in 1.0 L of 1.0 *M* NH_3?

(b) What mass of AgCl dissolves in 1.0 L of 1.0 *M* NH_3?

101. The following question is taken from a Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

Solve the following problem:

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$$

In a saturated solution of MgF_2 at 18 °C, the concentration of Mg^{2+} is 1.21 × $10^{–3}$ *M*. The equilibrium is represented by the preceding equation.

(a) Write the expression for the solubility-product constant, K_{sp}, and calculate its value at 18 °C.

(b) Calculate the equilibrium concentration of Mg^{2+} in 1.000 L of saturated MgF_2 solution at 18 °C to which 0.100 mol of solid KF has been added. The KF dissolves completely. Assume the volume change is negligible.

(c) Predict whether a precipitate of MgF_2 will form when 100.0 mL of a 3.00 × $10^{–3}$-*M* solution of $Mg(NO_3)_2$ is mixed with 200.0 mL of a 2.00 × $10^{–3}$-*M* solution of NaF at 18 °C. Show the calculations to support your prediction.

(d) At 27 °C the concentration of Mg^{2+} in a saturated solution of MgF_2 is 1.17 × $10^{–3}$ *M*. Is the dissolving of MgF_2 in water an endothermic or an exothermic process? Give an explanation to support your conclusion.

102. Which of the following compounds, when dissolved in a 0.01-*M* solution of $HClO_4$, has a solubility greater than in pure water: CuCl, $CaCO_3$, MnS, $PbBr_2$, CaF_2? Explain your answer.

103. Which of the following compounds, when dissolved in a 0.01-*M* solution of $HClO_4$, has a solubility greater than in pure water: AgBr, BaF_2, $Ca_3(PO_4)_2$, ZnS, PbI_2? Explain your answer.

104. What is the effect on the amount of solid $Mg(OH)_2$ that dissolves and the concentrations of Mg^{2+} and OH^- when each of the following are added to a mixture of solid $Mg(OH)_2$ and water at equilibrium?

(a) $MgCl_2$

(b) KOH

(c) $HClO_4$

(d) $NaNO_3$

(e) $Mg(OH)_2$

105. What is the effect on the amount of $CaHPO_4$ that dissolves and the concentrations of Ca^{2+} and $HPO_4{}^-$ when each of the following are added to a mixture of solid $CaHPO_4$ and water at equilibrium?

(a) $CaCl_2$

(b) HCl

(c) $KClO_4$

(d) NaOH

(e) $CaHPO_4$

106. Identify all chemical species present in an aqueous solution of $Ca_3(PO_4)_2$ and list these species in decreasing order of their concentrations. (Hint: Remember that the $PO_4{}^{3-}$ ion is a weak base.)

Chapter 16

Electrochemistry

Figure 16.1 Electric vehicles are powered by batteries, devices that harness the energy of spontaneous redox reactions. (credit: modification of work by Robert Couse-Baker)

Chapter Outline

Introduction

Another chapter in this text introduced the chemistry of reduction-oxidation (redox) reactions. This important reaction class is defined by changes in oxidation states for one or more reactant elements, and it includes a subset of reactions involving the transfer of electrons between reactant species. Around the turn of the nineteenth century, chemists began exploring ways these electrons could be transferred *indirectly* via an external circuit rather than directly via intimate contact of redox reactants. In the two centuries since, the field of *electrochemistry* has evolved to yield significant insights on the fundamental aspects of redox chemistry as well as a wealth of technologies ranging from industrial-scale metallurgical processes to robust, rechargeable batteries for electric vehicles (**Figure 16.1**). In this chapter, the essential concepts of electrochemistry will be addressed.

16.1 Review of Redox Chemistry

By the end of this section, you will be able to:

- Describe defining traits of redox chemistry
- Identify the oxidant and reductant of a redox reaction
- Balance chemical equations for redox reactions using the half-reaction method

Since reactions involving electron transfer are essential to the topic of electrochemistry, a brief review of redox chemistry is provided here that summarizes and extends the content of an earlier text chapter (see chapter on reaction stoichiometry). Readers wishing additional review are referred to the text chapter on reaction stoichiometry.

Oxidation Numbers

By definition, a redox reaction is one that entails changes in *oxidation number* (or *oxidation state*) for one or more of the elements involved. The oxidation number of an element in a compound is essentially an assessment of how the electronic environment of its atoms is different in comparison to atoms of the pure element. By this description, *the oxidation number of an atom in an element is equal to zero*. For an atom in a compound, *the oxidation number is equal to the charge the atom would have in the compound if the compound were ionic*. Consequential to these rules, *the sum of oxidation numbers for all atoms in a molecule is equal to the charge on the molecule*. To illustrate this formalism, examples from the two compound classes, ionic and covalent, will be considered.

Simple ionic compounds present the simplest examples to illustrate this formalism, since by definition the elements' oxidation numbers are numerically equivalent to ionic charges. Sodium chloride, NaCl, is comprised of Na^+ cations and Cl^- anions, and so oxidation numbers for sodium and chlorine are, +1 and −1, respectively. Calcium fluoride, CaF_2, is comprised of Ca^{2+} cations and F^- anions, and so oxidation numbers for calcium and fluorine are, +2 and −1, respectively.

Covalent compounds require a more challenging use of the formalism. Water is a covalent compound whose molecules consist of two H atoms bonded separately to a central O atom via polar covalent O−H bonds. The shared electrons comprising an O−H bond are more strongly attracted to the more electronegative O atom, and so it acquires a partial negative charge in the water molecule (relative to an O atom in elemental oxygen). Consequently, H atoms in a water molecule exhibit partial positive charges compared to H atoms in elemental hydrogen. The sum of the partial negative and partial positive charges for each water molecule is zero, and the water molecule is neutral.

Imagine that the polarization of shared electrons within the O−H bonds of water were 100% complete—the result would be *transfer* of electrons from H to O, and water would be an ionic compound comprised of O^{2-} anions and H^+ cations. And so, the oxidations numbers for oxygen and hydrogen in water are −2 and +1, respectively. Applying this same logic to carbon tetrachloride, CCl_4, yields oxidation numbers of +4 for carbon and −1 for chlorine. In the nitrate ion, NO_3^-, the oxidation number for nitrogen is +5 and that for oxygen is −2, summing to equal the 1− charge on the molecule:

$$(1\text{N atom})\left(\frac{+5}{\text{N atom}}\right) + (3\text{ O atoms})\left(\frac{-2}{\text{O atom}}\right) = +5 + -6 = -1$$

Balancing Redox Equations

The unbalanced equation below describes the decomposition of molten sodium chloride:

$$\text{NaCl}(l) \longrightarrow \text{Na}(l) + \text{Cl}_2(g) \qquad \textit{unbalanced}$$

This reaction satisfies the criterion for redox classification, since the oxidation number for Na is decreased from +1 to 0 (it undergoes *reduction*) and that for Cl is increased from −1 to 0 (it undergoes *oxidation*). The equation in this case is easily balanced by inspection, requiring stoichiometric coefficients of 2 for the NaCl and Na:

$$2\text{NaCl}(l) \longrightarrow 2\text{Na}(l) + \text{Cl}_2(g) \qquad \textit{balanced}$$

Redox reactions that take place in aqueous solutions are commonly encountered in electrochemistry, and many involve water or its characteristic ions, $H^+(aq)$ and $OH^-(aq)$, as reactants or products. In these cases, equations representing the redox reaction can be very challenging to balance by inspection, and the use of a systematic approach called the *half-reaction method* is helpful. This approach involves the following steps:

1. Write skeletal equations for the oxidation and reduction half-reactions.
2. Balance each half-reaction for all elements except H and O.
3. Balance each half-reaction for O by adding H_2O.
4. Balance each half-reaction for H by adding H^+.
5. Balance each half-reaction for charge by adding electrons.
6. If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.
7. Add the two half-reactions and simplify.
8. If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

The examples below demonstrate the application of this method to balancing equations for aqueous redox reactions.

Example 16.1

Balancing Equations for Redox Reactions in Acidic Solutions

Write the balanced equation representing reaction between solid copper and nitric acid to yield aqueous copper(II) ions and nitrogen monoxide gas.

Solution

Following the steps of the half-reaction method:

1. *Write skeletal equations for the oxidation and reduction half-reactions.*

   oxidation: $\text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq)$

   reduction: $\text{HNO}_3(aq) \longrightarrow \text{NO}(g)$

2. *Balance each half-reaction for all elements except H and O.*

   oxidation: $\text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq)$

   reduction: $\text{HNO}_3(aq) \longrightarrow \text{NO}(g)$

3. *Balance each half-reaction for O by adding H_2O.*

   oxidation: $\text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq)$

   reduction: $\text{HNO}_3(aq) \longrightarrow \text{NO}(g) + \mathbf{2H_2O(\mathit{l})}$

4. *Balance each half-reaction for H by adding H^+.*

   oxidation: $\text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq)$

   reduction: $\mathbf{3H^+(\mathit{aq})} + \text{HNO}_3(aq) \longrightarrow \text{NO}(g) + 2\text{H}_2\text{O}(l)$

5. *Balance each half-reaction for charge by adding electrons.*

   oxidation: $\text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq) + \mathbf{2e^-}$

   reduction: $\mathbf{3e^-} + 3\text{H}^+(aq) + \text{HNO}_3(aq) \longrightarrow \text{NO}(g) + 2\text{H}_2\text{O}(l)$

6. *If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.*

oxidation (×3): $\mathbf{3}\mathrm{Cu}(s) \longrightarrow \mathbf{3}\mathrm{Cu}^{2+}(aq) + \mathbf{6}\cancel{2}\mathrm{e}^-$

reduction (×2): $\mathbf{6}\cancel{3}\mathrm{e}^- + \mathbf{6}\cancel{3}\mathrm{H}^+(aq) + \mathbf{2}\mathrm{HNO}_3(aq) \longrightarrow \mathbf{2}\mathrm{NO}(g) + \mathbf{4}\cancel{2}\mathrm{H}_2\mathrm{O}(l)$

7. *Add the two half-reactions and simplify.*

   $3\mathrm{Cu}(s) + \cancel{\mathbf{6}}\mathbf{e}^- + 6\mathrm{H}^+(aq) + 2\mathrm{HNO}_3(aq) \longrightarrow 3\mathrm{Cu}^{2+}(aq) + \cancel{\mathbf{6}}\mathbf{e}^- + 2\mathrm{NO}(g)4\mathrm{H}_2\mathrm{O}(l)$

   $3\mathrm{Cu}(s) + 6\mathrm{H}^+(aq) + 2\mathrm{HNO}_3(aq) \longrightarrow 3\mathrm{Cu}^{2+}(aq) + 2\mathrm{NO}(g) + 4\mathrm{H}_2\mathrm{O}(l)$

8. *If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.*

   This step not necessary since the solution is stipulated to be acidic.

The balanced equation for the reaction in an acidic solution is then

$$3\mathrm{Cu}(s) + 6\mathrm{H}^+(aq) + 2\mathrm{HNO}_3(aq) \longrightarrow 3\mathrm{Cu}^{2+}(aq) + 2\mathrm{NO}(g) + 4\mathrm{H}_2\mathrm{O}(l)$$

Check Your Learning

The reaction above results when using relatively diluted nitric acid. If concentrated nitric acid is used, nitrogen dioxide is produced instead of nitrogen monoxide. Write a balanced equation for this reaction.

Answer: $\mathrm{Cu}(s) + 2\mathrm{H}^+(aq) + 2\mathrm{HNO}_3(aq) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\mathrm{NO}_2(g) + 2\mathrm{H}_2\mathrm{O}(l)$

Example 16.2

Balancing Equations for Redox Reactions in Basic Solutions

Write the balanced equation representing reaction between aqueous permanganate ion, $\mathrm{MnO_4}^-$, and solid chromium(III) hydroxide, $\mathrm{Cr(OH)_3}$, to yield solid manganese(IV) oxide, $\mathrm{MnO_2}$, and aqueous chromate ion, $\mathrm{CrO_4}^{2-}$ The reaction takes place in a basic solution.

Solution

Following the steps of the half-reaction method:

1. *Write skeletal equations for the oxidation and reduction half-reactions.*

   oxidation: $\mathrm{Cr(OH)}_3(s) \longrightarrow \mathrm{CrO_4}^{2-}(aq)$

   reduction: $\mathrm{MnO_4}^-(aq) \longrightarrow \mathrm{MnO}_2(s)$

2. *Balance each half-reaction for all elements except H and O.*

   oxidation: $\mathrm{Cr(OH)}_3(s) \longrightarrow \mathrm{CrO_4}^{2-}(aq)$

   reduction: $\mathrm{MnO_4}^-(aq) \longrightarrow \mathrm{MnO}_2(s)$

3. *Balance each half-reaction for O by adding H_2O.*

   oxidation: $\mathbf{H_2O}(\boldsymbol{l}) \mathbf{+} \mathrm{Cr(OH)}_3(s) \longrightarrow \mathrm{CrO_4}^{2-}(aq)$

   reduction: $\mathrm{MnO_4}^-(aq) \longrightarrow \mathrm{MnO}_2(s) \mathbf{+ 2H_2O}(\boldsymbol{l})$

4. *Balance each half-reaction for H by adding H^+.*

   oxidation: $\mathrm{H_2O}(l) + \mathrm{Cr(OH)}_3(s) \longrightarrow \mathrm{CrO_4}^{2-}(aq) \mathbf{+ 5H^+}(\boldsymbol{aq})$

   reduction: $\mathbf{4H^+}(\boldsymbol{aq}) \mathbf{+} \mathrm{MnO_4}^-(aq) \longrightarrow \mathrm{MnO}_2(s) + 2\mathrm{H_2O}(l)$

5. *Balance each half-reaction for charge by adding electrons.*

   oxidation: $\mathrm{H_2O}(l) + \mathrm{Cr(OH)}_3(s) \longrightarrow \mathrm{CrO_4}^{2-}(aq) + 5\mathrm{H}^+(aq) \mathbf{+ 3e^-}$

   reduction: $\mathbf{3e^-} \mathbf{+} 4\mathrm{H}^+(aq) + \mathrm{MnO_4}^-(aq) \longrightarrow \mathrm{MnO}_2(s) + 2\mathrm{H_2O}(l)$

6. *If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is*

equal to the number produced in the other.
This step is not necessary since the number of electrons is already in balance.

7. *Add the two half-reactions and simplify.*

$$\cancel{\mathbf{H_2O}(\boldsymbol{l})} + \mathrm{Cr(OH)_3}(s) + \cancel{\mathbf{3e^-}} + \cancel{\mathbf{4H^+}(\boldsymbol{aq})} + \mathrm{MnO_4}^-(aq) \longrightarrow \mathrm{CrO_4}^{2-}(aq) + \cancel{\mathbf{5}}\mathrm{H}^+(aq) + \cancel{\mathbf{3e^-}} + \mathrm{MnO_2}(s) + \mathbf{2}\mathrm{H_2O}(l)$$

$$\mathrm{Cr(OH)_3}(s) + \mathrm{MnO_4}^-(aq) \longrightarrow \mathrm{CrO_4}^{2-}(aq)\mathrm{H}^+(aq) + \mathrm{MnO_2}(s) + \mathrm{H_2O}(l)$$

8. *If the reaction takes place in a basic medium, add OH⁻ ions the equation obtained in step 7 to neutralize the H⁺ ions (add in equal numbers to both sides of the equation) and simplify.*

$$\mathbf{OH^-}(\boldsymbol{aq}) + \mathrm{Cr(OH)_3}(s) + \mathrm{MnO_4}^-(aq) \longrightarrow \mathrm{CrO_4}^{2-}(aq) + \mathrm{H}^+(aq) + \mathbf{OH^-}(\boldsymbol{aq}) + \mathrm{MnO_2}(s) + \mathrm{H_2O}(l)$$

$$\mathrm{OH}^-(aq) + \mathrm{Cr(OH)_3}(s) + \mathrm{MnO_4}^-(aq) \longrightarrow \mathrm{CrO_4}^{2-}(aq) + \mathrm{MnO_2}(s) + 2\mathrm{H_2O}(l)$$

Check Your Learning

Aqueous permanganate ion may also be reduced using aqueous bromide ion, Br^-, the products of this reaction being solid manganese(IV) oxide and aqueous bromate ion, $\mathrm{BrO_3}^-$. Write the balanced equation for this reaction occurring in a basic medium.

Answer: $\mathrm{H_2O}(l) + 2\mathrm{MnO_4}^-(aq) + \mathrm{Br}^-(aq) \longrightarrow 2\mathrm{MnO_2}(s) + \mathrm{BrO_3}^-(aq) + 2\mathrm{OH}^-(aq)$

16.2 Galvanic Cells

By the end of this section, you will be able to:

- Describe the function of a galvanic cell and its components
- Use cell notation to symbolize the composition and construction of galvanic cells

As demonstration of spontaneous chemical change, **Figure 16.2** shows the result of immersing a coiled wire of copper into an aqueous solution of silver nitrate. A gradual but visually impressive change spontaneously occurs as the initially colorless solution becomes increasingly blue, and the initially smooth copper wire becomes covered with a porous gray solid.

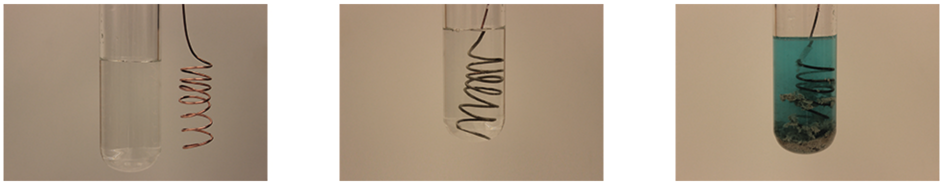


Figure 16.2 A copper wire and an aqueous solution of silver nitrate (left) are brought into contact (center) and a spontaneous transfer of electrons occurs, creating blue Cu^{2+}(*aq*) and gray Ag(*s*) (right).

These observations are consistent with (i) the oxidation of elemental copper to yield copper(II) ions, Cu^{2+}*(aq)*, which impart a blue color to the solution, and (ii) the reduction of silver(I) ions to yield elemental silver, which deposits as a fluffy solid on the copper wire surface. And so, *the direct transfer of electrons from the copper wire to the aqueous silver ions is spontaneous* under the employed conditions. A summary of this redox system is provided by these equations:

$$\begin{array}{ll} \text{overall reaction:} & \mathrm{Cu}(s) + 2\mathrm{Ag}^{+}(aq) \longrightarrow \mathrm{Cu}^{2\,+}(aq) + 2\mathrm{Ag}(s) \\ \text{oxidation half-reaction:} & \mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\mathrm{e}^{-} \\ \text{reduction half-reaction:} & 2\mathrm{Ag}^{+}(aq) + 2\mathrm{e}^{-} \longrightarrow 2\mathrm{Ag}(s) \end{array}$$

Consider the construction of a device that contains all the reactants and products of a redox system like the one here, but prevents physical contact between the reactants. Direct transfer of electrons is, therefore, prevented; transfer, instead, takes place indirectly through an external circuit that contacts the separated reactants. Devices of this sort are generally referred to as *electrochemical cells*, and those in which a spontaneous redox reaction takes place are called **galvanic cells** (or **voltaic cells**).

A galvanic cell based on the spontaneous reaction between copper and silver(I) is depicted in **Figure 16.3**. The cell is comprised of two **half-cells**, each containing the redox conjugate pair ("couple") of a single reactant. The half-cell shown at the left contains the Cu(0)/Cu(II) couple in the form of a solid copper foil and an aqueous solution of copper nitrate. The right half-cell contains the Ag(I)/Ag(0) couple as solid silver foil and an aqueous silver nitrate solution. An external circuit is connected to each half-cell at its solid foil, meaning the Cu and Ag foil each function as an *electrode*. By definition, the **anode** of an electrochemical cell is the electrode at which oxidation occurs (in this case, the Cu foil) and the **cathode** is the electrode where reduction occurs (the Ag foil). The redox reactions in a galvanic cell occur only at the interface between each half-cell's reaction mixture and its electrode. To keep the reactants separate while maintaining charge-balance, the two half-cell solutions are connected by a tube filled with inert electrolyte solution called a **salt bridge**. The spontaneous reaction in this cell produces Cu^{2+} cations in the anode half-cell and consumes Ag^{+} ions in the cathode half-cell, resulting in a compensatory flow of inert ions from the salt bridge that maintains charge balance. Increasing concentrations of Cu^{2+} in the anode half-cell are balanced by an influx of $\mathrm{NO_3}^{-}$ from the salt bridge, while a flow of Na^{+} into the cathode half-cell compensates for the decreasing Ag^{+} concentration.

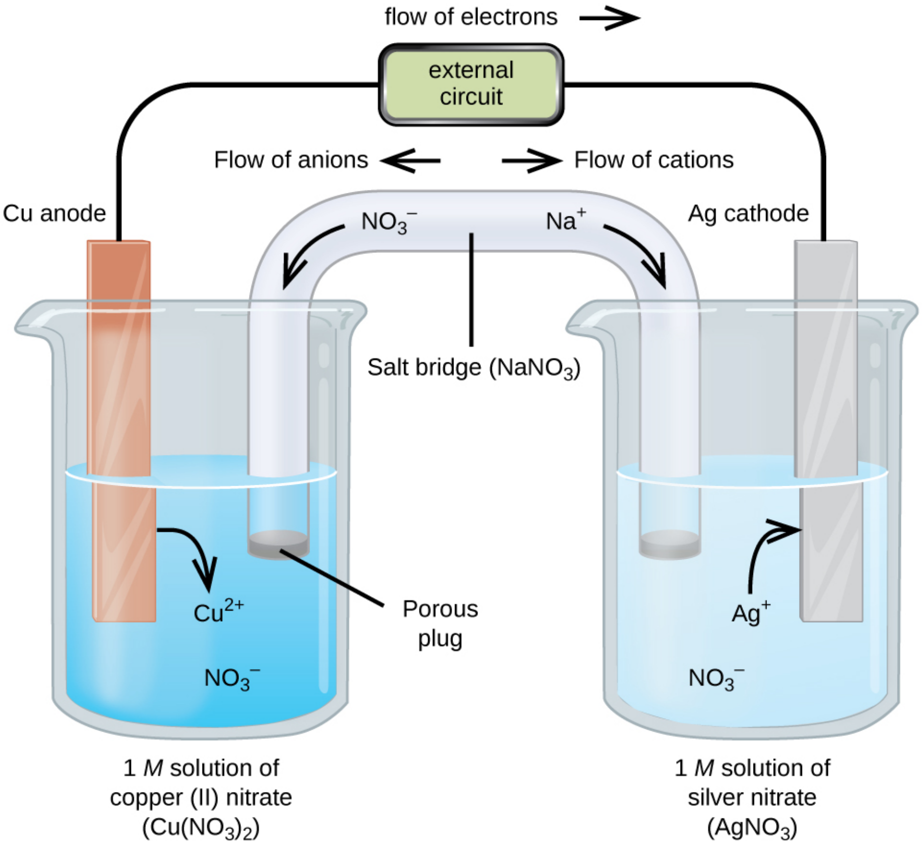


Figure 16.3 A galvanic cell based on the spontaneous reaction between copper and silver(I) ions.

Cell Notation

Abbreviated symbolism is commonly used to represent a galvanic cell by providing essential information on its composition and structure. These symbolic representations are called **cell notations** or **cell schematics**, and they are written following a few guidelines:

- The relevant components of each half-cell are represented by their chemical formulas or element symbols
- All interfaces between component phases are represented by vertical parallel lines; if two or more components are present in the same phase, their formulas are separated by commas
- By convention, the schematic begins with the anode and proceeds left-to-right identifying phases and interfaces encountered within the cell, ending with the cathode

A verbal description of the cell as viewed from anode-to-cathode is often a useful first-step in writing its schematic. For example, the galvanic cell shown in **Figure 16.3** consists of a solid copper anode immersed in an aqueous solution of copper(II) nitrate that is connected via a salt bridge to an aqueous silver(I) nitrate solution, immersed in which is a solid silver cathode. Converting this statement to symbolism following the above guidelines results in the cell schematic:

$$\text{Cu}(s) \mid 1\,M\ \text{Cu(NO}_3)_2(aq) \parallel 1\,M\ \text{AgNO}_3(aq) \mid \text{Ag}(s)$$

Consider a different galvanic cell (see **Figure 16.4**) based on the spontaneous reaction between solid magnesium and aqueous iron(III) ions:

$$\begin{array}{ll} \text{net cell reaction:} & \text{Mg}(s) + 2\text{Fe}^{3+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + 2\text{Fe}^{2+}(aq) \\ \text{oxidation half-reaction:} & \text{Mg}(s) \longrightarrow \text{Mg}^{2+}(aq) + 2\text{e}^- \\ \text{reduction half-reaction:} & 2\text{Fe}^{3+}(aq) + 2\text{e}^- \longrightarrow 2\text{Fe}^{2+}(aq) \end{array}$$

In this cell, a solid magnesium anode is immersed in an aqueous solution of magnesium chloride that is connected via a salt bridge to an aqueous solution containing a mixture of iron(III) chloride and iron(II) chloride, immersed in which is a platinum cathode. The cell schematic is then written as

$$\text{Mg}(s) \mid 0.1\,M\ \text{MgCl}_2(aq) \parallel 0.2\,M\ \text{FeCl}_3(aq),\ 0.3\,M\ \text{FeCl}_2(aq) \mid \text{Pt}(s)$$

Notice the cathode half-cell is different from the others considered thus far in that its electrode is comprised of a substance (Pt) that is neither a reactant nor a product of the cell reaction. This is required when neither member of the half-cell's redox couple can reasonably function as an electrode, which must be electrically conductive and in a phase separate from the half-cell solution. In this case, both members of the redox couple are solute species, and so Pt is used as an **inert electrode** that can simply provide or accept electrons to redox species in solution. Electrodes constructed from a member of the redox couple, such as the Mg anode in this cell, are called **active electrodes**.

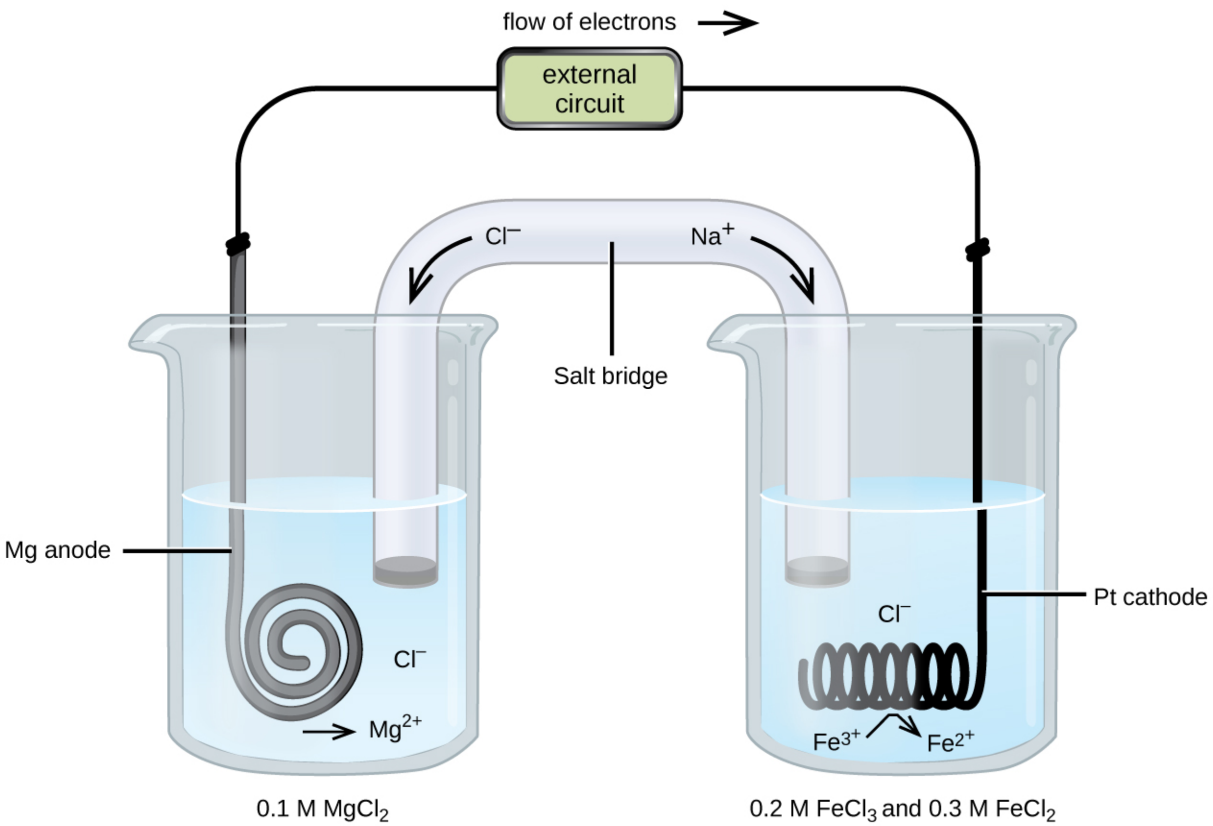


Figure 16.4 A galvanic cell based on the spontaneous reaction between magnesium and iron(III) ions.

Example 16.3

Writing Galvanic Cell Schematics

A galvanic cell is fabricated by connecting two half-cells with a salt bridge, one in which a chromium wire is immersed in a 1 M $CrCl_3$ solution and another in which a copper wire is immersed in 1 M $CuCl_2$. Assuming the chromium wire functions as an anode, write the schematic for this cell along with equations for the anode half-reaction, the cathode half-reaction, and the overall cell reaction.

Solution

Since the chromium wire is stipulated to be the anode, the schematic begins with it and proceeds left-to-right, symbolizing the other cell components until ending with the copper wire cathode:

$$\text{Cr}(s) \mid 1\ M\ \text{CrCl}_3(aq) \parallel 1\ M\ \text{CuCl}_2(aq) \mid \text{Cu}(s)$$

The half-reactions for this cell are

$$\begin{array}{ll} \text{anode (oxidation):} & \text{Cr}(s) \longrightarrow \text{Cr}^{3+}(aq) + 3\text{e}^- \\ \text{cathode (oxidation):} & \text{Cu}^{2+}(aq) + 2\text{e}^- \longrightarrow \text{Cu}(s) \end{array}$$

Multiplying to make the number of electrons lost by Cr and gained by Cu^{2+} equal yields

$$\begin{array}{ll} \text{anode (oxidation):} & 2\mathrm{Cr}(s) \longrightarrow 2\mathrm{Cr}^{3+}(aq) + 6\mathrm{e}^- \\ \text{cathode (reducation):} & 3\mathrm{Cu}^{2+}(aq) + 6\mathrm{e}^- \longrightarrow 3\mathrm{Cu}(s) \end{array}$$

Adding the half-reaction equations and simplifying yields an equation for the cell reaction:

$$2\mathrm{Cr}(s) + 3\mathrm{Cu}^{2+}(aq) \longrightarrow 2\mathrm{Cr}^{3+}(aq) + 3\mathrm{Cu}(s)$$

Check Your Learning

Omitting solute concentrations and spectator ion identities, write the schematic for a galvanic cell whose net cell reaction is shown below.

$$\mathrm{Sn}^{4+}(aq) + \mathrm{Zn}(s) \longrightarrow \mathrm{Sn}^{2+}(aq) + \mathrm{Zn}^{2+}(aq)$$

Answer: $\mathrm{Zn}(s) \mid \mathrm{Zn}^{2+}(aq) \parallel \mathrm{Sn}^{4+}(aq), \mathrm{Sn}^{2+}(aq) \mid \mathrm{Pt}(s)$

16.3 Electrode and Cell Potentials

By the end of this section, you will be able to:

- Describe and relate the definitions of electrode and cell potentials
- Interpret electrode potentials in terms of relative oxidant and reductant strengths
- Calculate cell potentials and predict redox spontaneity using standard electrode potentials

Unlike the spontaneous oxidation of copper by aqueous silver(I) ions described in section 17.2, immersing a copper wire in an aqueous solution of lead(II) ions yields no reaction. The two species, $\mathrm{Ag}^+(aq)$ and $\mathrm{Pb}^{2+}(aq)$, thus show a distinct difference in their redox activity towards copper: the silver ion spontaneously oxidized copper, but the lead ion did not. Electrochemical cells permit this relative redox activity to be quantified by an easily measured property, *potential*. This property is more commonly called *voltage* when referenced in regard to electrical applications, and it is a measure of energy accompanying the transfer of charge. Potentials are measured in the volt unit, defined as one joule of energy per one coulomb of charge, V = J/C.

When measured for purposes of electrochemistry, a potential reflects the driving force for a specific type of charge transfer process, namely, the transfer of electrons between redox reactants. Considering the nature of potential in this context, it is clear that the potential of a single half-cell or a single electrode can't be measured; "transfer" of electrons requires both a donor and recipient, in this case a reductant and an oxidant, respectively. Instead, a half-cell potential may only be assessed relative to that of another half-cell. It is only the *difference in potential* between two half-cells that may be measured, and these measured potentials are called **cell potentials, E_{cell}**, defined as

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

where E_{cathode} and E_{anode} are the potentials of two different half-cells functioning as specified in the subscripts. As for other thermodynamic quantities, the **standard cell potential, $E°_{\text{cell}}$**, is a cell potential measured when both half-cells are under standard-state conditions (1 *M* concentrations, 1 bar pressures, 298 K):

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

To simplify the collection and sharing of potential data for half-reactions, the scientific community has designated one particular half-cell to serve as a universal reference for cell potential measurements, assigning it a potential of exactly 0 V. This half-cell is the **standard hydrogen electrode (SHE)** and it is based on half-reaction below:

$$2\mathrm{H}^+(aq) + 2\mathrm{e}^- \longrightarrow \mathrm{H}_2(g)$$

A typical SHE contains an inert platinum electrode immersed in precisely 1 *M* aqueous H^+ and a stream of bubbling H_2 gas at 1 bar pressure, all maintained at a temperature of 298 K (see **Figure 16.5**).

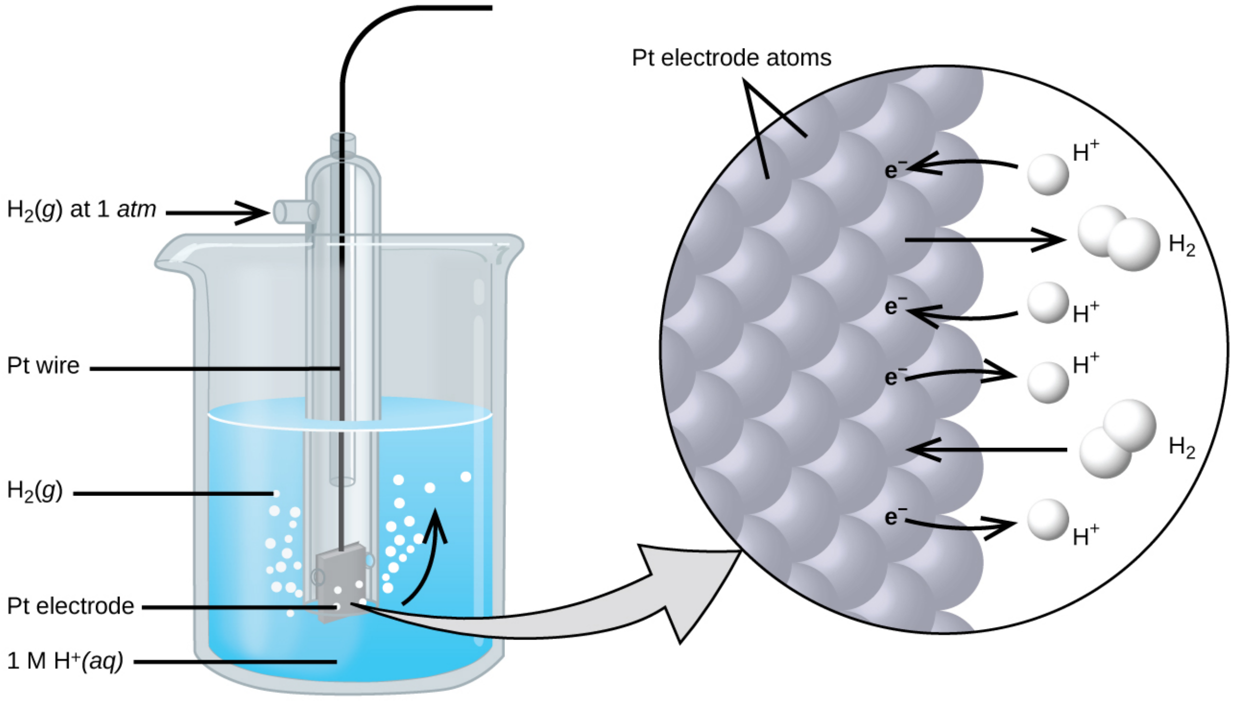


Figure 16.5 A standard hydrogen electrode (SHE).

The assigned potential of the SHE permits the definition of a conveniently measured potential for a single half-cell. The **electrode potential (E_X)** for a half-cell *X* is defined as *the potential measured for a cell comprised of X acting as cathode and the SHE acting as anode*:

$$E_{cell} = E_X - E_{SHE}$$
$$E_{SHE} = 0\text{ V (defined)}$$
$$E_{cell} = E_X$$

When the half-cell *X* is under standard-state conditions, its potential is the **standard electrode potential, $E°_X$**. Since the definition of cell potential requires the half-cells function as cathodes, these potentials are sometimes called *standard reduction potentials*.

This approach to measuring electrode potentials is illustrated in **Figure 16.6**, which depicts a cell comprised of an SHE connected to a copper(II)/copper(0) half-cell under standard-state conditions. A voltmeter in the external circuit allows measurement of the potential difference between the two half-cells. Since the Cu half-cell is designated as the cathode in the definition of cell potential, it is connected to the red (positive) input of the voltmeter, while the designated SHE anode is connected to the black (negative) input. These connections insure that the sign of the measured potential will be consistent with the sign conventions of electrochemistry per the various definitions discussed above. A cell potential of +0.337 V is measured, and so

$$E^\circ_{cell} = E^\circ_{Cu} = +0.337\text{ V}$$

Tabulations of E° values for other half-cells measured in a similar fashion are available as reference literature to permit calculations of cell potentials and the prediction of the spontaneity of redox processes.

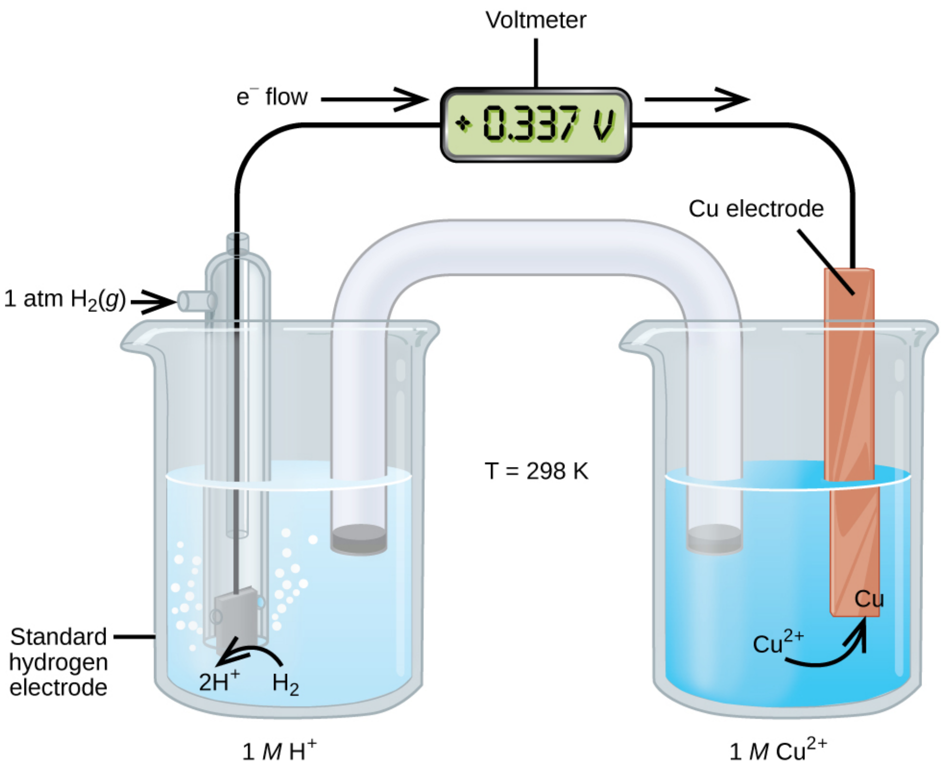


Figure 16.6 A cell permitting experimental measurement of the standard electrode potential for the half-reaction $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Table 16.1 provides a listing of standard electrode potentials for a selection of half-reactions in numerical order, and a more extensive alphabetical listing is given in **Appendix L**.

Selected Standard Reduction Potentials at 25 °C

Half-Reaction	*E*° (V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.866
$PbO_2(s) + SO_4{}^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$	+1.69
$MnO_4{}^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.507
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.498
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.35827
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	+1.229
$Pt^{2+}(aq) + 2e^- \longrightarrow Pt(s)$	+1.20
$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$	+1.0873
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.7996

Table 16.1

Selected Standard Reduction Potentials at 25 °C

Half-Reaction	*E*° (V)
$Hg_2{}^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.7973
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771
$MnO_4{}^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.558
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.5355
$NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq)$	+0.26808
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22233
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.151
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.1262
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.1375
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.257
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4{}^{2-}(aq)$	−0.3505
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.4030
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.447
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.744
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.185
$Zn(OH)_2(s) + 2e^- \longrightarrow Zn(s) + 2OH^-(aq)$	−1.245
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.7618
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.662
$Mg^{2}(aq) + 2e^- \longrightarrow Mg(s)$	−2.372
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.868

Table 16.1

Selected Standard Reduction Potentials at 25 °C

Half-Reaction	*E*° (V)
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.912
$K^+(aq) + e^- \longrightarrow K(s)$	−2.931
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.04

Table 16.1

Example 16.4

Calculating Standard Cell Potentials

What is the standard potential of the galvanic cell shown in **Figure 16.3**?

Solution

The cell in **Figure 16.3** is galvanic, the spontaneous cell reaction involving oxidation of its copper anode and reduction of silver(I) ions at its silver cathode:

cell reaction: $Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$
anode half-reaction: $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$
cathode half-reaction: $2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$

The standard cell potential computed as

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{\text{Ag}} - E^\circ_{\text{Cu}} \\ &= 0.7996\text{ V} - 0.34\text{ V} \\ &= +0.46\text{ V} \end{aligned}$$

Check Your Learning

What is the standard cell potential expected if the silver cathode half-cell in **Figure 16.3** is replaced with a lead half-cell: $Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$?

Answer: −0. 47 V

Intrepreting Electrode and Cell Potentials

Thinking carefully about the definitions of cell and electrode potentials and the observations of spontaneous redox change presented thus far, a significant relation is noted. The previous section described the spontaneous oxidation of copper by aqueous silver(I) ions, but no observed reaction with aqueous lead(II) ions. Results of the calculations in **Example 16.4** have just shown *the spontaneous process is described by a positive cell potential* while *the nonspontaneous process exhibits a negative cell potential*. And so, with regard to the relative effectiveness ("strength") with which aqueous Ag^+ and Pb^{2+} ions oxidize Cu under standard conditions, *the stronger oxidant is the one exhibiting the greater standard electrode potential, E°*. Since by convention electrode potentials are for reduction processes, an increased value of *E*° corresponds to an increased driving force behind the reduction of the species (hence increased effectiveness of its action as an *oxidizing agent* on some other species). Negative values for electrode potentials are simply a consequence of assigning a value of 0 V to the SHE, indicating the reactant of the half-reaction is a weaker oxidant than aqueous hydrogen ions.

Applying this logic to the numerically ordered listing of standard electrode potentials in **Table 16.1** shows this listing to be likewise in order of the oxidizing strength of the half-reaction's reactant species, decreasing from strongest oxidant (most positive $E°$) to weakest oxidant (most negative $E°$). Predictions regarding the spontaneity of redox reactions under standard state conditions can then be easily made by simply comparing the relative positions of their table entries. By definition, $E°_{\text{cell}}$ is positive when $E°_{\text{cathode}} > E°_{\text{anode}}$, and so any redox reaction in which the oxidant's entry is above the reductant's entry is predicted to be spontaneous.

Reconsideration of the two redox reactions in **Example 16.4** provides support for this fact. The entry for the silver(I)/silver(0) half-reaction is above that for the copper(II)/copper(0) half-reaction, and so the oxidation of Cu by Ag^+ is predicted to be spontaneous ($E°_{\text{cathode}} > E°_{\text{anode}}$ and so $E°_{\text{cell}} > 0$). Conversely, the entry for the lead(II)/lead(0) half-cell is beneath that for copper(II)/copper(0), and the oxidation of Cu by Pb^{2+} is nonspontaneous ($E°_{\text{cathode}} < E°_{\text{anode}}$ and so $E°_{\text{cell}} < 0$).

Recalling the chapter on thermodynamics, the spontaneities of the forward and reverse reactions of a reversible process show a reciprocal relationship: if a process is spontaneous in one direction, it is non-spontaneous in the opposite direction. As an indicator of spontaneity for redox reactions, the potential of a cell reaction shows a consequential relationship in its arithmetic sign. The spontaneous oxidation of copper by lead(II) ions is *not* observed,

$$\text{Cu}(s) + \text{Pb}^{2+}(aq) \longrightarrow \text{Cu}^{2+}(aq) + \text{Pb}(s) E^{\circ}_{\ forward} = -0.47\text{ V (negative, non-spontaneous)}$$

and so the reverse reaction, the oxidation of lead by copper(II) ions, is predicted to occur spontaneously:

$$\text{Pb}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Pb}^{2+}(aq) + \text{Cu}(s) E^{\circ}_{\ forward} = +0.47\text{ V (positive, spontaneous)}$$

Note that reversing the direction of a redox reaction effectively interchanges the identities of the cathode and anode half-reactions, and so the cell potential is calculated from electrode potentials in the reverse subtraction order than that for the forward reaction. In practice, a voltmeter would report a potential of −0.47 V with its red and black inputs connected to the Pb and Cu electrodes, respectively. If the inputs were swapped, the reported voltage would be +0.47 V.

Example 16.5

Predicting Redox Spontaneity

Are aqueous iron(II) ions predicted to spontaneously oxidize elemental chromium under standard state conditions? Assume the half-reactions to be those available in **Table 16.1**.

Solution

Referring to the tabulated half-reactions, the redox reaction in question can be represented by the equations below:

$$\text{Cr}(s) + \text{Fe}^{2+}(aq) \longrightarrow \text{Cr}^{3+}(aq) + \text{Fe}(s)$$

The entry for the putative oxidant, Fe^{2+}, appears *above* the entry for the reductant, Cr, and so a spontaneous reaction is predicted per the quick approach described above. Supporting this predication by calculating the standard cell potential for this reaction gives

$$\begin{aligned} \text{E}^{\circ}_{\ \text{cell}} &= \text{E}^{\circ}_{\ \text{cathode}} - \text{E}^{\circ}_{\ \text{anode}} \\ &= \text{E}^{\circ}_{\ \text{Fe(II)}} - \text{E}^{\circ}_{\ \text{Cr}} \\ &= -0.447\text{ V} - -0.774\text{ V} = +0.297\text{ V} \end{aligned}$$

The positive value for the standard cell potential indicates the process is spontaneous under standard state conditions.

Check Your Learning

Use the data in **Table 16.1** to predict the spontaneity of the oxidation of bromide ion by molecular iodine under standard state conditions, supporting the prediction by calculating the standard cell potential for the reaction. Repeat for the oxidation of iodide ion by molecular bromine.

Answer:

$$I_2(s) + 2Br^-(aq) \longrightarrow 2I^-(aq) + Br_2(l) \qquad E^\circ_{\text{cell}} = +0.5518 \text{ V (spontaneous)}$$

$$Br_2(s) + 2I^-(aq) \longrightarrow 2Br^-(aq) + I_2(l) \qquad E^\circ_{\text{cell}} = -0.5518 \text{ V (nonspontaneous)}$$

16.4 Potential, Free Energy, and Equilibrium

By the end of this section, you will be able to:

- Explain the relations between potential, free energy change, and equilibrium constants
- Perform calculations involving the relations between cell potentials, free energy changes, and equilibrium
- Use the Nernst equation to determine cell potentials under nonstandard conditions

So far in this chapter, the relationship between the cell potential and reaction *spontaneity* has been described, suggesting a link to the free energy change for the reaction (see chapter on thermodynamics). The interpretation of potentials as measures of oxidant *strength* was presented, bringing to mind similar measures of acid-base strength as reflected in equilibrium constants (see the chapter on acid-base equilibria). This section provides a summary of the relationships between potential and the related thermodynamic properties ΔG and K.

E° and ΔG°

The standard free energy change of a process, $\Delta G°$, was defined in a previous chapter as the maximum work that could be performed by a system, w_{max}. In the case of a redox reaction taking place within a galvanic cell under standard state conditions, essentially all the work is associated with transferring the electrons from reductant-to-oxidant, w_{elec}:

$$\Delta G° = w_{\text{max}} = w_{\text{elec}}$$

The work associated with transferring electrons is determined by the total amount of charge (coulombs) transferred and the cell potential:

$$\begin{aligned} \Delta G° = w_{\text{elec}} &= -nFE^\circ_{\text{cell}} \\ \Delta G° &= -nFE^\circ_{\text{cell}} \end{aligned}$$

where n is the number of moles of electrons transferred, F is **Faraday's constant**, and $E°_{\text{cell}}$ is the standard cell potential. The relation between free energy change and standard cell potential confirms the sign conventions and spontaneity criteria previously discussed for both of these properties: spontaneous redox reactions exhibit positive potentials and negative free energy changes.

E° and K

Combining a previously derived relation between ΔG° and K (see the chapter on thermodynamics) and the equation above relating ΔG° and $E°_{\text{cell}}$ yields the following:

$$\begin{aligned} \Delta G° &= -RT \ln K = -nFE^\circ_{\text{cell}} \\ E^\circ_{\text{cell}} &= \left(\frac{RT}{nF}\right) \ln K \end{aligned}$$

This equation indicates redox reactions with large (positive) standard cell potentials will proceed far towards completion, reaching equilibrium when the majority of reactant has been converted to product. A summary of the relations between $E°$, $\Delta G°$ and K is depicted in **Figure 16.7**, and a table correlating reaction spontaneity to values of these properties is provided in **Table 16.2**.

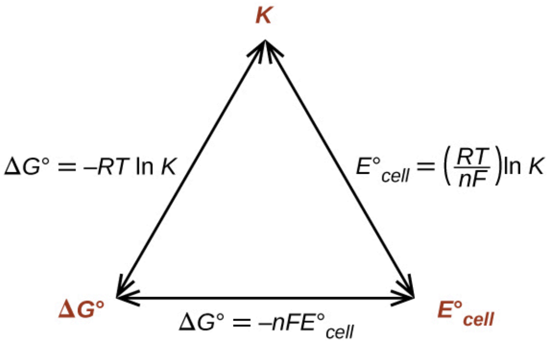


Figure 16.7 Graphic depicting the relation between three important thermodynamic properties.

K	$\Delta G°$	$E°_{\text{cell}}$	
> 1	< 0	> 0	Reaction is spontaneous under standard conditions Products more abundant at equilibrium
< 1	> 0	< 0	Reaction is non-spontaneous under standard conditions Reactants more abundant at equilibrium
= 1	= 0	= 0	Reaction is at equilibrium under standard conditions Reactants and products equally abundant

Table 16.2

Example 16.6

Equilibrium Constants, Standard Cell Potentials, and Standard Free Energy Changes

Use data from **Appendix L** to calculate the standard cell potential, standard free energy change, and equilibrium constant for the following reaction at 25 °C. Comment on the spontaneity of the forward reaction and the composition of an equilibrium mixture of reactants and products.

$$2\text{Ag}^+(aq) + \text{Fe}(s) \rightleftharpoons 2\text{Ag}(s) + \text{Fe}^{2+}(aq)$$

Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in **Appendix L**.

$$\begin{array}{llrcl}
\text{anode (oxidation):} & \text{Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 2\text{e}^- & E°_{\text{Fe}^{2+}/\text{Fe}} & = & -0.447\text{ V} \\
\text{cathode (reduction):} & 2 \times (\text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)) & E°_{\text{Ag}^+/\text{Ag}} & = & 0.7996\text{ V} \\
 & E°_{\text{cell}} = E°_{\text{cathode}} - E°_{\text{anode}} = & E°_{\text{Ag}^+/\text{Ag}} - E°_{\text{Fe}^{2+}/\text{Fe}} & = & +1.247\text{ V}
\end{array}$$

With $n = 2$, the equilibrium constant is then

$$\begin{aligned} E^\circ_\text{cell} &= \frac{0.0592\ \text{V}}{n}\log K \\ K &= 10^{n \times E^\circ_\text{cell}/0.0592\ \text{V}} \\ K &= 10^{2 \times 1.247\ \text{V}/0.0592\ \text{V}} \\ K &= 10^{42.128} \\ K &= 1.3 \times 10^{42} \end{aligned}$$

The standard free energy is then

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ_\text{cell} \\ \Delta G^\circ &= -2 \times 96{,}485\ \frac{\text{C}}{\text{mol}} \times 1.247\ \frac{\text{J}}{\text{C}} = -240.6\ \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

The reaction is spontaneous, as indicated by a negative free energy change and a positive cell potential. The K value is very large, indicating the reaction proceeds to near completion to yield an equilibrium mixture containing mostly products.

Check Your Learning

What is the standard free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?

$$\text{Sn}(s) + 2\text{Cu}^{2+}(aq) \rightleftharpoons \text{Sn}^{2+}(aq) + 2\text{Cu}^{+}(aq)$$

Answer: Spontaneous; $n = 2$; $E^\circ_\text{cell} = +0.291$ V; $\Delta G^\circ = -56.2\ \frac{\text{kJ}}{\text{mol}}$; $K = 6.8 \times 10^{9}$.

Potentials at Nonstandard Conditions: The Nernst Equation

Most of the redox processes that interest science and society do not occur under standard state conditions, and so the potentials of these systems under nonstandard conditions are a property worthy of attention. Having established the relationship between potential and free energy change in this section, the previously discussed relation between free energy change and reaction mixture composition can be used for this purpose.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Notice the reaction quotient, Q, appears in this equation, making the free energy change dependent upon the composition of the reaction mixture. Substituting the equation relating free energy change to cell potential yields the **Nernst equation**:

$$-nFE_\text{cell} = -nFE^\circ_\text{cell} + RT \ln Q$$

$$E_\text{cell} = E^\circ_\text{cell} - \frac{RT}{nF}\ln Q$$

This equation describes how the potential of a redox system (such as a galvanic cell) varies from its standard state value, specifically, showing it to be a function of the number of electrons transferred, n, the temperature, T, and the reaction mixture composition as reflected in Q. A convenient form of the Nernst equation for most work is one in which values for the fundamental constants (R and F) and a factor converting from natural to base-10 logarithms have been included:

$$E_\text{cell} = -E^\circ_\text{cell} - \frac{0.0592\text{V}}{n}\ln Q$$

Example 16.7

Predicting Redox Spontaneity Under Nonstandard Conditions

Use the Nernst equation to predict the spontaneity of the redox reaction shown below.

$$\text{Co}(s) + \text{Fe}^{2+}(aq,\ 1.94\ M) \longrightarrow \text{Co}^{2+}(aq, 0.15\ M) + \text{Fe}(s)$$

Solution

Collecting information from **Appendix L** and the problem,

$$\begin{array}{lllll} \text{Anode (oxidation):} & \mathrm{Co}(s) \longrightarrow \mathrm{Co}^{2+}(aq) + 2\mathrm{e}^- & E^\circ_{\mathrm{Co}^{2+}/\mathrm{Co}} & = & -0.28\ \mathrm{V} \\ \text{Cathode (reduction):} & \mathrm{Fe}^{2+}(aq) + 2\mathrm{e}^- \longrightarrow \mathrm{Fe}(s) & E^\circ_{\mathrm{Fe}^{2+}/\mathrm{Fe}} & = & -0.447\ \mathrm{V} \\ & E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{cathode}} - E^\circ_{\mathrm{anode}} = & -0.447\ \mathrm{V} - (-0.28\ \mathrm{V}) & = & -0.17\ \mathrm{V} \end{array}$$

Notice the negative value of the standard cell potential indicates the process is not spontaneous under standard conditions. Substitution of the Nernst equation terms for the nonstandard conditions yields:

$$\begin{aligned} Q &= \frac{[\mathrm{Co}^{2+}]}{[\mathrm{Fe}^{2+}]} = \frac{0.15\ M}{1.94\ M} = 0.077 \\ E_{\mathrm{cell}} &= E^\circ_{\mathrm{cell}} - \frac{0.0592\ \mathrm{V}}{n} \log Q \\ E_{\mathrm{cell}} &= -0.17\ \mathrm{V} - \frac{0.0592\ \mathrm{V}}{2} \log 0.077 \\ E_{\mathrm{cell}} &= -0.17\ \mathrm{V} + 0.033\ \mathrm{V} = -0.014\ \mathrm{V} \end{aligned}$$

The cell potential remains negative (slightly) under the specified conditions, and so the reaction remains nonspontaneous.

Check Your Learning

For the cell schematic below, identify values for n and Q, and calculate the cell potential, E_{cell}.

$$\mathrm{Al}(s) \mid \mathrm{Al}^{3+}(aq,\ 0.15\ M) \parallel \mathrm{Cu}^{2+}(aq,\ 0.025\ M) \mid \mathrm{Cu}(s)$$

Answer: $n = 6$; $Q = 1440$; $E_{\mathrm{cell}} = +1.97$ V, spontaneous.

A **concentration cell** is constructed by connecting two nearly identical half-cells, each based on the same half-reaction and using the same electrode, varying only in the concentration of one redox species. The potential of a concentration cell, therefore, is determined only by the difference in concentration of the chosen redox species. The example problem below illustrates the use of the Nernst equation in calculations involving concentration cells.

Example 16.8

Concentration Cells

What is the cell potential of the concentration cell described by

$$\mathrm{Zn}(s) \mid \mathrm{Zn}^{2+}(aq, 0.10\ M) \parallel \mathrm{Zn}^{2+}(aq, 0.50\ M) \mid \mathrm{Zn}(s)$$

Solution

From the information given:

$$\begin{array}{lllll} \text{Anode:} & \mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq, 0.10\ M) + 2\mathrm{e}^- & E^\circ_{\mathrm{anode}} & = & -0.7618\ \mathrm{V} \\ \text{Cathode:} & \mathrm{Zn}^{2+}(aq, 0.50\ M) + 2\mathrm{e}^- \longrightarrow \mathrm{Zn}(s) & E^\circ_{\mathrm{cathode}} & = & -0.7618\ \mathrm{V} \\ \hline \text{Overall:} & \mathrm{Zn}^{2+}(aq, 0.50\ M) \longrightarrow \mathrm{Zn}^{2+}(aq, 0.10\ M) & E^\circ_{\mathrm{cell}} & = & 0.000\ \mathrm{V} \end{array}$$

Substituting into the Nernst equation,

$$E_{\mathrm{cell}} = 0.000\ \mathrm{V} - \frac{0.0592\ \mathrm{V}}{2} \log \frac{0.10}{0.50} = +0.021\ \mathrm{V}$$

The positive value for cell potential indicates the overall cell reaction (see above) is spontaneous. This spontaneous reaction is one in which the zinc ion concentration in the cathode falls (it is reduced to elemental zinc) while that in the anode rises (it is produced by oxidation of the zinc anode). A greater driving force for zinc reduction is present in the cathode, where the zinc(II) ion concentration is greater ($E_{\text{cathode}} > E_{\text{anode}}$).

Check Your Learning

The concentration cell above was allowed to operate until the cell reaction reached equilibrium. What are the cell potential and the concentrations of zinc(II) in each half-cell for the cell now?

Answer: $E_{\text{cell}} = 0.000$ V; $[\text{Zn}^{2+}]_{\text{cathode}} = [\text{Zn}^{2+}]_{\text{anode}} = 0.30\ M$

16.5 Batteries and Fuel Cells

By the end of this section, you will be able to:

- Describe the electrochemistry associated with several common batteries
- Distinguish the operation of a fuel cell from that of a battery

There are many technological products associated with the past two centuries of electrochemistry research, none more immediately obvious than the battery. A **battery** is a galvanic cell that has been specially designed and constructed in a way that best suits its intended use a source of electrical power for specific applications. Among the first successful batteries was the *Daniell cell*, which relied on the spontaneous oxidation of zinc by copper(II) ions (Figure 16.8):

$$\text{Zn}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$$

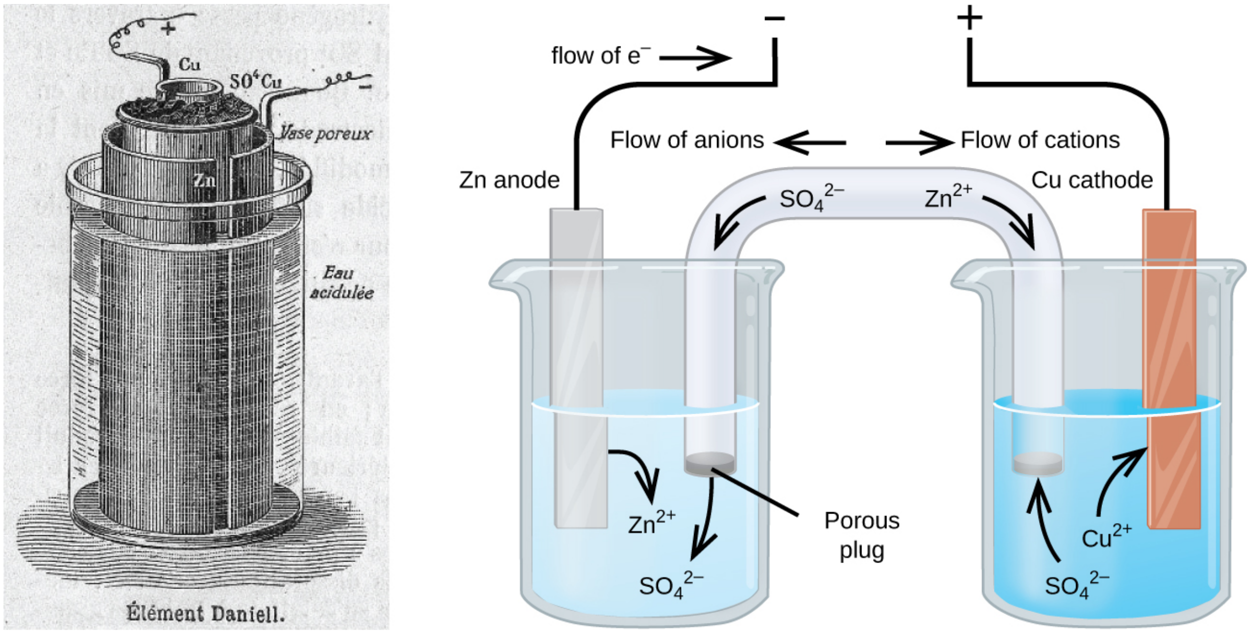


Figure 16.8 Illustration of a Daniell cell taken from a 1904 journal publication (left) along with a simplified illustration depicting the electrochemistry of the cell (right). The 1904 design used a porous clay pot to both contain one of the half-cell’s content and to serve as a salt bridge to the other half-cell.

Modern batteries exist in a multitude of forms to accommodate various applications, from tiny button batteries that provide the modest power needs of a wristwatch to the very large batteries used to supply backup energy to municipal power grids. Some batteries are designed for single-use applications and cannot be recharged (**primary cells**), while others are based on conveniently reversible cell reactions that allow recharging by an external power source (**secondary cells**). This section will provide a summary of the basic electrochemical aspects of several batteries familiar to most consumers, and will introduce a related electrochemical device called a *fuel cell* that can offer improved performance in certain applications.

Link to Learning

Visit this site (http://openstaxcollege.org/l/16batteries) to learn more about batteries.

Single-Use Batteries

A common primary battery is the **dry cell**, which uses a zinc can as both container and anode ("–" terminal) and a graphite rod as the cathode ("+" terminal). The Zn can is filled with an electrolyte paste containing manganese(IV) oxide, zinc(II) chloride, ammonium chloride, and water. A graphite rod is immersed in the electrolyte paste to complete the cell. The spontaneous cell reaction involves the oxidation of zinc:

$$\text{anode reaction: } \text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + 2\text{e}^-$$

and the reduction of manganese(IV)

$$\text{reduction reaction: } 2\text{MnO}_2(s) + 2\text{NH}_4\text{Cl}(aq) + 2\,\text{e}^- \longrightarrow \text{Mn}_2\text{O}_3(s) + 2\text{NH}_3(aq) + \text{H}_2\text{O}(l) + 2\text{Cl}^-$$

which together yield the cell reaction:

$$\text{cell reaction: } 2\text{MnO}_2(s) + 2\text{NH}_4\text{Cl}(aq) + \text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + \text{Mn}_2\text{O}_3(s) + 2\text{NH}_3(aq) + \text{H}_2\text{O}(l) + 2\text{Cl}^- \quad E_\text{cell} \sim 1.5\text{ V}$$

The voltage (*cell potential*) of a dry cell is approximately 1.5 V. Dry cells are available in various sizes (e.g., D, C, AA, AAA). All sizes of dry cells comprise the same components, and so they exhibit the same voltage, but larger cells contain greater amounts of the redox reactants and therefore are capable of transferring correspondingly greater amounts of charge. Like other galvanic cells, dry cells may be connected in series to yield batteries with greater voltage outputs, if needed.

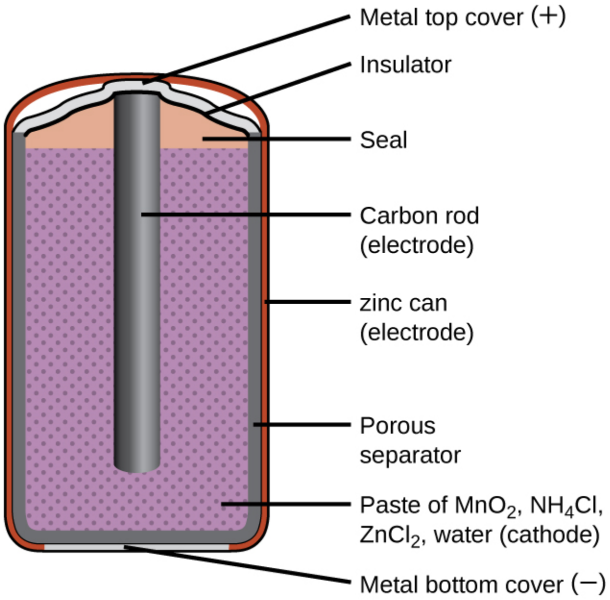


Figure 16.9 A schematic diagram shows a typical dry cell.

Link to Learning

Visit this site (http://openstaxcollege.org/l/16zinccarbon) to learn more about zinc-carbon batteries.

Alkaline batteries (Figure 16.10) were developed in the 1950s to improve on the performance of the dry cell, and they were designed around the same redox couples. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide. The reactions are

$$\begin{array}{lll}
\text{anode:} & \text{Zn}(s) + 2\text{OH}^-(aq) \longrightarrow \text{ZnO}(s) + \text{H}_2\text{O}(l) + 2\text{e}^- & \\
\text{cathode:} & 2\text{MnO}_2(s) + \text{H}_2\text{O}(l) + 2\text{e}^- \longrightarrow \text{Mn}_2\text{O}_3(s) + 2\text{OH}^-(aq) & \\
\hline
\text{cell:} & \text{Zn}(s) + 2\text{MnO}_2(s) \longrightarrow \text{ZnO}(s) + \text{Mn}_2\text{O}_3(s) & E_\text{cell} = +1.43\text{ V}
\end{array}$$

An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size. Alkaline batteries are prone to leaking potassium hydroxide, so they should be removed from devices for long-term storage. While some alkaline batteries are rechargeable, most are not. Attempts to recharge an alkaline battery that is not rechargeable often leads to rupture of the battery and leakage of the potassium hydroxide electrolyte.

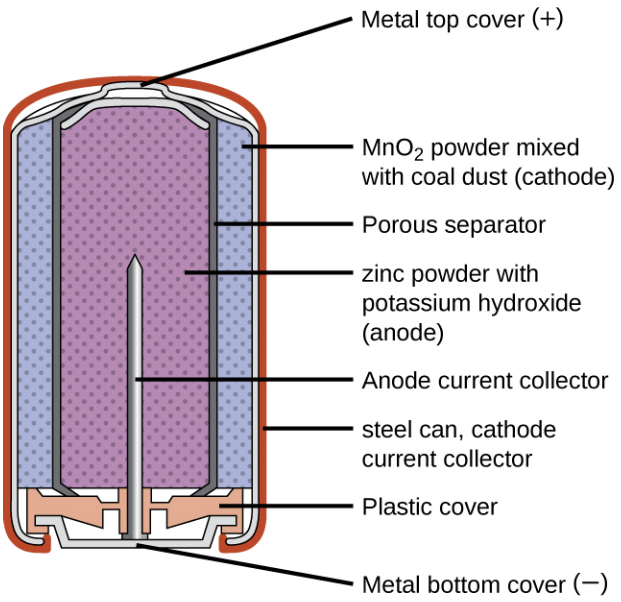


Figure 16.10 Alkaline batteries were designed as improved replacements for zinc-carbon (dry cell) batteries.

Link to Learning

Visit this site (http://openstaxcollege.org/l/16alkaline) to learn more about alkaline batteries.

Rechargeable (Secondary) Batteries

Nickel-cadmium, or NiCd, batteries (Figure 16.11) consist of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrode. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a "jelly-roll" design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery. The reactions are

$$\begin{array}{ll}\text{anode:} & \text{Cd}(s) + 2\text{OH}^-(aq) \longrightarrow \text{Cd(OH)}_2(s) + 2\text{e}^- \\ \text{cathode:} & \text{NiO}_2(s) + 2\text{H}_2\text{O}(l) + 2\text{e}^- \longrightarrow \text{Ni(OH)}_2(s) + 2\text{OH}^-(aq) \\ \hline \text{cell:} & \text{Cd}(s) + \text{NiO}_2(s) + 2\text{H}_2\text{O}(l) \longrightarrow \text{Cd(OH)}_2(s) + \text{Ni(OH)}_2(s) \qquad E_\text{cell} \sim 1.2\text{ V}\end{array}$$

When properly treated, a NiCd battery can be recharged about 1000 times. Cadmium is a toxic heavy metal so NiCd batteries should never be ruptured or incinerated, and they should be disposed of in accordance with relevant toxic waste guidelines.

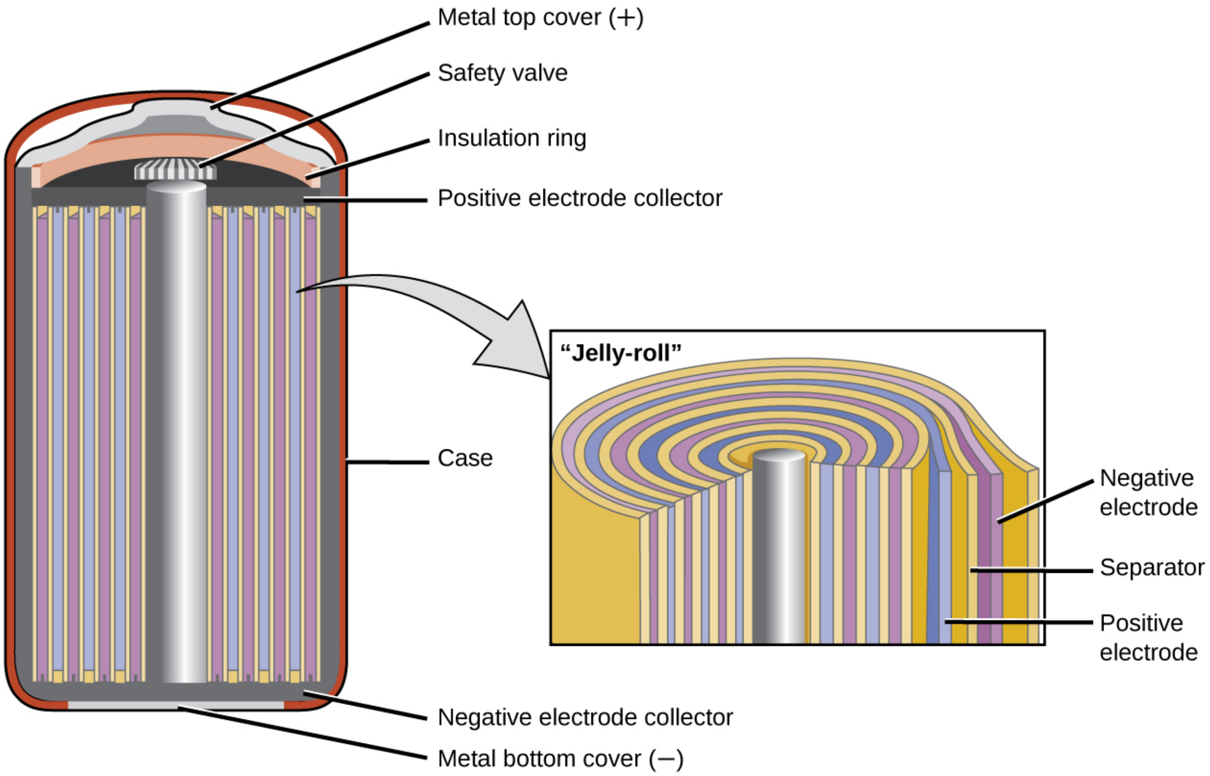


Figure 16.11 NiCd batteries use a "jelly-roll" design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery.

Link to Learning

Visit this site (http://openstaxcollege.org/l/16NiCdrecharge) for more information about nickel cadmium rechargeable batteries.

Lithium ion batteries (Figure 16.12) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

$$\begin{array}{lrcl} \text{anode:} & \mathrm{LiCoO_2} & \rightleftharpoons & \mathrm{Li_{1-\mathit{x}}CoO_2} + x\,\mathrm{Li^+} + x\,\mathrm{e^-} \\ \text{cathode:} & x\,\mathrm{Li^+} + x\,\mathrm{e^-} + x\,\mathrm{C_6} & \rightleftharpoons & x\,\mathrm{LiC_6} \\ \hline \text{cell:} & \mathrm{LiCoO_2} + x\,\mathrm{C_6} & \rightleftharpoons & \mathrm{Li_{1-\mathit{x}}CoO_2} + x\,\mathrm{LiC_6} \qquad E_\mathrm{cell} \sim 3.7\ \mathrm{V} \end{array}$$

The variable stoichiometry of the cell reaction leads to variation in cell voltages, but for typical conditions, x is usually no more than 0.5 and the cell voltage is approximately 3.7 V. Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

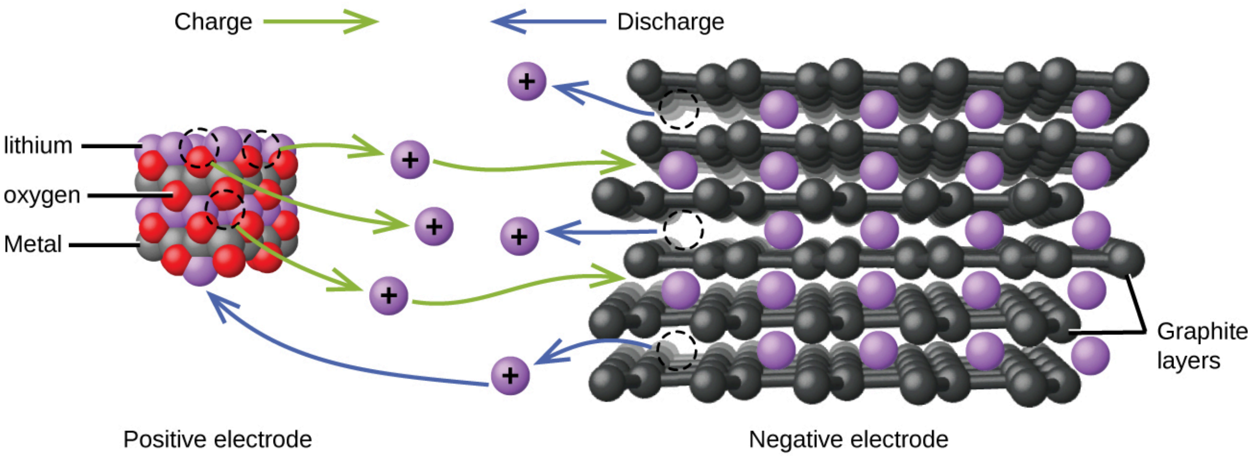


Figure 16.12 In a lithium ion battery, charge flows as the lithium ions are transferred between the anode and cathode.

Link to Learning

Visit this site (http://openstaxcollege.org/l/16lithiumion) for more information about lithium ion batteries.

The **lead acid battery** (Figure 16.13) is the type of secondary battery commonly used in automobiles. It is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are

$$\begin{array}{ll} \text{anode:} & Pb(s) + HSO_4{}^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2e^- \\ \text{cathode:} & PbO_2(s) + HSO_4{}^-(aq) + 3H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l) \\ \hline \text{cell:} & Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l) \qquad E_\text{cell} \sim 2\text{ V} \end{array}$$

Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, $H_2SO_4(aq)$, but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.

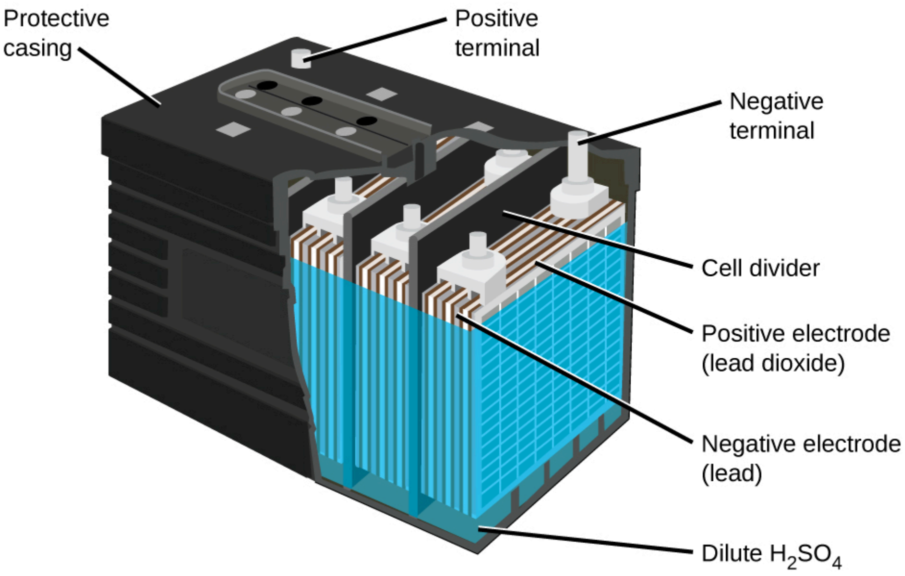


Figure 16.13 The lead acid battery in your automobile consists of six cells connected in series to give 12 V.

Link to Learning

Visit this site (http://openstaxcollege.org/l/16leadacid) for more information about lead acid batteries.

Fuel Cells

A **fuel cell** is a galvanic cell that uses traditional combustive fuels, most often hydrogen or methane, that are continuously fed into the cell along with an oxidant. (An alternative, but not very popular, name for a fuel cell is a *flow battery*.) Within the cell, fuel and oxidant undergo the same redox chemistry as when they are combusted, but via a catalyzed electrochemical that is significantly more efficient. For example, a typical hydrogen fuel cell uses graphite electrodes embedded with platinum-based catalysts to accelerate the two half-cell reactions:

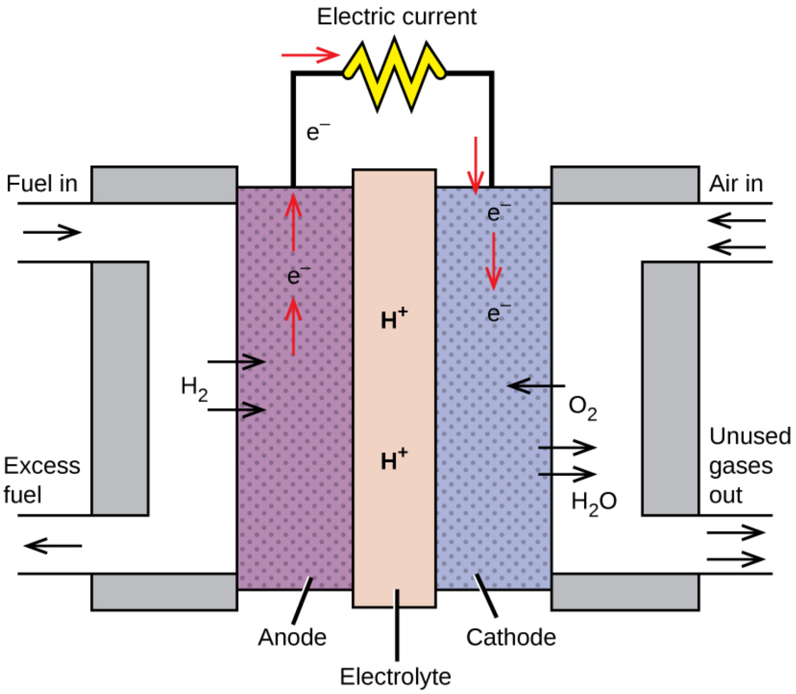


Figure 16.14 In this hydrogen fuel cell, oxygen from the air reacts with hydrogen, producing water and electricity.

$$\begin{array}{ll} \text{Anode:} & 2H_2(g) \longrightarrow 4H^+(aq) + 4e^- \\ \text{Cathode:} & O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(g) \\ \hline \text{Cell:} & 2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) \qquad E_{\text{cell}} \sim 1.2\text{ V} \end{array}$$

These types of fuel cells generally produce voltages of approximately 1.2 V. Compared to an internal combustion engine, the energy efficiency of a fuel cell using the same redox reaction is typically more than double (~20%–25% for an engine versus ~50%–75% for a fuel cell). Hydrogen fuel cells are commonly used on extended space missions, and prototypes for personal vehicles have been developed, though the technology remains relatively immature.

Link to Learning

Check out this link (http://openstaxcollege.org/l/16fuelcells) to learn more about fuel cells.

16.6 Corrosion

By the end of this section, you will be able to:

- Define corrosion
- List some of the methods used to prevent or slow corrosion

Corrosion is usually defined as the degradation of metals by a naturally occurring electrochemical process. The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper are all examples of corrosion. The total cost of corrosion remediation in the United States is significant, with estimates in excess of half a trillion dollars a year.

Chemistry in Everyday Life

Statue of Liberty: Changing Colors

The Statue of Liberty is a landmark every American recognizes. The Statue of Liberty is easily identified by its height, stance, and unique blue-green color (**Figure 16.15**). When this statue was first delivered from France, its appearance was not green. It was brown, the color of its copper "skin." So how did the Statue of Liberty change colors? The change in appearance was a direct result of corrosion. The copper that is the primary component of the statue slowly underwent oxidation from the air. The oxidation-reduction reactions of copper metal in the environment occur in several steps. Copper metal is oxidized to copper(I) oxide (Cu_2O), which is red, and then to copper(II) oxide, which is black

$$2\text{Cu}(s) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{Cu}_2\text{O}(s) \qquad \text{(red)}$$
$$\text{Cu}_2\text{O}(s) + \frac{1}{2}\text{O}_2(g) \longrightarrow 2\text{CuO}(s) \qquad \text{(black)}$$

Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, atmospheric sulfur trioxide, carbon dioxide, and water all reacted with the CuO

$$2\text{CuO}(s) + \text{CO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow \text{Cu}_2\text{CO}_3(\text{OH})_2(s) \qquad \text{(green)}$$
$$3\text{CuO}(s) + 2\text{CO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow \text{Cu}_2(\text{CO}_3)_2(\text{OH})_2(s) \qquad \text{(blue)}$$
$$4\text{CuO}(s) + \text{SO}_3(g) + 3\text{H}_2\text{O}(l) \longrightarrow \text{Cu}_4\text{SO}_4(\text{OH})_6(s) \qquad \text{(green)}$$

These three compounds are responsible for the characteristic blue-green patina seen on the Statue of Liberty (and other outdoor copper structures). Fortunately, formation of patina creates a protective layer on the copper surface, preventing further corrosion of the underlying copper. The formation of the protective layer is called *passivation*, a phenomenon discussed further in another chapter of this text.

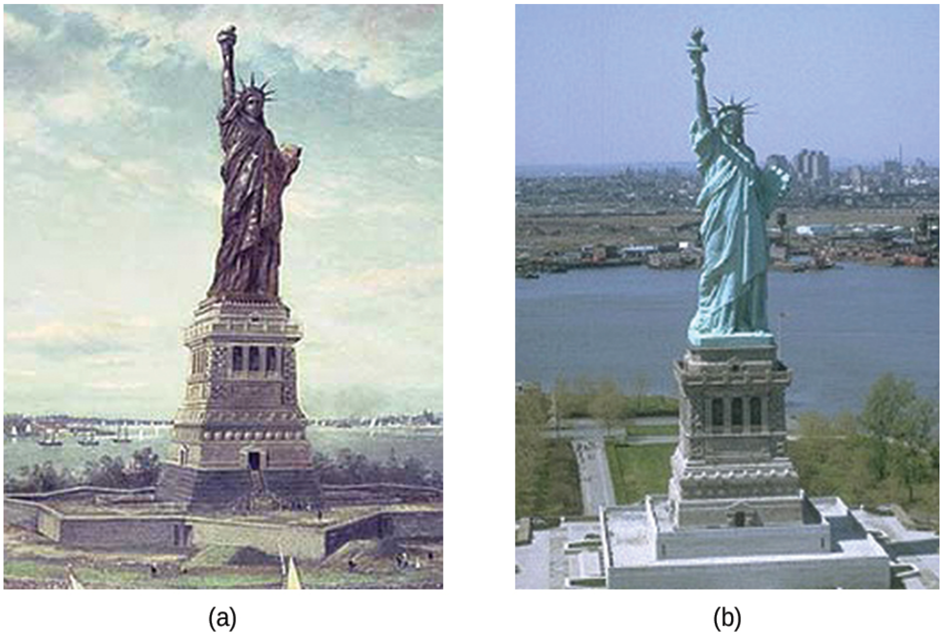


Figure 16.15 (a) The Statue of Liberty is covered with a copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today.

Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. Rust formation involves the creation of a galvanic cell at an iron surface, as illustrated in **Figure**

16.15. The relevant redox reactions are described by the following equations:

$$\begin{array}{llrl} \text{anode:} & \mathrm{Fe}(s) \longrightarrow \mathrm{Fe}^{2+}(aq) + 2\mathrm{e}^- & E^\circ_{\mathrm{Fe}^{2+}/\mathrm{Fe}} & = -0.44\ \mathrm{V} \\ \text{cathode:} & \mathrm{O}_2(g) + 4\mathrm{H}^+(aq) + 4\mathrm{e}^- \longrightarrow 2\mathrm{H}_2\mathrm{O}(l) & E^\circ_{\mathrm{O}_2/\mathrm{O}^2} & = +1.23\ \mathrm{V} \\ \text{overall:} & 2\mathrm{Fe}(s) + \mathrm{O}_2(g) + 4\mathrm{H}^+(aq) \longrightarrow 2\mathrm{Fe}^{2+}(aq) + 2\mathrm{H}_2\mathrm{O}(l) & E^\circ_{\text{cell}} & = +1.67\ \mathrm{V} \end{array}$$

Further reaction of the iron(II) product in humid air results in the production of an iron(III) oxide hydrate known as rust:

$$4\mathrm{Fe}^{2+}(aq) + \mathrm{O}_2(g) + (4 + 2x)\,\mathrm{H}_2\mathrm{O}(l) \longrightarrow 2\mathrm{Fe}_2\mathrm{O}_3{\cdot}x\mathrm{H}_2\mathrm{O}(s) + 8\mathrm{H}^+(aq)$$

The stoichiometry of the hydrate varies, as indicated by the use of x in the compound formula. Unlike the patina on copper, the formation of rust does not create a protective layer and so corrosion of the iron continues as the rust flakes off and exposes fresh iron to the atmosphere.

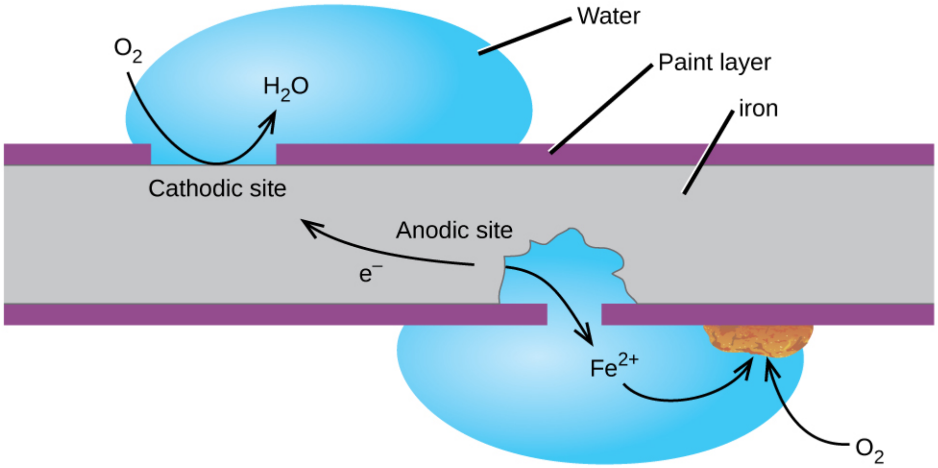


Figure 16.16 Corrosion can occur when a painted iron or steel surface is exposed to the environment by a scratch through the paint. A galvanic cell results that may be approximated by the simplified cell schematic Fe(*s*) | Fe^{2+}(*aq*) ||O_2(*aq*), H_2O(*l*) | Fe(*s*).

One way to keep iron from corroding is to keep it painted. The layer of paint prevents the water and oxygen necessary for rust formation from coming into contact with the iron. As long as the paint remains intact, the iron is protected from corrosion.

Other strategies include alloying the iron with other metals. For example, stainless steel is an alloy of iron containing a small amount of chromium. The chromium tends to collect near the surface, where it corrodes and forms a passivating an oxide layer that protects the iron.

Iron and other metals may also be protected from corrosion by **galvanization**, a process in which the metal to be protected is coated with a layer of a more readily oxidized metal, usually zinc. When the zinc layer is intact, it prevents air from contacting the underlying iron and thus prevents corrosion. If the zinc layer is breached by either corrosion or mechanical abrasion, the iron may still be protected from corrosion by a *cathodic protection* process, which is described in the next paragraph.

Another important way to protect metal is to make it the cathode in a galvanic cell. This is **cathodic protection** and can be used for metals other than just iron. For example, the rusting of underground iron storage tanks and pipes can be prevented or greatly reduced by connecting them to a more active metal such as zinc or magnesium (**Figure 16.17**). This is also used to protect the metal parts in water heaters. The more active metals (lower reduction potential) are called **sacrificial anodes** because as they get used up as they corrode (oxidize) at the anode. The metal being protected serves as the cathode for the reduction of oxygen in air, and so it simply serves to conduct (not react with) the electrons being transferred. When the anodes are properly monitored and periodically replaced, the useful lifetime of the iron storage tank can be greatly extended.

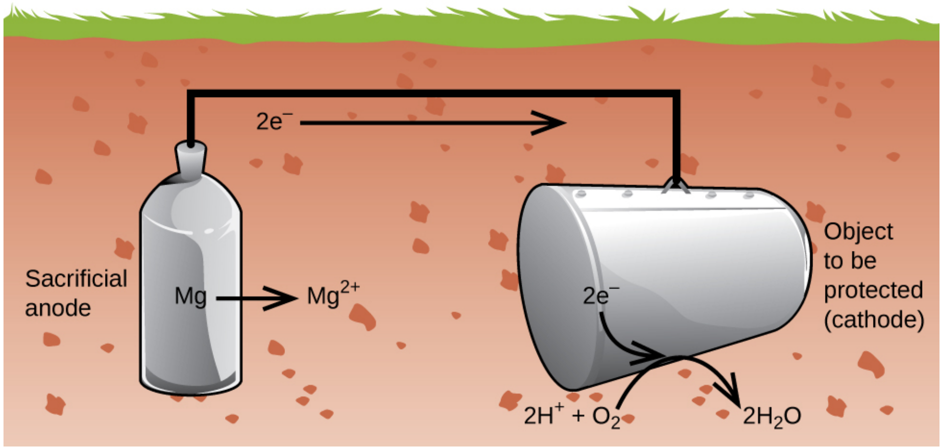


Figure 16.17 Cathodic protection is a useful approach to electrochemically preventing corrosion of underground storage tanks.

16.7 Electrolysis

By the end of this section you will be able to:

- Describe the process of electrolysis
- Compare the operation of electrolytic cells with that of galvanic cells
- Perform stoichiometric calculations for electrolytic processes

Electrochemical cells in which spontaneous redox reactions take place (*galvanic cells*) have been the topic of discussion so far in this chapter. In these cells, *electrical work is done by a redox system on its surroundings* as electrons produced by the redox reaction are transferred through an external circuit. This final section of the chapter will address an alternative scenario in which *an external circuit does work on a redox system* by imposing a voltage sufficient to drive an otherwise nonspontaneous reaction, a process known as **electrolysis**. A familiar example of electrolysis is recharging a battery, which involves use of an external power source to drive the spontaneous (discharge) cell reaction in the reverse direction, restoring to some extent the composition of the half-cells and the voltage of the battery. Perhaps less familiar is the use of electrolysis in the refinement of metallic ores, the manufacture of commodity chemicals, and the *electroplating* of metallic coatings on various products (e.g., jewelry, utensils, auto parts). To illustrate the essential concepts of electrolysis, a few specific processes will be considered.

The Electrolysis of Molten Sodium Chloride

Metallic sodium, Na, and chlorine gas, Cl_2, are used in numerous applications, and their industrial production relies on the large-scale electrolysis of molten sodium chloride, NaCl(*l*). The industrial process typically uses a *Downs cell* similar to the simplified illustration shown in **Figure 16.18**. The reactions associated with this process are:

$$\begin{array}{ll} \text{anode:} & 2\text{Cl}^-(l) \longrightarrow \text{Cl}_2(g) + 2\text{e}^- \\ \text{cathode:} & \text{Na}^+(l) + \text{e}^- \longrightarrow \text{Na}(l) \\ \hline \text{cell:} & 2\text{Na}^+(l) + 2\text{Cl}^-(l) \longrightarrow 2\text{Na}(l) + \text{Cl}_2(g) \end{array}$$

The cell potential for the above process is negative, indicating the reaction as written (decomposition of liquid NaCl) is not spontaneous. To force this reaction, *a positive potential of magnitude greater than the negative cell potential* must be applied to the cell.

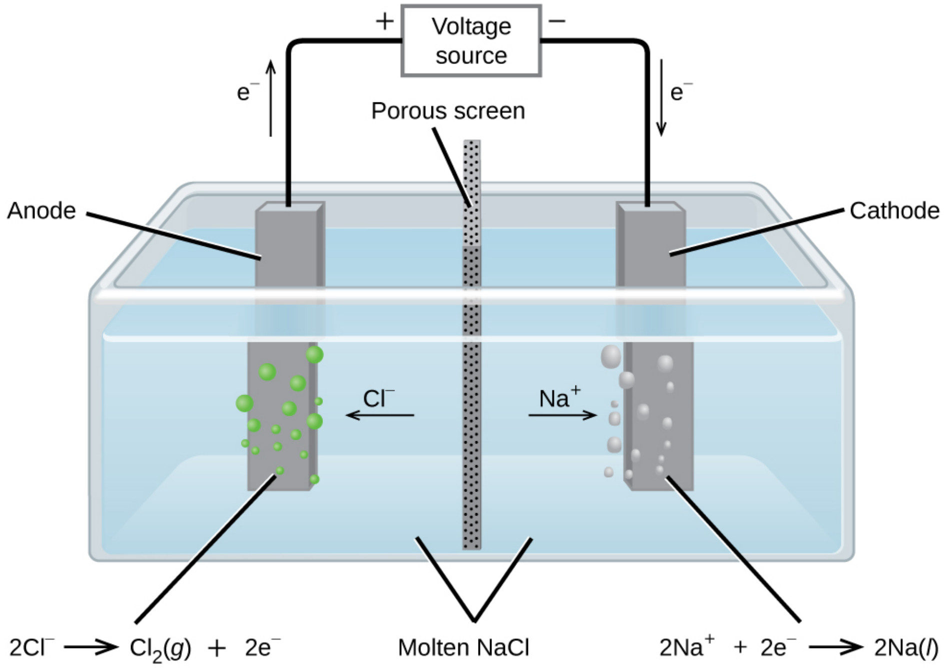


Figure 16.18 Cells of this sort (a cell for the electrolysis of molten sodium chloride) are used in the *Downs process* for production of sodium and chlorine, and they typically use iron cathodes and carbon anodes.

The Electrolysis of Water

Water may be electrolytically decomposed in a cell similar to the one illustrated in **Figure 16.19**. To improve electrical conductivity without introducing a different redox species, the hydrogen ion concentration of the water is typically increased by addition of a strong acid. The redox processes associated with this cell are

$$\begin{array}{llll} \text{anode:} & 2\text{H}_2\text{O}(l) \longrightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- & E^\circ_\text{anode} & = +1.229\text{ V} \\ \text{cathode:} & 2\text{H}^+(aq) + 2\text{e}^- \longrightarrow \text{H}_2(g) & E^\circ_\text{cathode} & = 0\text{ V} \\ \hline \text{cell:} & 2\text{H}_2\text{O}(l) \longrightarrow 2\text{H}_2(g) + \text{O}_2(g) & E^\circ_\text{cell} & = -1.229\text{ V} \end{array}$$

Again, the cell potential as written is negative, indicating a nonspontaneous cell reaction that must be driven by imposing a cell voltage greater than +1.229 V. Keep in mind that *standard* electrode potentials are used to inform thermodynamic predictions here, though the cell is *not* operating under standard state conditions. Therefore, at best, calculated cell potentials should be considered ballpark estimates.

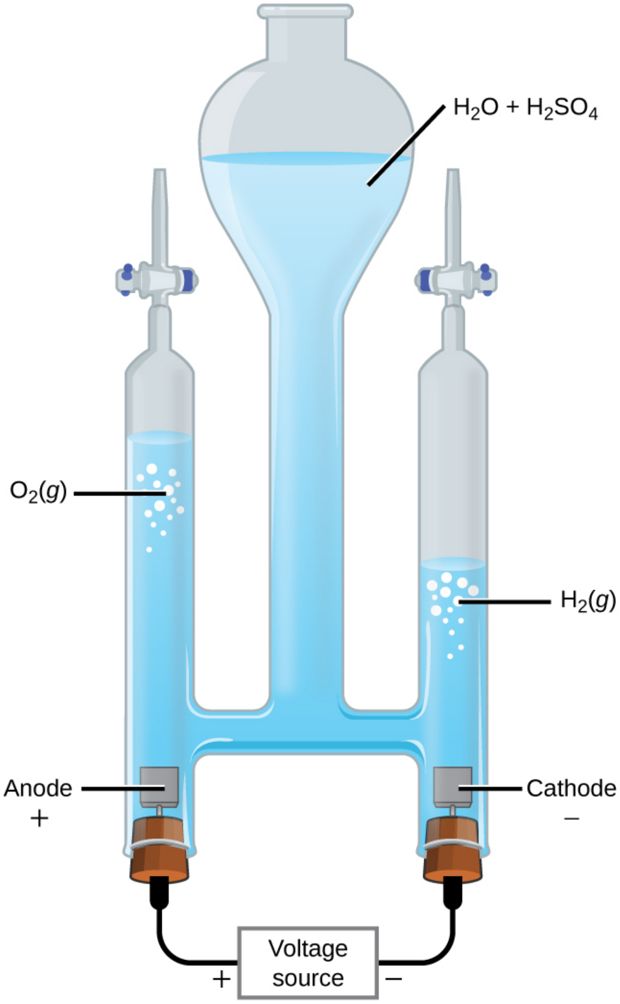


Figure 16.19 The electrolysis of water produces stoichiometric amounts of oxygen gas at the anode and hydrogen at the anode.

The Electrolysis of Aqueous Sodium Chloride

When aqueous solutions of ionic compounds are electrolyzed, the anode and cathode half-reactions may involve the electrolysis of either water species (H_2O, H^+, OH^-) or solute species (the cations and anions of the compound). As an example, the electrolysis of aqueous sodium chloride could involve either of these two anode reactions:

$$\begin{aligned} &\text{(i) } 2\text{Cl}^-(aq) \longrightarrow \text{Cl}_2(g) + 2\,\text{e}^- && E^\circ_\text{anode} = +1.35827\text{ V} \\ &\text{(ii) } 2\text{H}_2\text{O}(l) \longrightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- && E^\circ_\text{anode} = +1.229\text{ V} \end{aligned}$$

The standard electrode (*reduction*) potentials of these two half-reactions indicate water may be *oxidized* at a less negative/more positive potential (–1.229 V) than chloride ion (–1.358 V). Thermodynamics thus predicts that water would be more readily oxidized, though in practice it is observed that both water and chloride ion are oxidized under typical conditions, producing a mixture of oxygen and chlorine gas.

Turning attention to the cathode, the possibilities for reduction are:

$$\begin{aligned} &\text{(iii) } 2\text{H}^+(aq) + 2\text{e}^- \longrightarrow \text{H}_2(g) && E^\circ_{\text{cathode}} = 0\text{ V} \\ &\text{(iv) } 2\text{H}_2\text{O}(l) + 2\text{e}^- \longrightarrow \text{H}_2(g) + 2\text{OH}^-(aq) && E^\circ_{\text{cathode}} = -0.8277\text{ V} \\ &\text{(v) Na}^+(aq) + \text{e}^- \longrightarrow \text{Na}(s) && E^\circ_{\text{cathode}} = -2.71\text{ V} \end{aligned}$$

Comparison of these *standard* half-reaction potentials suggests the reduction of hydrogen ion is thermodynamically favored. However, in a neutral aqueous sodium chloride solution, the concentration of hydrogen ion is far below the standard state value of 1 *M* (approximately 10^{-7} *M*), and so the observed cathode reaction is actually reduction of water. The net cell reaction in this case is then

$$\text{cell: } 2\text{H}_2\text{O}(l) + 2\text{Cl}^-(aq) \longrightarrow \text{H}_2(g) + \text{Cl}_2(g) + 2\text{OH}^-(aq) \qquad E^\circ_{\text{cell}} = -2.186\text{ V}$$

This electrolysis reaction is part of the *chlor-alkali process* used by industry to produce chlorine and sodium hydroxide (lye).

Chemistry in Everyday Life

Electroplating

An important use for electrolytic cells is in **electroplating**. Electroplating results in a thin coating of one metal on top of a conducting surface. Reasons for electroplating include making the object more corrosion resistant, strengthening the surface, producing a more attractive finish, or for purifying metal. The metals commonly used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. Common consumer products include silver-plated or gold-plated tableware, chrome-plated automobile parts, and jewelry. The silver plating of eating utensils is used here to illustrate the process. (Figure 16.20).

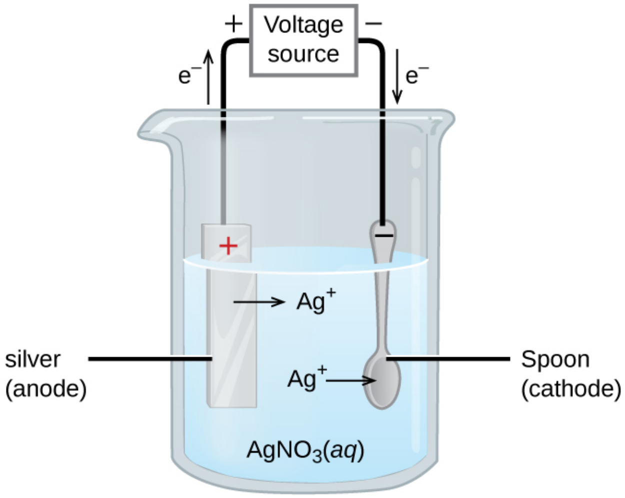


Figure 16.20 This schematic shows an electrolytic cell for silver plating eating utensils.

In the figure, the anode consists of a silver electrode, shown on the left. The cathode is located on the right and is the spoon, which is made from inexpensive metal. Both electrodes are immersed in a solution of silver nitrate. Applying a sufficient potential results in the oxidation of the silver anode

$$\text{anode: Ag}(s) \longrightarrow \text{Ag}^+(aq) + \text{e}^-$$

and reduction of silver ion at the (spoon) cathode:

$$\text{cathode: Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)$$

The net result is the transfer of silver metal from the anode to the cathode. Several experimental factors must be carefully controlled to obtain high-quality silver coatings, including the exact composition of the electrolyte solution, the cell voltage applied, and the rate of the electrolysis reaction (electrical current).

Quantitative Aspects of Electrolysis

Electrical current is defined as the rate of flow for any charged species. Most relevant to this discussion is the flow of electrons. Current is measured in a composite unit called an ampere, defined as one coulomb per second (A = 1 C/s). The charge transferred, Q, by passage of a constant current, I, over a specified time interval, t, is then given by the simple mathematical product

$$Q = It$$

When electrons are transferred during a redox process, the stoichiometry of the reaction may be used to derive the total amount of (electronic) charge involved. For example, the generic reduction process

$$\mathrm{M}^{\mathrm{n}+}(aq) + \mathrm{ne}^- \longrightarrow \mathrm{M}(s)$$

involves the transfer of n mole of electrons. The charge transferred is, therefore,

$$Q = nF$$

where F is Faraday's constant, the charge in coulombs for one mole of electrons. If the reaction takes place in an electrochemical cell, the current flow is conveniently measured, and it may be used to assist in stoichiometric calculations related to the cell reaction.

Example 16.9

Converting Current to Moles of Electrons

In one process used for electroplating silver, a current of 10.23 A was passed through an electrolytic cell for exactly 1 hour. How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

Solution

Faraday's constant can be used to convert the charge (Q) into moles of electrons (n). The charge is the current (I) multiplied by the time

$$n = \frac{Q}{F} = \frac{\frac{10.23\text{ C}}{\text{s}} \times 1\text{ hr} \times \frac{60\text{ min}}{\text{hr}} \times \frac{60\text{ s}}{\text{min}}}{96{,}485\text{ C/mol e}^-} = \frac{36{,}830\text{ C}}{96{,}485\text{ C/mol e}^-} = 0.3817\text{ mol e}^-$$

From the problem, the solution contains $AgNO_3$, so the reaction at the cathode involves 1 mole of electrons for each mole of silver

$$\text{cathode: Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)$$

The atomic mass of silver is 107.9 g/mol, so

$$\text{mass Ag} = 0.3817\text{ mol e}^- \times \frac{1\text{ mol Ag}}{1\text{ mol e}^-} \times \frac{107.9\text{ g Ag}}{1\text{ mol Ag}} = 41.19\text{ g Ag}$$

Check Your Learning

Aluminum metal can be made from aluminum(III) ions by electrolysis. What is the half-reaction at the cathode? What mass of aluminum metal would be recovered if a current of 25.0 A passed through the solution for 15.0 minutes?

Answer: $\text{Al}^{3+}(aq) + 3\text{ e}^- \longrightarrow \text{Al}(s)$; 0.0777 mol Al = 2.10 g Al.

Example 16.10

Time Required for Deposition

In one application, a 0.010-mm layer of chromium must be deposited on a part with a total surface area of 3.3 m^2 from a solution of containing chromium(III) ions. How long would it take to deposit the layer of chromium if the current was 33.46 A? The density of chromium (metal) is 7.19 g/cm^3.

Solution

First, compute the volume of chromium that must be produced (equal to the product of surface area and thickness):

$$\text{volume} = \left(0.010\text{ mm} \times \frac{1\text{ cm}}{10\text{ mm}}\right) \times \left(3.3\text{ m}^2 \times \left(\frac{10{,}000\text{ cm}^2}{1\text{ m}^2}\right)\right) = 33\text{ cm}^3$$

Use the computed volume and the provided density to calculate the molar amount of chromium required:

$$\text{mass} = \text{volume} \times \text{density} = 33\ \cancel{\text{cm}^3} \times \frac{7.19\ \text{g}}{\cancel{\text{cm}^3}} = 237\ \text{g Cr}$$

$$\text{mol Cr} = 237\ \text{g Cr} \times \frac{1\ \text{mol Cr}}{52.00\ \text{g Cr}} = 4.56\ \text{mol Cr}$$

The stoichiometry of the chromium(III) reduction process requires three moles of electrons for each mole of chromium(0) produced, and so the total charge required is:

$$Q = 4.56\ \text{mol Cr} \times \frac{3\ \text{mol e}^-}{1\ \text{mol Cr}} \times \frac{96485\ \text{C}}{\text{mol e}^-} = 1.32 \times 10^6\ \text{C}$$

Finally, if this charge is passed at a rate of 33.46 C/s, the required time is:

$$t = \frac{Q}{I} = \frac{1.32 \times 10^6\ \text{C}}{33.46\ \text{C/s}} = 3.95 \times 10^4\ \text{s} = 11.0\ \text{hr}$$

Check Your Learning

What mass of zinc is required to galvanize the top of a 3.00 m × 5.50 m sheet of iron to a thickness of 0.100 mm of zinc? If the zinc comes from a solution of $Zn(NO_3)_2$ and the current is 25.5 A, how long will it take to galvanize the top of the iron? The density of zinc is 7.140 g/cm^3.

Answer: 11.8 kg Zn requires 382 hours.

Key Terms

active electrode electrode that participates as a reactant or product in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

alkaline battery primary battery similar to a *dry cell* that uses an alkaline (often potassium hydroxide) electrolyte; designed to be an improved replacement for the dry cell, but with more energy storage and less electrolyte leakage than typical dry cell

anode electrode in an electrochemical cell at which oxidation occurs

battery single or series of galvanic cells designed for use as a source of electrical power

cathode electrode in an electrochemical cell at which reduction occurs

cathodic protection approach to preventing corrosion of a metal object by connecting it to a *sacrificial anode* composed of a more readily oxidized metal

cell notation (schematic) symbolic representation of the components and reactions in an electrochemical cell

cell potential (E_cell) difference in potential of the cathode and anode half-cells

concentration cell galvanic cell comprising half-cells of identical composition but for the concentration of one redox reactant or product

corrosion degradation of metal via a natural electrochemical process

dry cell primary battery, also called a zinc-carbon battery, based on the spontaneous oxidation of zinc by manganese(IV)

electrode potential (E_X) the potential of a cell in which the half-cell of interest acts as a cathode when connected to the standard hydrogen electrode

electrolysis process using electrical energy to cause a nonspontaneous process to occur

electrolytic cell electrochemical cell in which an external source of electrical power is used to drive an otherwise nonspontaneous process

Faraday's constant (F) charge on 1 mol of electrons; F = 96,485 C/mol e^-

fuel cell devices similar to galvanic cells that require a continuous feed of redox reactants; also called a *flow battery*

galvanic (voltaic) cell electrochemical cell in which a spontaneous redox reaction takes place; also called a *voltaic cell*

galvanization method of protecting iron or similar metals from corrosion by coating with a thin layer of more easily oxidized zinc.

half cell component of a cell that contains the redox conjugate pair ("couple") of a single reactant

inert electrode electrode that conducts electrons to and from the reactants in a half-cell but that is not itself oxidized or reduced

lead acid battery rechargeable battery commonly used in automobiles; it typically comprises six galvanic cells based on Pb half-reactions in acidic solution

lithium ion battery widely used rechargeable battery commonly used in portable electronic devices, based on lithium ion transfer between the anode and cathode

Nernst equation relating the potential of a redox system to its composition

nickel-cadmium battery rechargeable battery based on Ni/Cd half-cells with applications similar to those of lithium ion batteries

primary cell nonrechargeable battery, suitable for single use only

sacrificial anode electrode constructed from an easily oxidized metal, often magnesium or zinc, used to prevent corrosion of metal objects via cathodic protection

salt bridge tube filled with inert electrolyte solution

secondary cell battery designed to allow recharging

standard cell potential (E°_cell) the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 *M* for solutes), usually at 298.15 K

standard electrode potential ((E°_X) **)** electrode potential measured under standard conditions (1 bar or 1 atm for gases; 1 *M* for solutes) usually at 298.15 K

standard hydrogen electrode (SHE) half-cell based on hydrogen ion production, assigned a potential of exactly 0 V under standard state conditions, used as the universal reference for measuring electrode potential

Key Equations

- $E^\circ_\text{cell} = E^\circ_\text{cathode} - E^\circ_\text{anode}$
- $E^\circ_\text{cell} = \frac{RT}{nF} \ln K$
- $E^\circ_\text{cell} = \frac{0.0257\text{ V}}{n} \ln K = \frac{0.0592\text{ V}}{n} \log K$ (at 298.15 K)
- $E_\text{cell} = E^\circ_\text{cell} - \frac{RT}{nF} \ln Q$ (Nernst equation)
- $E^\circ_\text{cell} - \frac{0.0592\text{ V}}{n} \log Q$ (at 298.15 K)
- $\Delta G = -nFE_\text{cell}$
- $\Delta G^\circ = -nFE^\circ_\text{cell}$
- $w_\text{ele} = w_\text{max} = -nFE_\text{cell}$
- $Q = I \times t = n \times F$

Summary

16.1 Review of Redox Chemistry

Redox reactions are defined by changes in reactant oxidation numbers, and those most relevant to electrochemistry involve actual transfer of electrons. Aqueous phase redox processes often involve water or its characteristic ions, H^+ and OH^-, as reactants in addition to the oxidant and reductant, and equations representing these reactions can be challenging to balance. The half-reaction method is a systematic approach to balancing such equations that involves separate treatment of the oxidation and reduction half-reactions.

16.2 Galvanic Cells

Galvanic cells are devices in which a spontaneous redox reaction occurs indirectly, with the oxidant and reductant redox couples contained in separate half-cells. Electrons are transferred from the reductant (in the anode half-cell) to the oxidant (in the cathode half-cell) through an external circuit, and inert solution phase ions are transferred between half-cells, through a salt bridge, to maintain charge neutrality. The construction and composition of a galvanic cell may be succinctly represented using chemical formulas and others symbols in the form of a cell schematic (cell notation).

16.3 Electrode and Cell Potentials

The property of potential, E, is the energy associated with the separation/transfer of charge. In electrochemistry, the potentials of cells and half-cells are thermodynamic quantities that reflect the driving force or the spontaneity of their redox processes. The cell potential of an electrochemical cell is the difference in between its cathode and anode. To permit easy sharing of half-cell potential data, the standard hydrogen electrode (SHE) is assigned a potential of exactly 0 V and used to define a single electrode potential for any given half-cell. The electrode potential of a half-cell, E_X, is the cell potential of said half-cell acting as a cathode when connected to a SHE acting as an anode. When the half-cell is operating under standard state conditions, its potential is the standard electrode potential, $E°_{\text{X}}$. Standard electrode potentials reflect the relative oxidizing strength of the half-reaction's reactant, with stronger oxidants exhibiting larger (more positive) $E°_X$ values. Tabulations of standard electrode potentials may be used to compute standard cell potentials, $E°_{cell}$, for many redox reactions. The arithmetic sign of a cell potential indicates the spontaneity of the cell reaction, with positive values for spontaneous reactions and negative values for nonspontaneous reactions (spontaneous in the reverse direction).

16.4 Potential, Free Energy, and Equilibrium

Potential is a thermodynamic quantity reflecting the intrinsic driving force of a redox process, and it is directly related to the free energy change and equilibrium constant for the process. For redox processes taking place in electrochemical cells, the maximum (electrical) work done by the system is easily computed from the cell potential and the reaction stoichiometry and is equal to the free energy change for the process. The equilibrium constant for a redox reaction is logarithmically related to the reaction's cell potential, with larger (more positive) potentials indicating reactions with greater driving force that equilibrate when the reaction has proceeded far towards completion (large value of K). Finally, the potential of a redox process varies with the composition of the reaction mixture, being related to the reactions standard potential and the value of its reaction quotient, Q, as described by the Nernst equation.

16.5 Batteries and Fuel Cells

Galvanic cells designed specifically to function as electrical power supplies are called batteries. A variety of both single-use batteries (primary cells) and rechargeable batteries (secondary cells) are commercially available to serve a variety of applications, with important specifications including voltage, size, and lifetime. Fuel cells, sometimes called flow batteries, are devices that harness the energy of spontaneous redox reactions normally associated with combustion processes. Like batteries, fuel cells enable the reaction's electron transfer via an external circuit, but they require continuous input of the redox reactants (fuel and oxidant) from an external reservoir. Fuel cells are typically much more efficient in converting the energy released by the reaction to useful work in comparison to internal combustion engines.

16.6 Corrosion

Spontaneous oxidation of metals by natural electrochemical processes is called corrosion, familiar examples including the rusting of iron and the tarnishing of silver. Corrosion process involve the creation of a galvanic cell in which different sites on the metal object function as anode and cathode, with the corrosion taking place at the anodic site. Approaches to preventing corrosion of metals include use of a protective coating of zinc (galvanization) and the use of sacrificial anodes connected to the metal object (cathodic protection).

16.7 Electrolysis

Nonspontaneous redox processes may be forced to occur in electrochemical cells by the application of an appropriate potential using an external power source—a process known as electrolysis. Electrolysis is the basis for certain ore refining processes, the industrial production of many chemical commodities, and the electroplating of metal coatings on various products. Measurement of the current flow during electrolysis permits stoichiometric calculations.

Exercises

16.1 Review of Redox Chemistry

1. Identify each half-reaction below as either oxidation or reduction.

(a) $\text{Fe}^{3+} + 3\text{e}^- \longrightarrow \text{Fe}$

(b) $\text{Cr} \longrightarrow \text{Cr}^{3+} + 3\text{e}^-$

(c) $\text{MnO}_4{}^{2-} \longrightarrow \text{MnO}_4{}^- + \text{e}^-$

(d) $\text{Li}^+ + \text{e}^- \longrightarrow \text{Li}$

2. Identify each half-reaction below as either oxidation or reduction.

(a) $\text{Cl}^- \longrightarrow \text{Cl}_2$

(b) $\text{Mn}^{2+} \longrightarrow \text{MnO}_2$

(c) $\text{H}_2 \longrightarrow \text{H}^+$

(d) $\text{NO}_3{}^- \longrightarrow \text{NO}$

3. Assuming each pair of half-reactions below takes place in an acidic solution, write a balanced equation for the overall reaction.

(a) $\text{Ca} \longrightarrow \text{Ca}^{2+} + 2\text{e}^-, \quad \text{F}_2 + 2\text{e}^- \longrightarrow 2\text{F}^-$

(b) $\text{Li} \longrightarrow \text{Li}^+ + \text{e}^-, \quad \text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$

(c) $\text{Fe} \longrightarrow \text{Fe}^{3+} + 3\text{e}^-, \quad \text{Br}_2 + 2\text{e}^- \longrightarrow 2\text{Br}^-$

(d) $\text{Ag} \longrightarrow \text{Ag}^+ + \text{e}^-, \quad \text{MnO}_4{}^- + 4\text{H}^+ + 3\text{e}^- \longrightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$

4. Balance the equations below assuming they occur in an acidic solution.

(a) $\text{H}_2\text{O}_2 + \text{Sn}^{2+} \longrightarrow \text{H}_2\text{O} + \text{Sn}^{4+}$

(b) $\text{PbO}_2 + \text{Hg} \longrightarrow \text{Hg}_2{}^{2+} + \text{Pb}^{2+}$

(c) $\text{Al} + \text{Cr}_2\text{O}_7{}^{2-} \longrightarrow \text{Al}^{3+} + \text{Cr}^{3+}$

5. Identify the oxidant and reductant of each reaction of the previous exercise.

6. Balance the equations below assuming they occur in a basic solution.

(a) $\text{SO}_3{}^{2-}(aq) + \text{Cu(OH)}_2(s) \longrightarrow \text{SO}_4{}^{2-}(aq) + \text{Cu(OH)}(s)$

(b) $\text{O}_2(g) + \text{Mn(OH)}_2(s) \longrightarrow \text{MnO}_2(s)$

(c) $\text{NO}_3{}^-(aq) + \text{H}_2(g) \longrightarrow \text{NO}(g)$

(d) $\text{Al}(s) + \text{CrO}_4{}^{2-}(aq) \longrightarrow \text{Al(OH)}_3(s) + \text{Cr(OH)}_4{}^-(aq)$

7. Identify the oxidant and reductant of each reaction of the previous exercise.

8. Why don’t hydroxide ions appear in equations for half-reactions occurring in acidic solution?

9. Why don’t hydrogen ions appear in equations for half-reactions occurring in basic solution?

10. Why must the charge balance in oxidation-reduction reactions?

16.2 Galvanic Cells

11. Write cell schematics for the following cell reactions, using platinum as an inert electrode as needed.

(a) $\text{Mg}(s) + \text{Ni}^{2+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{Ni}(s)$

(b) $2\text{Ag}^{+}(aq) + \text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq) + 2\text{Ag}(s)$

(c) $\text{Mn}(s) + \text{Sn}(\text{NO}_3)_2(aq) \longrightarrow \text{Mn}(\text{NO}_3)_2(aq) + \text{Au}(s)$

(d) $3\text{CuNO}_3(aq) + \text{Au}(\text{NO}_3)_3(aq) \longrightarrow 3\text{Cu}(\text{NO}_3)_2(aq) + \text{Au}(s)$

12. Assuming the schematics below represent galvanic cells as written, identify the half-cell reactions occurring in each.

(a) $\text{Mg}(s) \mid \text{Mg}^{2+}(aq) \parallel \text{Cu}^{2+}(aq) \mid \text{Cu}(s)$

(b) $\text{Ni}(s) \mid \text{Ni}^{2+}(aq) \parallel \text{Ag}^{+}(aq) \mid \text{Ag}(s)$

13. Write a balanced equation for the cell reaction of each cell in the previous exercise.

14. Balance each reaction below, and write a cell schematic representing the reaction as it would occur in a galvanic cell.

(a) $\text{Al}(s) + \text{Zr}^{4+}(aq) \longrightarrow \text{Al}^{3+}(aq) + \text{Zr}(s)$

(b) $\text{Ag}^{+}(aq) + \text{NO}(g) \longrightarrow \text{Ag}(s) + \text{NO}_3{}^{-}(aq)$ (acidic solution)

(c) $\text{SiO}_3{}^{2-}(aq) + \text{Mg}(s) \longrightarrow \text{Si}(s) + \text{Mg(OH)}_2(s)$ (basic solution)

(d) $\text{ClO}_3{}^{-}(aq) + \text{MnO}_2(s) \longrightarrow \text{Cl}^{-}(aq) + \text{MnO}_4{}^{-}(aq)$ (basic solution)

15. Identify the oxidant and reductant in each reaction of the previous exercise.

16. From the information provided, use cell notation to describe the following systems:

(a) In one half-cell, a solution of $\text{Pt}(\text{NO}_3)_2$ forms Pt metal, while in the other half-cell, Cu metal goes into a $\text{Cu}(\text{NO}_3)_2$ solution with all solute concentrations 1 *M*.

(b) The cathode consists of a gold electrode in a 0.55 *M* $\text{Au}(\text{NO}_3)_3$ solution and the anode is a magnesium electrode in 0.75 *M* $\text{Mg}(\text{NO}_3)_2$ solution.

(c) One half-cell consists of a silver electrode in a 1 *M* AgNO_3 solution, and in the other half-cell, a copper electrode in 1 *M* $\text{Cu}(\text{NO}_3)_2$ is oxidized.

17. Why is a salt bridge necessary in galvanic cells like the one in **Figure 16.3**?

18. An active (metal) electrode was found to gain mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode an anode or a cathode? Explain.

19. An active (metal) electrode was found to lose mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode an anode or a cathode? Explain.

20. The masses of three electrodes (A, B, and C), each from three different galvanic cells, were measured before and after the cells were allowed to pass current for a while. The mass of electrode A increased, that of electrode B was unchanged, and that of electrode C decreased. Identify each electrode as active or inert, and note (if possible) whether it functioned as anode or cathode.

16.3 Electrode and Cell Potentials

21. Calculate the standard cell potential for each reaction below, and note whether the reaction is spontaneous under standard state conditions.

(a) $\text{Mg}(s) + \text{Ni}^{2+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{Ni}(s)$

(b) $2\text{Ag}^{+}(aq) + \text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq) + 2\text{Ag}(s)$

(c) $\text{Mn}(s) + \text{Sn(NO}_3\text{)}_2(aq) \longrightarrow \text{Mn(NO}_3\text{)}_2(aq) + \text{Sn}(s)$

(d) $3\text{Fe(NO}_3\text{)}_2(aq) + \text{Au(NO}_3\text{)}_3(aq) \longrightarrow 3\text{Fe(NO}_3\text{)}_3(aq) + \text{Au}(s)$

22. Calculate the standard cell potential for each reaction below, and note whether the reaction is spontaneous under standard state conditions.

(a) $\text{Mn}(s) + \text{Ni}^{2+}(aq) \longrightarrow \text{Mn}^{2+}(aq) + \text{Ni}(s)$

(b) $3\text{Cu}^{2+}(aq) + 2\text{Al}(s) \longrightarrow 2\text{Al}^{3+}(aq) + 3\text{Cu}(s)$

(c) $\text{Na}(s) + \text{LiNO}_3(aq) \longrightarrow \text{NaNO}_3(aq) + \text{Li}(s)$

(d) $\text{Ca(NO}_3\text{)}_2(aq) + \text{Ba}(s) \longrightarrow \text{Ba(NO}_3\text{)}_2(aq) + \text{Ca}(s)$

23. Write the balanced cell reaction for the cell schematic below, calculate the standard cell potential, and note whether the reaction is spontaneous under standard state conditions.

$\text{Cu}(s) \mid \text{Cu}^{2+}(aq) \parallel \text{Au}^{3+}(aq) \mid \text{Au}(s)$

24. Determine the cell reaction and standard cell potential at 25 °C for a cell made from a cathode half-cell consisting of a silver electrode in 1 *M* silver nitrate solution and an anode half-cell consisting of a zinc electrode in 1 *M* zinc nitrate. Is the reaction spontaneous at standard conditions?

25. Determine the cell reaction and standard cell potential at 25 °C for a cell made from an anode half-cell containing a cadmium electrode in 1 *M* cadmium nitrate and an anode half-cell consisting of an aluminum electrode in 1 *M* aluminum nitrate solution. Is the reaction spontaneous at standard conditions?

26. Write the balanced cell reaction for the cell schematic below, calculate the standard cell potential, and note whether the reaction is spontaneous under standard state conditions.

$\text{Pt}(s) \mid \text{H}_2(g) \mid \text{H}^{+}(aq) \parallel \text{Br}_2(aq),\ \text{Br}^{-}(aq) \mid \text{Pt}(s)$

16.4 Potential, Free Energy, and Equilibrium

27. For each pair of standard cell potential and electron stoichiometry values below, calculate a corresponding standard free energy change (kJ).

(a) 0.000 V, n = 2

(b) +0.434 V, n = 2

(c) −2.439 V, n = 1

28. For each pair of standard free energy change and electron stoichiometry values below, calculate a corresponding standard cell potential.

(a) 12 kJ/mol, n = 3

(b) −45 kJ/mol, n = 1

29. Determine the standard cell potential and the cell potential under the stated conditions for the electrochemical reactions described here. State whether each is spontaneous or nonspontaneous under each set of conditions at 298.15 K.

(a) $\mathrm{Hg}(l) + \mathrm{S}^{2-}(aq, 0.10\ M) + 2\mathrm{Ag}^{+}(aq, 0.25\ M) \longrightarrow 2\mathrm{Ag}(s) + \mathrm{HgS}(s)$

(b) The cell made from an anode half-cell consisting of an aluminum electrode in 0.015 *M* aluminum nitrate solution and a cathode half-cell consisting of a nickel electrode in 0.25 *M* nickel(II) nitrate solution.

(c) The cell made of a half-cell in which 1.0 *M* aqueous bromide is oxidized to 0.11 *M* bromine ion and a half-cell in which aluminum ion at 0.023 *M* is reduced to aluminum metal.

30. Determine ΔG and $\Delta G°$ for each of the reactions in the previous problem.

31. Use the data in **Appendix L** to calculate equilibrium constants for the following reactions. Assume 298.15 K if no temperature is given.

(a) $\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{Cl}^{-}(aq)$

(b) $\mathrm{CdS}(s) \rightleftharpoons \mathrm{Cd}^{2+}(aq) + \mathrm{S}^{2-}(aq)$ at 377 K

(c) $\mathrm{Hg}^{2+}(aq) + 4\mathrm{Br}^{-}(aq) \rightleftharpoons [\mathrm{HgBr}_4]^{2-}(aq)$

(d) $\mathrm{H}_2\mathrm{O}(l) \rightleftharpoons \mathrm{H}^{+}(aq) + \mathrm{OH}^{-}(aq)$ at 25 °C

16.5 Batteries and Fuel Cells

32. Consider a battery made from one half-cell that consists of a copper electrode in 1 *M* $\mathrm{CuSO_4}$ solution and another half-cell that consists of a lead electrode in 1 *M* $\mathrm{Pb(NO_3)_2}$ solution.

(a) What is the standard cell potential for the battery?

(b) What are the reactions at the anode, cathode, and the overall reaction?

(c) Most devices designed to use dry-cell batteries can operate between 1.0 and 1.5 V. Could this cell be used to make a battery that could replace a dry-cell battery? Why or why not.

(d) Suppose sulfuric acid is added to the half-cell with the lead electrode and some $\mathrm{PbSO_4}(s)$ forms. Would the cell potential increase, decrease, or remain the same?

33. Consider a battery with the overall reaction: $\mathrm{Cu}(s) + 2\mathrm{Ag}^{+}(aq) \longrightarrow 2\mathrm{Ag}(s) + \mathrm{Cu}^{2+}(aq).$

(a) What is the reaction at the anode and cathode?

(b) A battery is "dead" when its cell potential is zero. What is the value of *Q* when this battery is dead?

(c) If a particular dead battery was found to have $[\mathrm{Cu}^{2+}] = 0.11\ M$, what was the concentration of silver ion?

34. Why do batteries go dead, but fuel cells do not?

35. Use the Nernst equation to explain the drop in voltage observed for some batteries as they discharge.

36. Using the information thus far in this chapter, explain why battery-powered electronics perform poorly in low temperatures.

16.6 Corrosion

37. Which member of each pair of metals is more likely to corrode (oxidize)?

(a) Mg or Ca

(b) Au or Hg

(c) Fe or Zn

(d) Ag or Pt

38. Consider the following metals: Ag, Au, Mg, Ni, and Zn. Which of these metals could be used as a sacrificial anode in the cathodic protection of an underground steel storage tank? Steel is an alloy composed mostly of iron, so use −0.447 V as the standard reduction potential for steel.

39. Aluminum $(E^\circ_{\text{Al}^{3+}/\text{Al}} = -2.07\text{ V})$ is more easily oxidized than iron $(E^\circ_{\text{Fe}^{3+}/\text{Fe}} = -0.477\text{ V}),$ and yet when both are exposed to the environment, untreated aluminum has very good corrosion resistance while the corrosion resistance of untreated iron is poor. What might explain this observation?

40. If a sample of iron and a sample of zinc come into contact, the zinc corrodes but the iron does not. If a sample of iron comes into contact with a sample of copper, the iron corrodes but the copper does not. Explain this phenomenon.

41. Suppose you have three different metals, A, B, and C. When metals A and B come into contact, B corrodes and A does not corrode. When metals A and C come into contact, A corrodes and C does not corrode. Based on this information, which metal corrodes and which metal does not corrode when B and C come into contact?

42. Why would a sacrificial anode made of lithium metal be a bad choice

16.7 Electrolysis

43. If a 2.5 A current flows through a circuit for 35 minutes, how many coulombs of charge moved through the circuit?

44. For the scenario in the previous question, how many electrons moved through the circuit?

45. Write the half-reactions and cell reaction occurring during electrolysis of each molten salt below.

(a) $CaCl_2$

(b) LiH

(c) $AlCl_3$

(d) $CrBr_3$

46. What mass of each product is produced in each of the electrolytic cells of the previous problem if a total charge of 3.33×10^5 C passes through each cell?

47. How long would it take to reduce 1 mole of each of the following ions using the current indicated?

(a) Al^{3+}, 1.234 A

(b) Ca^{2+}, 22.2 A

(c) Cr^{5+}, 37.45 A

(d) Au^{3+}, 3.57 A

48. A current of 2.345 A passes through the cell shown in **Figure 16.19** for 45 minutes. What is the volume of the hydrogen collected at room temperature if the pressure is exactly 1 atm? (Hint: Is hydrogen the only gas present above the water?)

49. An irregularly shaped metal part made from a particular alloy was galvanized with zinc using a $Zn(NO_3)_2$ solution. When a current of 2.599 A was used, it took exactly 1 hour to deposit a 0.01123-mm layer of zinc on the part. What was the total surface area of the part? The density of zinc is 7.140 g/cm^3.

Chapter 17

Kinetics

Figure 17.1 An agama lizard basks in the sun. As its body warms, the chemical reactions of its metabolism speed up.

Chapter Outline

Introduction

The lizard in the photograph is not simply enjoying the sunshine or working on its tan. The heat from the sun's rays is critical to the lizard's survival. A warm lizard can move faster than a cold one because the chemical reactions that allow its muscles to move occur more rapidly at higher temperatures. A cold lizard is a slower lizard and an easier meal for predators.

From baking a cake to determining the useful lifespan of a bridge, rates of chemical reactions play important roles in our understanding of processes that involve chemical changes. Two questions are typically posed when planning to carry out a chemical reaction. The first is: "Will the reaction produce the desired products in useful quantities?" The second question is: "How rapidly will the reaction occur?" A third question is often asked when investigating reactions in greater detail: "What specific molecular-level processes take place as the reaction occurs?" Knowing the answer to this question is of practical importance when the yield or rate of a reaction needs to be controlled.

The study of chemical kinetics concerns the second and third questions—that is, the rate at which a reaction yields products and the molecular-scale means by which a reaction occurs. This chapter examines the factors that influence the rates of chemical reactions, the mechanisms by which reactions proceed, and the quantitative techniques used to describe the rates at which reactions occur.

17.1 Chemical Reaction Rates

By the end of this section, you will be able to:

- Define chemical reaction rate
- Derive rate expressions from the balanced equation for a given chemical reaction
- Calculate reaction rates from experimental data

A *rate* is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The **rate of reaction** is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution’s conductivity.

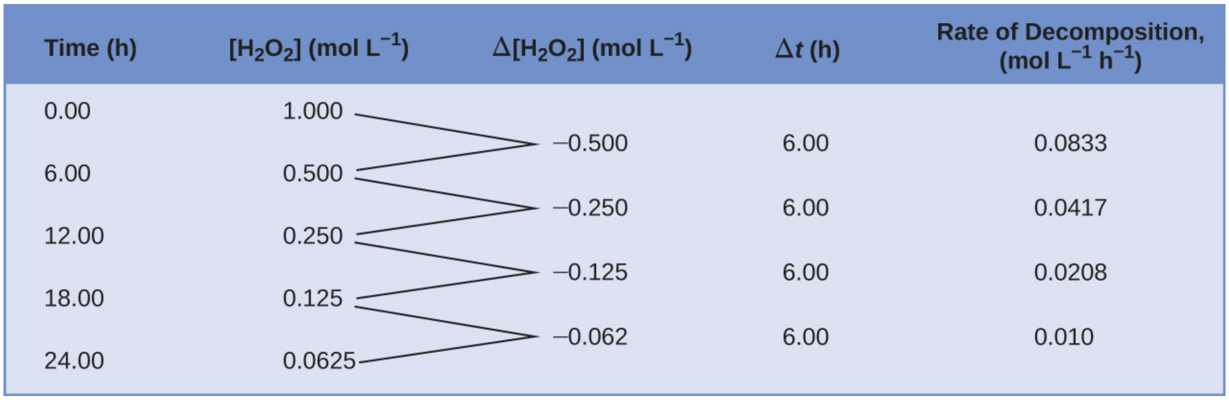
For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. For example, the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution changes slowly over time as it decomposes according to the equation:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

$$\begin{aligned} \text{rate of decomposition of } H_2O_2 &= -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= -\frac{[H_2O_2]_{t_2} - [H_2O_2]_{t_1}}{t_2 - t_1} \\ &= -\frac{\Delta[H_2O_2]}{\Delta t} \end{aligned}$$

This mathematical representation of the change in species concentration over time is the **rate expression** for the reaction. The brackets indicate molar concentrations, and the symbol delta (Δ) indicates “change in.” Thus, $[H_2O_2]_{t_1}$ represents the molar concentration of hydrogen peroxide at some time t_1; likewise, $[H_2O_2]_{t_2}$ represents the molar concentration of hydrogen peroxide at a later time t_2; and $\Delta[H_2O_2]$ represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[H_2O_2]$ is a negative quantity. Reaction rates are, by convention, positive quantities, and so this negative change in concentration is multiplied by −1. **Figure 17.2** provides an example of data collected during the decomposition of H_2O_2.



Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol L^{-1} h^{-1})
0.00	1.000			
		−0.500	6.00	0.0833
6.00	0.500			
		−0.250	6.00	0.0417
12.00	0.250			
		−0.125	6.00	0.0208
18.00	0.125			
		−0.062	6.00	0.010
24.00	0.0625			

Figure 17.2 The rate of decomposition of H_2O_2 in an aqueous solution decreases as the concentration of H_2O_2 decreases.

To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40 °C. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

$$\frac{-\Delta[\mathrm{H_2O_2}]}{\Delta t} = \frac{-(0.500\ \mathrm{mol/L} - 1.000\ \mathrm{mol/L})}{(6.00\ \mathrm{h} - 0.00\ \mathrm{h})} = 0.0833\ \mathrm{mol\ L^{-1}\ h^{-1}}$$

Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

$$\frac{-\Delta[\mathrm{H_2O_2}]}{\Delta t} = \frac{-(0.0625\ \mathrm{mol/L} - 0.125\ \mathrm{mol/L})}{(24.00\ \mathrm{h} - 18.00\ \mathrm{h})} = 0.010\ \mathrm{mol\ L^{-1}\ h^{-1}}$$

This behavior indicates the reaction continually slows with time. Using the concentrations at the beginning and end of a time period over which the reaction rate is changing results in the calculation of an **average rate** for the reaction over this time interval. At any specific time, the rate at which a reaction is proceeding is known as its **instantaneous rate**. The instantaneous rate of a reaction at "time zero," when the reaction commences, is its **initial rate**. Consider the analogy of a car slowing down as it approaches a stop sign. The vehicle's initial rate—analogous to the beginning of a chemical reaction—would be the speedometer reading at the moment the driver begins pressing the brakes (t_0). A few moments later, the instantaneous rate at a specific moment—call it t_1—would be somewhat slower, as indicated by the speedometer reading at that point in time. As time passes, the instantaneous rate will continue to fall until it reaches zero, when the car (or reaction) stops. Unlike instantaneous speed, the car's average speed is not indicated by the speedometer; but it can be calculated as the ratio of the distance traveled to the time required to bring the vehicle to a complete stop (Δt). Like the decelerating car, the average rate of a chemical reaction will fall somewhere between its initial and final rates.

The instantaneous rate of a reaction may be determined one of two ways. If experimental conditions permit the measurement of concentration changes over very short time intervals, then average rates computed as described earlier provide reasonably good approximations of instantaneous rates. Alternatively, a graphical procedure may be used that, in effect, yields the results that would be obtained if short time interval measurements were possible. In a plot of the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of H_2O_2 at any time t is given by the slope of a straight line that is tangent to the curve at that time (**Figure 17.3**). These tangent line slopes may be evaluated using calculus, but the procedure for doing so is beyond the scope of this chapter.

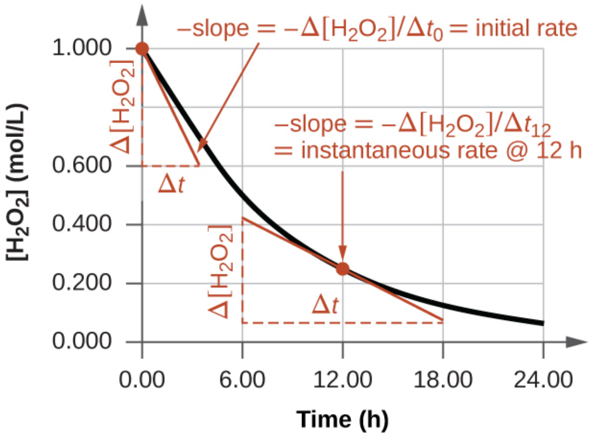


Figure 17.3 This graph shows a plot of concentration versus time for a 1.000 *M* solution of H_2O_2. The rate at any time is equal to the negative of the slope of a line tangent to the curve at that time. Tangents are shown at *t* = 0 h ("initial rate") and at *t* = 12 h ("instantaneous rate" at 12 h).

Chemistry in Everyday Life

Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (**Figure 17.4**). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in color upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:

$$C_6H_{12}O_6 + O_2 \xrightarrow{\text{catalyst}} C_6H_{10}O_6 + H_2O_2$$
$$2H_2O_2 + 2I^- \xrightarrow{\text{catalyst}} I_2 + 2H_2O + O_2$$

The first equation depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colorless iodide ion to yield brown iodine, which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct color change.

The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of *catalysis*, a topic discussed later in this chapter. A typical glucose test strip for use with urine requires approximately 30 seconds for completion of the color-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it actually is (a *false-negative* result). Waiting too long to assess the color change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ion by other substances found in urine.

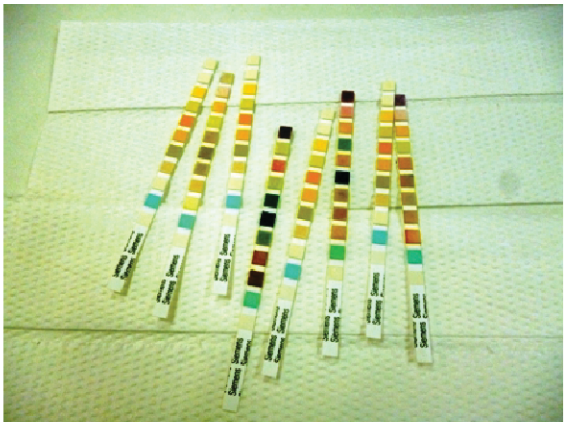


Figure 17.4 Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman)

Relative Rates of Reaction

The rate of a reaction may be expressed as the change in concentration of any reactant or product. For any given reaction, these rate expressions are all related simply to one another according to the reaction stoichiometry. The rate of the general reaction

$$\text{aA} \longrightarrow \text{bB}$$

can be expressed in terms of the decrease in the concentration of A or the increase in the concentration of B. These two rate expressions are related by the stoichiometry of the reaction:

$$\text{rate} = -\left(\frac{1}{\text{a}}\right)\left(\frac{\Delta\text{A}}{\Delta t}\right) = \left(\frac{1}{\text{b}}\right)\left(\frac{\Delta\text{B}}{\Delta t}\right)$$

the reaction represented by the following equation:

$$2\text{NH}_3(g) \longrightarrow \text{N}_2(g) + 3\text{H}_2(g)$$

The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

$$-\frac{\Delta\text{mol NH}_3}{\Delta t} \times \frac{1\text{ mol N}_2}{2\text{ mol NH}_3} = \frac{\Delta\text{mol N}_2}{\Delta t}$$

This may be represented in an abbreviated format by omitting the units of the stoichiometric factor:

$$-\frac{1}{2}\frac{\Delta\text{mol NH}_3}{\Delta t} = \frac{\Delta\text{mol N}_2}{\Delta t}$$

Note that a negative sign has been included as a factor to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). For homogeneous reactions, both the reactants and products are present in the same solution and thus occupy the same volume, so the molar amounts may be replaced with molar concentrations:

$$-\frac{1}{2}\frac{\Delta[\text{NH}_3]}{\Delta t} = \frac{\Delta[\text{N}_2]}{\Delta t}$$

Similarly, the rate of formation of H_2 is three times the rate of formation of N_2 because three moles of H_2 are produced for each mole of N_2 produced.

$$\frac{1}{3}\frac{\Delta[\mathrm{H_2}]}{\Delta t} = \frac{\Delta[\mathrm{N_2}]}{\Delta t}$$

Figure 17.5 illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. Slopes of the tangent lines at t = 500 s show that the instantaneous rates derived from all three species involved in the reaction are related by their stoichiometric factors. The rate of hydrogen production, for example, is observed to be three times greater than that for nitrogen production:

$$\frac{2.91 \times 10^{-6}\ M/\mathrm{s}}{9.70 \times 10^{-7}\ M/\mathrm{s}} \approx 3$$

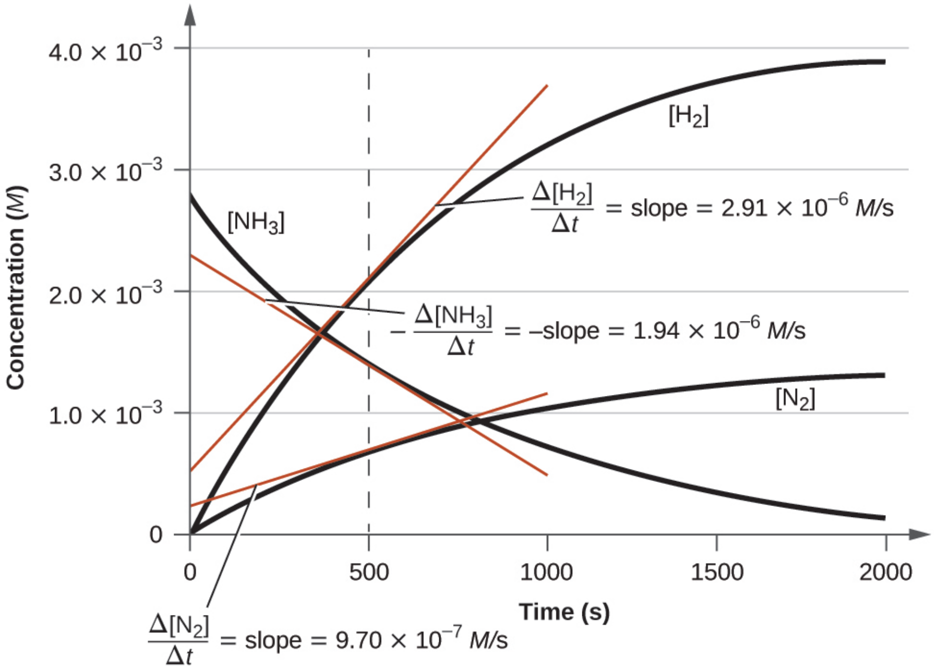


Figure 17.5 Changes in concentrations of the reactant and products for the reaction $2\mathrm{NH_3} \longrightarrow \mathrm{N_2} + 3\mathrm{H_2}$. The rates of change of the three concentrations are related by the reaction stoichiometry, as shown by the different slopes of the tangents at t = 500 s.

Example 17.1

Expressions for Relative Reaction Rates

The first step in the production of nitric acid is the combustion of ammonia:

$$4\mathrm{NH_3}(g) + 5\mathrm{O_2}(g) \longrightarrow 4\mathrm{NO}(g) + 6\mathrm{H_2O}(g)$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Solution

Considering the stoichiometry of this homogeneous reaction, the rates for the consumption of reactants and formation of products are:

$$-\frac{1}{4}\frac{\Delta[\mathrm{NH_3}]}{\Delta t} = -\frac{1}{5}\frac{\Delta[\mathrm{O_2}]}{\Delta t} = \frac{1}{4}\frac{\Delta[\mathrm{NO}]}{\Delta t} = \frac{1}{6}\frac{\Delta[\mathrm{H_2O}]}{\Delta t}$$

Check Your Learning

The rate of formation of Br_2 is 6.0 × 10^{-6} mol/L/s in a reaction described by the following net ionic equation:

$$5Br^- + BrO_3{}^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Answer: $-\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3{}^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$

Example 17.2

Reaction Rate Expressions for Decomposition of H_2O_2

The graph in **Figure 17.3** shows the rate of the decomposition of H_2O_2 over time:

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Based on these data, the instantaneous rate of decomposition of H_2O_2 at t = 11.1 h is determined to be 3.20 × 10^{-2} mol/L/h, that is:

$$-\frac{\Delta[H_2O_2]}{\Delta t} = 3.20 \times 10^{-2}\,\text{mol L}^{-1}\,\text{h}^{-1}$$

What is the instantaneous rate of production of H_2O and O_2?

Solution

The reaction stoichiometry shows that

$$-\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Therefore:

$$\frac{1}{2} \times 3.20 \times 10^{-2}\,\text{mol L}^{-1}\,\text{h}^{-1} = \frac{\Delta[O_2]}{\Delta t}$$

and

$$\frac{\Delta[O_2]}{\Delta t} = 1.60 \times 10^{-2}\,\text{mol L}^{-1}\,\text{h}^{-1}$$

Check Your Learning

If the rate of decomposition of ammonia, NH_3, at 1150 K is 2.10 × 10^{-6} mol/L/s, what is the rate of production of nitrogen and hydrogen?

Answer: 1.05 × 10^{-6} mol/L/s, N_2 and 3.15 × 10^{-6} mol/L/s, H_2.

17.2 Factors Affecting Reaction Rates

By the end of this section, you will be able to:

- Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. Five factors typically affecting the rates of chemical reactions will be explored in this section: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

The Physical States of the Reactants

A chemical reaction between two or more substances requires intimate contact between the reactants. When reactants are in different physical states, or phases (solid, liquid, gaseous, dissolved), the reaction takes place only at the interface between the phases. Consider the heterogeneous reaction between a solid phase and either a liquid or gaseous phase. Compared with the reaction rate for large solid particles, the rate for smaller particles will be greater because the surface area in contact with the other reactant phase is greater. For example, large pieces of iron react more slowly with acids than they do with finely divided iron powder (**Figure 17.6**). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.


(a) (b)

Figure 17.6 (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas: $2Fe(s) + 6HCl(aq) \longrightarrow 2FeCl_3(aq) + 3H_2(g)$. (b) An iron nail reacts more slowly because the surface area exposed to the acid is much less.

Link to Learning

Watch **this video (http://openstaxcollege.org/l/16cesium)** to see the reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.

Temperature of the Reactants

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. Gas burners, hot plates, and ovens are often used in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. For many chemical processes, reaction rates are approximately doubled when the temperature is raised by 10 °C.

Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate ($CaCO_3$) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (**Figure 17.7**). An acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$SO_2(g) + H_2O(g) \longrightarrow H_2SO_3(aq)$$

Calcium carbonate reacts with sulfurous acid as follows:

$$CaCO_3(s) + H_2SO_3(aq) \longrightarrow CaSO_3(aq) + CO_2(g) + H_2O(l)$$

In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.

Figure 17.7 Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III)

Link to Learning

Phosphorous burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen is higher. Watch this **video (http://openstaxcollege.org/l/16phosphor)** to see an example.

The Presence of a Catalyst

Relatively dilute aqueous solutions of hydrogen peroxide, H_2O_2, are commonly used as topical antiseptics. Hydrogen peroxide decomposes to yield water and oxygen gas according to the equation:

$$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$$

Under typical conditions, this decomposition occurs very slowly. When dilute $H_2O_2(aq)$ is poured onto an open wound, however, the reaction occurs rapidly and the solution foams because of the vigorous production of oxygen gas. This dramatic difference is caused by the presence of substances within the wound's exposed tissues that accelerate the decomposition process. Substances that function to increase the rate of a reaction are called **catalysts**, a topic treated in greater detail later in this chapter.

Link to Learning

Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modeling simulations to predict how the parameters discussed earlier will influence the rate of a reaction. Use the **PhET Reactions & Rates interactive (http://openstaxcollege.org/l/16PHETreaction)** to explore how temperature, concentration, and the nature of the reactants affect reaction rates.

17.3 Rate Laws

By the end of this section, you will be able to:

- Explain the form and function of a rate law
- Use rate laws to calculate reaction rates
- Use rate and concentration data to identify reaction orders and derive rate laws

As described in the previous module, the rate of a reaction is often affected by the concentrations of reactants. **Rate laws** (sometimes called *differential rate laws*) or **rate equations** are mathematical expressions that describe the relationship between the rate of a chemical reaction and the concentration of its reactants. As an example, consider the reaction described by the chemical equation

$$aA + bB \longrightarrow products$$

where a and b are stoichiometric coefficients. The rate law for this reaction is written as:

$$\text{rate} = k[A]^m[B]^n$$

in which $[A]$ and $[B]$ represent the molar concentrations of reactants, and k is the **rate constant**, which is specific for a particular reaction at a particular temperature. The exponents m and n are the **reaction orders** and are typically positive integers, though they can be fractions, negative, or zero. The rate constant k and the reaction orders m and n must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed. The rate constant k is independent of the reactant concentrations, but it does vary with temperature.

The reaction orders in a rate law describe the mathematical dependence of the rate on reactant concentrations. Referring to the generic rate law above, the reaction is m order with respect to A and n order with respect to B. For example, if $m = 1$ and $n = 2$, the reaction is first order in A and second order in B. The **overall reaction order** is simply the sum of orders for each reactant. For the example rate law here, the reaction is third order overall $(1 + 2 = 3)$. A few specific examples are shown below to further illustrate this concept.

The rate law:

$$\text{rate} = k[\text{H}_2\text{O}_2]$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$$\text{rate} = k[\text{C}_4\text{H}_6]^2$$

describes a reaction that is second order in C_4H_6 and second order overall. The rate law:

$$\text{rate} = k[\text{H}^+][\text{OH}^-]$$

describes a reaction that is first order in H^+, first order in OH^-, and second order overall.

Example 17.3

Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\text{NO}_2(g) + \text{CO}(g) \longrightarrow \text{NO}(g) + \text{CO}_2(g)$$

is second order in NO_2 and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate} = k[\text{NO}_2]^m[\text{CO}]^n$$

The reaction is second order in NO_2; thus $m = 2$. The reaction is zero order in CO; thus $n = 0$. The rate law is:

$$\text{rate} = k[\text{NO}_2]^2[\text{CO}]^0 = k[\text{NO}_2]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[\text{CO}]^0 = 1$, which is why the CO concentration term may be omitted from the rate law: the rate of reaction is solely dependent on the concentration of NO_2. A later chapter section on reaction mechanisms will explain how a reactant's concentration can have no effect on a reaction rate despite being involved in the reaction.

Check Your Learning

The rate law for the reaction:

$$\text{H}_2(g) + 2\text{NO}(g) \longrightarrow \text{N}_2\text{O}(g) + \text{H}_2\text{O}(g)$$

has been determined to be rate = $k[\text{NO}]^2[\text{H}_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer: order in NO = 2; order in H_2 = 1; overall order = 3

Check Your Learning

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($CH_3CH_2OCOCH_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$\text{CH}_3\text{OH} + \text{CH}_3\text{CH}_2\text{OCOCH}_3 \longrightarrow \text{CH}_3\text{OCOCH}_3 + \text{CH}_3\text{CH}_2\text{OH}$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, determined to be:

$$\text{rate} = k[\text{CH}_3\text{OH}]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer: order in CH_3OH = 1; order in $CH_3CH_2OCOCH_3$ = 0; overall order = 1

A common experimental approach to the determination of rate laws is the **method of initial rates**. This method involves measuring reaction rates for multiple experimental trials carried out using different initial reactant concentrations. Comparing the measured rates for these trials permits determination of the reaction orders and, subsequently, the rate constant, which together are used to formulate a rate law. This approach is illustrated in the next two example exercises.

Example 17.4

Determining a Rate Law from Initial Rates

Ozone in the upper atmosphere is depleted when it reacts with nitrogen oxides. The rates of the reactions of nitrogen oxides with ozone are important factors in deciding how significant these reactions are in the formation of the ozone hole over Antarctica (Figure 17.8). One such reaction is the combination of nitric oxide, NO, with ozone, O_3:

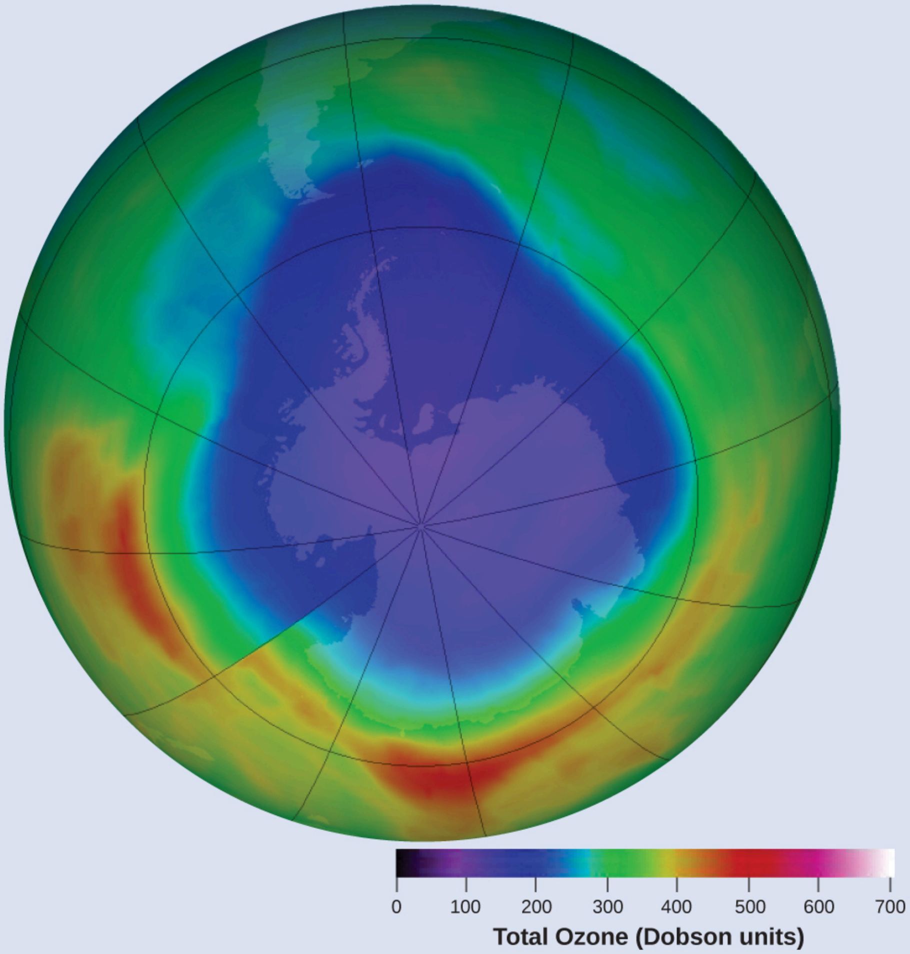


Figure 17.8 A contour map showing stratospheric ozone concentration and the “ozone hole” that occurs over Antarctica during its spring months. (credit: modification of work by NASA)

$$\mathrm{NO}(g) + \mathrm{O}_3(g) \longrightarrow \mathrm{NO}_2(g) + \mathrm{O}_2(g)$$

This reaction has been studied in the laboratory, and the following rate data were determined at 25 °C.

Trial	[NO] (mol/L)	$[O_3]$ (mol/L)	$\frac{\Delta[NO_2]}{\Delta t}$ (mol L^{-1} s^{-1})
1	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}
2	1.00×10^{-6}	6.00×10^{-6}	1.32×10^{-4}
3	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
4	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
5	3.00×10^{-6}	9.00×10^{-6}	5.94×10^{-4}

Determine the rate law and the rate constant for the reaction at 25 °C.

Solution

The rate law will have the form:

$$\text{rate} = k[\text{NO}]^m[\text{O}_3]^n$$

Determine the values of *m*, *n*, and *k* from the experimental data using the following three-part process:

Step 1. *Determine the value of* m *from the data in which [NO] varies and [O_3] is constant.* In the last three experiments, [NO] varies while [O_3] remains constant. When [NO] doubles from trial 3 to 4, the rate doubles, and when [NO] triples from trial 3 to 5, the rate also triples. Thus, the rate is also directly proportional to [NO], and *m* in the rate law is equal to 1.

Step 2. *Determine the value of* n *from data in which [O_3] varies and [NO] is constant.* In the first three experiments, [NO] is constant and [O_3] varies. The reaction rate changes in direct proportion to the change in [O_3]. When [O_3] doubles from trial 1 to 2, the rate doubles; when [O_3] triples from trial 1 to 3, the rate increases also triples. Thus, the rate is directly proportional to [O_3], and *n* is equal to 1.The rate law is thus:

$$\text{rate} = k[\text{NO}]^1[\text{O}_3]^1 = k[\text{NO}][\text{O}_3]$$

Step 3. *Determine the value of* k *from one set of concentrations and the corresponding rate*. The data from trial 1 are used below:

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{NO}][\text{O}_3]} \\ &= \frac{6.60 \times 10^{-5}\ \cancel{\text{mol L}^{-1}}\text{s}^{-1}}{\left(1.00 \times 10^{-6}\ \cancel{\text{mol L}^{-1}}\right)(3.00 \times 10^{-6}\ \text{mol L}^{-1})} \\ &= 2.20 \times 10^{7}\ \text{L mol}^{-1}\ \text{s}^{-1} \end{aligned}$$

Check Your Learning

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:

$$\text{CH}_3\text{CHO}(g) \longrightarrow \text{CH}_4(g) + \text{CO}(g)$$

Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	$[CH_3CHO]$ (mol/L)	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t}$ (mol L^{-1} s^{-1})
1	1.75×10^{-3}	2.06×10^{-11}
2	3.50×10^{-3}	8.24×10^{-11}

Trial	$[CH_3CHO]$ (mol/L)	$-\frac{\Delta[CH_3CHO]}{\Delta t}\,(\text{mol L}^{-1}\,\text{s}^{-1})$
3	7.00×10^{-3}	3.30×10^{-10}

Answer: $\text{rate} = k[CH_3CHO]^2$ with $k = 6.73 \times 10^{-6}$ L/mol/s

Example 17.5

Determining Rate Laws from Initial Rates

Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

Trial	[NO] (mol/L)	$[Cl_2]$ (mol/L)	$-\frac{\Delta[NO]}{\Delta t}\,(\text{mol L}^{-1}\,\text{s}^{-1})$
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Solution

The rate law for this reaction will have the form:

$$\text{rate} = k[NO]^m[Cl_2]^n$$

As in **Example 17.4**, approach this problem in a stepwise fashion, determining the values of m and n from the experimental data and then using these values to determine the value of k. In this example, however, an explicit algebraic approach (vs. the implicit approach of the previous example) will be used to determine the values of m and n:

Step 1. *Determine the value of* m *from the data in which [NO] varies and [Cl$_2$] is constant*. Write the ratios with the subscripts x and y to indicate data from two different trials:

$$\frac{\text{rate}_x}{\text{rate}_y} = \frac{k[NO]_x^m[Cl_2]_x^n}{k[NO]_y^m[Cl_2]_y^n}$$

Using the third trial and the first trial, in which $[Cl_2]$ does not vary, gives:

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{0.00675}{0.00300} = \frac{k(0.15)^m(0.10)^n}{k(0.10)^m(0.10)^n}$$

Canceling equivalent terms in the numerator and denominator leaves:

$$\frac{0.00675}{0.00300} = \frac{(0.15)^m}{(0.10)^m}$$

which simplifies to:

$$2.25 = (1.5)^m$$

Use logarithms to determine the value of the exponent m:

$$\begin{aligned}\ln(2.25) &= m\ln(1.5)\\ \frac{\ln(2.25)}{\ln(1.5)} &= m\\ 2 &= m\end{aligned}$$

Confirm the result

$$1.5^2 = 2.25$$

Step 2. *Determine the value of* n *from data in which [Cl₂] varies and [NO] is constant.*

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{0.00450}{0.00300} = \frac{k(0.10)^m(0.15)^n}{k(0.10)^m(0.10)^n}$$

Cancelation gives:

$$\frac{0.0045}{0.0030} = \frac{(0.15)^n}{(0.10)^n}$$

which simplifies to:

$$1.5 = (1.5)^n$$

Thus n must be 1, and the form of the rate law is:

$$\text{rate} = k[\text{NO}]^m[\text{Cl}_2]^n = k[\text{NO}]^2[\text{Cl}_2]$$

Step 3. *Determine the numerical value of the rate constant* k *with appropriate units.* The units for the rate of a reaction are mol/L/s. The units for k are whatever is needed so that substituting into the rate law expression affords the appropriate units for the rate. In this example, the concentration units are mol^3/L^3. The units for k should be $\text{mol}^{-2}\ \text{L}^2/\text{s}$ so that the rate is in terms of mol/L/s.

To determine the value of k once the rate law expression has been solved, simply plug in values from the first experimental trial and solve for k:

$$\begin{aligned}0.00300\ \text{mol L}^{-1}\ \text{s}^{-1} &= k\left(0.10\ \text{mol L}^{-1}\right)^2\left(0.10\ \text{mol L}^{-1}\right)^1\\ k &= 3.0\ \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-1}\end{aligned}$$

Check Your Learning

Use the provided initial rate data to derive the rate law for the reaction whose equation is:

$$\text{OCl}^-(aq) + \text{I}^-(aq) \longrightarrow \text{OI}^-(aq) + \text{Cl}^-(aq)$$

Trial	$[\text{OCl}^-]$ (mol/L)	$[\text{I}^-]$ (mol/L)	Initial Rate (mol/L/s)
1	0.0040	0.0020	0.00184
2	0.0020	0.0040	0.00092
3	0.0020	0.0020	0.00046

Determine the rate law expression and the value of the rate constant k with appropriate units for this reaction.

Answer:

$$\frac{\text{rate 2}}{\text{rate 3}} = \frac{0.00092}{0.00046} = \frac{k(0.0020)^x(0.0040)^y}{k(0.0020)^x(0.0020)^y}$$

$$2.00 = 2.00^y$$

$$y = 1$$

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{0.00184}{0.00092} = \frac{k(0.0040)^x(0.0020)^y}{k(0.0020)^x(0.0040)^y}$$

$$\begin{aligned} 2.00 &= \frac{2^x}{2^y} \\ 2.00 &= \frac{2^x}{2^1} \\ 4.00 &= 2^x \\ x &= 2 \end{aligned}$$

Substituting the concentration data from trial 1 and solving for k yields:

$$\begin{aligned} \text{rate} &= k[\text{OCl}^-]^2[\text{I}^-]^1 \\ 0.00184 &= k(0.0040)^2(0.0020)^1 \\ k &= 5.75 \times 10^4\ \text{mol}^{-2}\ \text{L}^2\,\text{s}^{-1} \end{aligned}$$

Reaction Order and Rate Constant Units

In some of our examples, the reaction orders in the rate law happen to be the same as the coefficients in the chemical equation for the reaction. This is merely a coincidence and very often not the case.

Rate laws may exhibit fractional orders for some reactants, and negative reaction orders are sometimes observed when an increase in the concentration of one reactant causes a decrease in reaction rate. A few examples illustrating these points are provided:

$$\begin{aligned} &\text{NO}_2 + \text{CO} \longrightarrow \text{NO} + \text{CO}_2 && \text{rate} = k[\text{NO}_2]^2 \\ &\text{CH}_3\text{CHO} \longrightarrow \text{CH}_4 + \text{CO} && \text{rate} = k[\text{CH}_3\text{CHO}]^2 \\ &2\text{N}_2\text{O}_5 \longrightarrow 2\text{NO}_2 + \text{O}_2 && \text{rate} = k[\text{N}_2\text{O}_5] \\ &2\text{NO}_2 + \text{F}_2 \longrightarrow 2\text{NO}_2\text{F} && \text{rate} = k[\text{NO}_2][\text{F}_2] \\ &2\text{NO}_2\text{Cl} \longrightarrow 2\text{NO}_2 + \text{Cl}_2 && \text{rate} = k[\text{NO}_2\text{Cl}] \end{aligned}$$

It is important to note that *rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry.*

The units for a rate constant will vary as appropriate to accommodate the overall order of the reaction. The unit of the rate constant for the second-order reaction described in **Example 17.4** was determined to be $\text{L mol}^{-1}\ \text{s}^{-1}$. For the third-order reaction described in **Example 17.5**, the unit for k was derived to be $\text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$. Dimensional analysis requires the rate constant unit for a reaction whose overall order is x to be $\text{L}^{x-1}\ \text{mol}^{1-x}\ \text{s}^{-1}$. **Table 17.1** summarizes the rate constant units for common reaction orders.

Rate Constant Units for Common Reaction Orders

Overall Reaction Order (x)	Rate Constant Unit ($\text{L}^{x-1}\ \text{mol}^{1-x}\ \text{s}^{-1}$)
0 (zero)	$\text{mol L}^{-1}\ \text{s}^{-1}$
1 (first)	s^{-1}
2 (second)	$\text{L mol}^{-1}\ \text{s}^{-1}$
3 (third)	$\text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$

Table 17.1

Note that the units in this table were derived using specific units for concentration (mol/L) and time (s), though any valid units for these two properties may be used.

17.4 Integrated Rate Laws

By the end of this section, you will be able to:

- Explain the form and function of an integrated rate law
- Perform integrated rate law calculations for zero-, first-, and second-order reactions
- Define half-life and carry out related calculations
- Identify the order of a reaction from concentration/time data

The rate laws discussed thus far relate the rate and the concentrations of reactants. We can also determine a second form of each rate law that relates the concentrations of reactants and time. These are called **integrated rate laws**. We can use an integrated rate law to determine the amount of reactant or product present after a period of time or to estimate the time required for a reaction to proceed to a certain extent. For example, an integrated rate law is used to determine the length of time a radioactive material must be stored for its radioactivity to decay to a safe level.

Using calculus, the differential rate law for a chemical reaction can be integrated with respect to time to give an equation that relates the amount of reactant or product present in a reaction mixture to the elapsed time of the reaction. This process can either be very straightforward or very complex, depending on the complexity of the differential rate law. For purposes of discussion, we will focus on the resulting integrated rate laws for first-, second-, and zero-order reactions.

First-Order Reactions

Integration of the rate law for a simple first-order reaction (rate = $k[A]$) results in an equation describing how the reactant concentration varies with time:

$$[A]_t = [A]_0 e^{-kt}$$

where $[A]t$ is the concentration of A at any time t, $[A]_0$ is the initial concentration of A, and k is the first-order rate constant.

For mathematical convenience, this equation may be rearranged to other formats, including direct and indirect proportionalities:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = kt \qquad \text{or} \qquad \ln\left(\frac{[A]_0}{[A]_t}\right) = -kt$$

and a format showing a linear dependence of concentration in time:

$$\ln[A]_t = \ln[A]_0 - kt$$

Example 17.6

The Integrated Rate Law for a First-Order Reaction

The rate constant for the first-order decomposition of cyclobutane, C_4H_8 at 500 °C is $9.2 \times 10^{-3}\ s^{-1}$:

$$C_4H_8 \longrightarrow 2C_2H_4$$

How long will it take for 80.0% of a sample of C_4H_8 to decompose?

Solution

Since the relative change in reactant concentration is provided, a convenient format for the integrated rate law is:

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

The initial concentration of C_4H_8, $[A]_0$, is not provided, but the provision that 80.0% of the sample has decomposed is enough information to solve this problem. Let x be the initial concentration, in which case the concentration after 80.0% decomposition is 20.0% of x or $0.200x$. Rearranging the rate law to isolate t and substituting the provided quantities yields:

$$\begin{aligned} t &= \ln \frac{[x]}{[0.200x]} \times \frac{1}{k} \\ &= \ln 5 \times \frac{1}{9.2 \times 10^{-3}\ \text{s}^{-1}} \\ &= 1.609 \times \frac{1}{9.2 \times 10^{-3}\ \text{s}^{-1}} \\ &= 1.7 \times 10^{2}\ \text{s} \end{aligned}$$

Check Your Learning

Iodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer. Iodine-131 decays to xenon-131 according to the equation:

$$\text{I-131} \longrightarrow \text{Xe-131} + \text{electron}$$

The decay is first-order with a rate constant of 0.138 d^{-1}. How many days will it take for 90% of the iodine−131 in a 0.500 *M* solution of this substance to decay to Xe-131?

Answer: 16.7 days

In the next example exercise, a linear format for the integrated rate law will be convenient:

$$\begin{aligned} \ln[A]_t &= (-k)(t) + \ln[A]_0 \\ y &= mx + b \end{aligned}$$

A plot of $\ln[A]_t$ versus t for a first-order reaction is a straight line with a slope of $-k$ and a y-intercept of $\ln[A]_0$. If a set of rate data are plotted in this fashion but do *not* result in a straight line, the reaction is not first order in A.

Example 17.7

Graphical Determination of Reaction Order and Rate Constant

Show that the data in **Figure 17.2** can be represented by a first-order rate law by graphing $\ln[H_2O_2]$ versus time. Determine the rate constant for the decomposition of H_2O_2 from these data.

Solution

The data from **Figure 17.2** are tabulated below, and a plot of $\ln[H_2O_2]$ is shown in **Figure 17.9**.

Trial	Time (h)	$[H_2O_2]$ (*M*)	$\ln[H_2O_2]$
1	0.00	1.000	0.000
2	6.00	0.500	−0.693
3	12.00	0.250	−1.386
4	18.00	0.125	−2.079
5	24.00	0.0625	−2.772

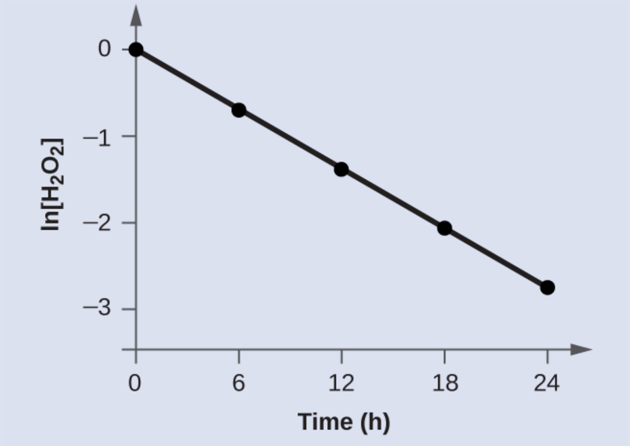


Figure 17.9 A linear relationship between ln[H_2O_2] and time suggests the decomposition of hydrogen peroxide is a first-order reaction.

The plot of ln[H_2O_2] versus time is linear, indicating that the reaction may be described by a first-order rate law.

According to the linear format of the first-order integrated rate law, the rate constant is given by the negative of this plot's slope.

$$\text{slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln\left[\text{H}_2\text{O}_2\right]}{\Delta t}$$

The slope of this line may be derived from two values of ln[H_2O_2] at different values of t (one near each end of the line is preferable). For example, the value of ln[H_2O_2] when t is 0.00 h is 0.000; the value when t = 24.00 h is −2.772

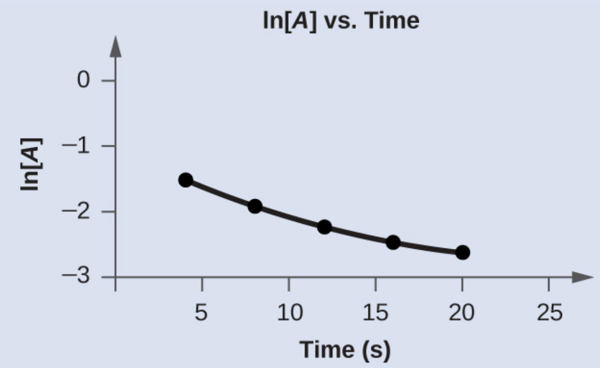
$$\begin{aligned} \text{slope} &= \frac{-2.772 - 0.000}{24.00 - 0.00\text{ h}} \\ &= \frac{-2.772}{24.00\text{ h}} \\ &= -0.116\text{ h}^{-1} \\ k &= -\text{slope} = -\left(-0.116\text{ h}^{-1}\right) = 0.116\text{ h}^{-1} \end{aligned}$$

Check Your Learning

Graph the following data to determine whether the reaction $A \longrightarrow B + C$ is first order.

Trial	Time (s)	[*A*]
1	4.0	0.220
2	8.0	0.144
3	12.0	0.110
4	16.0	0.088
5	20.0	0.074

Answer: The plot of ln$[A]_t$ vs. t is not linear, indicating the reaction is not first order:



Second-Order Reactions

The equations that relate the concentrations of reactants and the rate constant of second-order reactions can be fairly complicated. To illustrate the point with minimal complexity, only the simplest second-order reactions will be described here, namely, those whose rates depend on the concentration of just one reactant. For these types of reactions, the differential rate law is written as:

$$\text{rate} = k[A]^2$$

For these second-order reactions, the integrated rate law is:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

where the terms in the equation have their usual meanings as defined earlier.

Example 17.8

The Integrated Rate Law for a Second-Order Reaction

The reaction of butadiene gas (C_4H_6) to yield C_8H_{12} gas is described by the equation:

$$2C_4H_6(g) \longrightarrow C_8H_{12}(g)$$

This "dimerization" reaction is second order with a rate constant equal to 5.76×10^{-2} L mol^{-1} min^{-1} under certain conditions. If the initial concentration of butadiene is 0.200 *M*, what is the concentration after 10.0 min?

Solution

For a second-order reaction, the integrated rate law is written

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

We know three variables in this equation: $[A]_0 = 0.200$ mol/L, $k = 5.76 \times 10^{-2}$ L/mol/min, and $t = 10.0$ min. Therefore, we can solve for [*A*], the fourth variable: