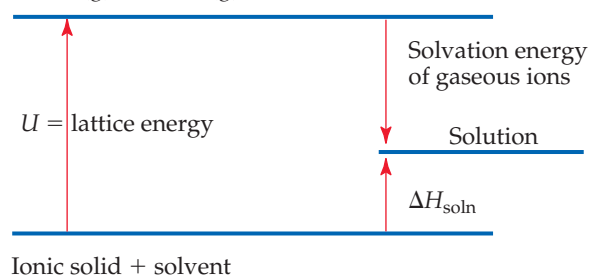


it to be more soluble in nonpolar  $\text{CCl}_4$ . (b) Dioxane can act as a hydrogen bond acceptor, so it will be more soluble than cyclohexane in water. **13.33** (a)  $\text{CCl}_4$  is more soluble because dispersion forces among nonpolar  $\text{CCl}_4$  molecules are similar to dispersion forces in hexane. (b)  $\text{C}_6\text{H}_6$  is a nonpolar hydrocarbon and will be more soluble in the similarly nonpolar hexane. (c) The long, rodlike hydrocarbon chain of octanoic acid forms strong dispersion interactions and causes it to be more soluble in hexane. **13.35** (a) A sealed container is required to maintain a partial pressure of  $\text{CO}_2(\text{g})$  greater than 1 atm above the beverage. (b) Since the solubility of gases increases with decreasing temperature, more  $\text{CO}_2(\text{g})$  will remain dissolved in the beverage if it is kept cool. **13.37**  $S_{\text{He}} = 5.6 \times 10^{-4} \text{ M}$ ,  $S_{\text{N}_2} = 9.0 \times 10^{-4} \text{ M}$  **13.39** (a) 2.15%  $\text{Na}_2\text{SO}_4$  by mass (b) 3.15 ppm Ag **13.41** (a)  $X_{\text{CH}_3\text{OH}} = 0.0427$  (b) 7.35%  $\text{CH}_3\text{OH}$  by mass (c) 2.48 *m*  $\text{CH}_3\text{OH}$  **13.43** (a)  $1.46 \times 10^{-2} \text{ M Mg}(\text{NO}_3)_2$  (b) 1.12 *M*  $\text{LiClO}_4 \cdot 3 \text{ H}_2\text{O}$  (c) 0.350 *M*  $\text{HNO}_3$  **13.45** (a) 4.70 *m*  $\text{C}_6\text{H}_6$  (b) 0.235 *m*  $\text{NaCl}$  **13.47** (a) 43.01%  $\text{H}_2\text{SO}_4$  by mass (b)  $X_{\text{H}_2\text{SO}_4} = 0.122$  (c) 7.69 *m*  $\text{H}_2\text{SO}_4$  (d) 5.827 *M*  $\text{H}_2\text{SO}_4$  **13.49** (a)  $X_{\text{CH}_3\text{OH}} = 0.227$  (b) 7.16 *m*  $\text{CH}_3\text{OH}$  (c) 4.58 *M*  $\text{CH}_3\text{OH}$  **13.51** (a) 0.150 mol  $\text{SrBr}_2$  (b)  $1.56 \times 10^{-2}$  mol  $\text{KCl}$  (c)  $4.44 \times 10^{-2}$  mol  $\text{C}_6\text{H}_{12}\text{O}_6$  **13.53** (a) Weigh out 1.3 g  $\text{KBr}$ , dissolve in water, dilute with stirring to 0.75 L. (b) Weigh out 2.62 g  $\text{KBr}$ , dissolve it in 122.38 g  $\text{H}_2\text{O}$  to make exactly 125 g of 0.180 *m* solution. (c) Dissolve 244 g  $\text{KBr}$  in water, dilute with stirring to 1.85 L. (d) Weigh 10.1 g  $\text{KBr}$ , dissolve it in a small amount of water, and dilute to 0.568 L. **13.55** 71%  $\text{HNO}_3$  by mass **13.57** (a) 3.82 *m*  $\text{Zn}$  (b) 26.8 *M*  $\text{Zn}$  **13.59**  $1.8 \times 10^{-3} \text{ MCO}_2$  **13.61** Freezing point depression,  $\Delta T_f = K_f(m)$ ; boiling-point elevation,  $\Delta T_b = K_b(m)$ ; osmotic pressure,  $\Pi = MRT$ ; vapor pressure lowering,  $P_A = X_A P_A^\circ$  **13.63** (a) Sucrose has a greater molar mass than glucose, so the sucrose solution will contain fewer particles and have a higher vapor pressure. **13.65** (a)  $P_{\text{H}_2\text{O}} = 186.4$  torr (b) 78.9 g  $\text{C}_3\text{H}_8\text{O}_2$  **13.67** (a)  $X_{\text{Eth}} = 0.2812$  (b)  $P_{\text{soln}} = 238$  torr (c)  $X_{\text{Eth}}$  in vapor = 0.472 **13.69** (a) Because  $\text{NaCl}$  is a strong electrolyte, one mole of  $\text{NaCl}$  produces twice as many dissolved particles as one mole of the molecular solute  $\text{C}_6\text{H}_{12}\text{O}_6$ . Boiling-point elevation is directly related to total moles of dissolved particles, so 0.10 *m*  $\text{NaCl}$  has the higher boiling point. (b) 0.10 *m*  $\text{NaCl}$ :  $\Delta T_b = 0.101^\circ\text{C}$ ,  $T_b = 100.1^\circ\text{C}$ ; 0.10 *m*  $\text{C}_6\text{H}_{12}\text{O}_6$ :  $\Delta T_b = 0.051^\circ\text{C}$ ,  $T_b = 100.1^\circ\text{C}$  (c) Interactions between ions in solution result in nonideal behavior. **13.71** 0.050 *m*  $\text{LiBr} < 0.120 \text{ m glucose} < 0.050 \text{ m Zn}(\text{NO}_3)_2$  **13.73** (a)  $T_f = -115.0^\circ\text{C}$ ,  $T_b = 78.7^\circ\text{C}$  (b)  $T_f = -67.3^\circ\text{C}$ ,  $T_b = 64.2^\circ\text{C}$  (c)  $T_f = -0.4^\circ\text{C}$ ,  $T_b = 100.1^\circ\text{C}$  (c)  $T_f = -0.6^\circ\text{C}$ ,  $T_b = 100.2^\circ\text{C}$  **13.75** 167 g  $\text{C}_2\text{H}_6\text{O}_2$  **13.77**  $\Pi = 0.0168 \text{ atm} = 12.7 \text{ torr}$  **13.79** Experimental molar mass of adrenaline is  $1.8 \times 10^2 \text{ g}$ . The structure shows a molecular formula of  $\text{C}_9\text{H}_{13}\text{NO}_3$ , with a molar mass of 183 g. The two values agree to two significant figures, the precision of the experiment. **13.81** Molar mass of lysozyme =  $1.39 \times 10^4 \text{ g}$  **13.83** (a)  $i = 2.8$  (b) The more concentrated the solution, the greater the ion pairing and the smaller the measured value of  $i$ . **13.85** (a) In the gaseous state, particles are far apart and intermolecular attractive forces are small. When two gases combine, all terms in Equation 13.1 are essentially zero and the mixture is always homogeneous. (b) To determine whether Faraday's dispersion is a true solution or a colloid, shine a beam of light on it. If light is scattered, the dispersion is a colloid. **13.87** (a) Hydrophobic (b) hydrophilic (c) hydrophobic (d) hydrophobic (but stabilized by adsorbed charges). **13.89** When electrolytes are added to a suspension of proteins, dissolved ions form ion pairs with the protein surface charges, effectively neutralizing them. The protein's capacity for ion-dipole interactions with water is diminished and the colloid separates into a protein layer and a water layer. **13.91** The periphery of the BHT molecule is mostly hydrocarbon-like groups, such as  $-\text{CH}_3$ . The one  $-\text{OH}$  group is rather buried inside and probably does little to enhance solubility in water. Thus, BHT is more likely to be soluble in the nonpolar hydrocarbon hexane,  $\text{C}_6\text{H}_{14}$ , than in polar water. **13.94** (a)  $k_{\text{Rn}} = 7.27 \times 10^{-3} \text{ mol/L-atm}$  (b)  $P_{\text{Rn}} = 1.1 \times 10^{-4} \text{ atm}$ ;  $S_{\text{Rn}} = 8.1 \times 10^{-7} \text{ M}$  **13.98** (a) 2.69 *m*  $\text{LiBr}$  (b)  $X_{\text{LiBr}} = 0.0994$  (c) 81.1%  $\text{LiBr}$  by mass **13.100**  $X_{\text{H}_2\text{O}} = 0.808$ ; 0.0273 mol ions; 0.0136 mol  $\text{NaCl}$  **13.103** (a)  $-0.6^\circ\text{C}$  (b)  $-0.4^\circ\text{C}$  **13.106** (a)  $\text{CF}_4$ ,  $1.7 \times 10^{-4} \text{ m}$ ;  $\text{CClF}_3$ ,  $9 \times 10^{-4} \text{ m}$ ;  $\text{CCl}_2\text{F}_2$ ,  $2.3 \times 10^{-2} \text{ m}$ ;  $\text{CHClF}_2$ ,

$3.5 \times 10^{-2} \text{ m}$  (b) Molality and molarity are numerically similar when kilograms solvent and liters solution are nearly equal. This is true when solutions are dilute and when the density of the solvent is nearly 1 g/mL, as in this exercise. (c) Water is a polar solvent; the solubility of solutes increases as their polarity increases. Nonpolar  $\text{CF}_4$  has the lowest solubility and the most polar fluorocarbon,  $\text{CHClF}_2$ , has the greatest solubility in  $\text{H}_2\text{O}$ . (d) The Henry's law constant for  $\text{CHClF}_2$  is  $3.5 \times 10^{-2} \text{ mol/L-atm}$ . This value is greater than the Henry's law constant for  $\text{N}_2(\text{g})$  because  $\text{N}_2(\text{g})$  is nonpolar and of lower molecular mass than  $\text{CHClF}_2$ .

**13.109**

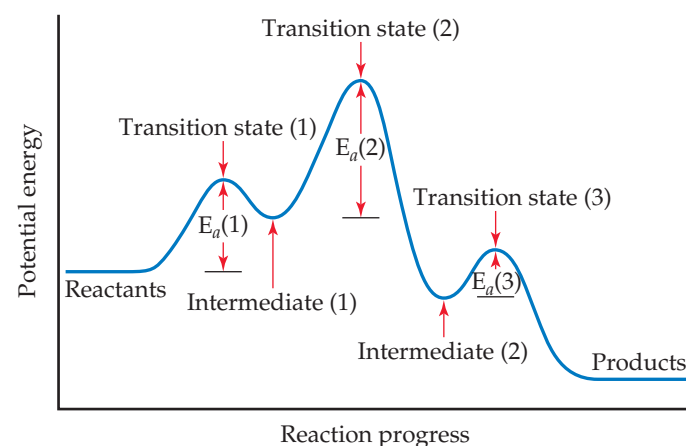
(a) cation (g) + anion (g) + solvent



(b) Lattice energy ( $U$ ) is inversely related to the distance between ions, so salts with large cations like  $(\text{CH}_3)_4\text{N}^+$  have smaller lattice energies than salts with simple cations like  $\text{Na}^+$ . Also the  $-\text{CH}_3$  groups in the large cation are capable of dispersion interactions with nonpolar groups of the solvent molecules, resulting in a more negative solvation energy of the gaseous ions. Overall, for salts with larger cations, lattice energy is smaller (less positive), the solvation energy of the gaseous ions is more negative, and  $\Delta H_{\text{soln}}$  is less endothermic. These salts are more soluble in polar nonaqueous solvents. **13.112** The freezing point of the  $\text{LiOH}(\text{aq})$  solution is essentially zero,  $T_f = -0.00058^\circ\text{C}$ .

**CHAPTER 14**

**14.1** Vessel 2 **14.3** Equation (d) **14.9** (1) Total potential energy of the reactants (2)  $E_a$ , activation energy of the reaction (3)  $\Delta E$ , net energy change for the reaction (4) total potential energy of the products **14.12** (a)  $\text{NO}_2 + \text{F}_2 \longrightarrow \text{NO}_2\text{F} + \text{F}$ ;  $\text{NO}_2 + \text{F} \longrightarrow \text{NO}_2\text{F}$  (b)  $2\text{NO}_2 + \text{F}_2 \longrightarrow 2\text{NO}_2\text{F}$  (c) F (atomic fluorine) is the intermediate (d) rate =  $k[\text{NO}_2][\text{F}_2]$

**14.16**

**14.17** (a) Reaction rate is the change in the amount of products or reactants in a given amount of time. (b) Rates depend on concentration of reactants, surface area of reactants, temperature, and presence of catalyst. (c) The stoichiometry of the reaction (mole ratios of reactants and products) must be known to relate rate of disappearance of reactants to rate of appearance of products.

## 14.19

Time (min)	Mol A	(a) Mol B	[A] (mol/L)	$\Delta[A]$ (mol/L)	(b) Rate (M/s)
0	0.065	0.000	0.65		
10	0.051	0.014	0.51	-0.14	$2.3 \times 10^{-4}$
20	0.042	0.023	0.42	-0.09	$1.5 \times 10^{-4}$
30	0.036	0.029	0.36	-0.06	$1.0 \times 10^{-4}$
40	0.031	0.034	0.31	-0.05	$0.8 \times 10^{-4}$

(c)  $\Delta[B]_{\text{avg}}/\Delta t = 1.3 \times 10^{-4} \text{ M/s}$ 

14.21 (a)

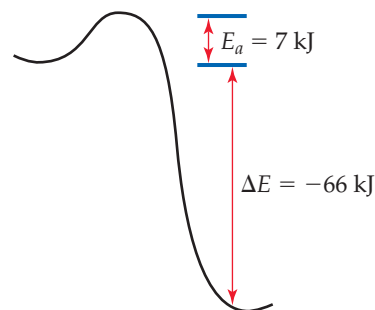
Time (s)	Time Interval (s)	Concentration (M)	$\Delta M$	Rate (M/s)
0		0.0165		
2,000	2,000	0.0110	-0.0055	$28 \times 10^{-7}$
5,000	3,000	0.00591	-0.0051	$17 \times 10^{-7}$
8,000	3,000	0.00314	-0.00277	$9.23 \times 10^{-7}$
12,000	4,000	0.00137	-0.00177	$4.43 \times 10^{-7}$
15,000	3,000	0.00074	-0.00063	$2.1 \times 10^{-7}$

(b) The average rate of reaction is  $1.05 \times 10^{-6} \text{ M/s}$ . (c) From the slopes of the tangents to the graph, the rates are  $12 \times 10^{-7} \text{ M/s}$  at 5000 s,  $5.8 \times 10^{-7} \text{ M/s}$  at 8000 s.

14.23

(a)  $-\Delta[\text{H}_2\text{O}_2]/\Delta t = \Delta[\text{H}_2]/\Delta t = \Delta[\text{O}_2]/\Delta t$ (b)  $-\frac{1}{2}\Delta[\text{N}_2\text{O}]/\Delta t = \frac{1}{2}\Delta[\text{N}_2]/\Delta t = \Delta[\text{O}_2]/\Delta t$ (c)  $-\Delta[\text{N}_2]/\Delta t = -1/3\Delta[\text{H}_2]/\Delta t = -1/2\Delta[\text{NH}_3]/2\Delta t$ (d)  $-\Delta[\text{C}_2\text{H}_5\text{NH}_2]/\Delta t = \Delta[\text{C}_2\text{H}_4]/\Delta t = \Delta[\text{NH}_3]/\Delta t$ 14.25 (a)  $-\Delta[\text{O}_2]/\Delta t = 0.24 \text{ mol/s}$ ;  $\Delta[\text{H}_2\text{O}]/\Delta t = 0.48 \text{ mol/s}$ (b)  $P_{\text{total}}$  decreases by 28 torr/min. 14.27 (a) If  $[\text{A}]$  doubles, there is no change in the rate or the rate constant. The overall rate is unchanged because  $[\text{A}]$  does not appear in the rate law; the rate constant changes only with a change in temperature. (b) The reaction is zero order in A, second order in B, and second order overall. (c) units of  $k = \text{M}^{-1}\text{s}^{-1}$ 14.29 (a) Rate =  $k[\text{N}_2\text{O}_5]$  (b) Rate =  $1.16 \times 10^{-4} \text{ M/s}$  (c) When the concentration of  $\text{N}_2\text{O}_5$  doubles, the rate doubles. (d) When the concentration of  $\text{N}_2\text{O}_5$  is halved, the rate doubles.14.31 (a, b)  $k = 1.7 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$  (c) If  $[\text{OH}^-]$  is tripled, the rate triples. (d) If  $[\text{OH}^-]$  and  $[\text{CH}_3\text{Br}]$  both triple, the rate increases by a factor of 9. 14.33 (a) Rate =  $k[\text{OCl}^-][\text{I}^-]$  (b)  $k = 60 \text{ M}^{-1}\text{s}^{-1}$ (c) Rate =  $6.0 \times 10^{-5} \text{ M/s}$  14.35 (a) Rate =  $k[\text{BF}_3][\text{NH}_3]$  (b) The reaction is second order overall. (c)  $k_{\text{avg}} = 3.41 \text{ M}^{-1}\text{s}^{-1}$  (d)  $0.170 \text{ M/s}$ 14.37 (a) Rate =  $k[\text{NO}]^2[\text{Br}_2]$  (b)  $k_{\text{avg}} = 1.2 \times 10^4 \text{ M}^{-2}\text{s}^{-1}$ (c)  $\frac{1}{2}\Delta[\text{NOBr}]/\Delta t = -\Delta[\text{Br}_2]/\Delta t$  (d)  $-\Delta[\text{Br}_2]/\Delta t = 8.4 \text{ M/s}$ 14.39 (a)  $[\text{A}]_0$  is the molar concentration of reactant A at time zero.  $[\text{A}]_t$  is the molar concentration of reactant A at time  $t$ .  $t_{1/2}$  is the time required to reduce  $[\text{A}]_0$  by a factor of 2.  $k$  is the rate constant for a particular reaction. (b) A graph of  $\ln[\text{A}]$  versus time yields a straight line for a first-order reaction. (c) On a graph of  $\ln[\text{A}]$  versus time, the rate constant is the (-slope) of the straight line. 14.41 Plot  $[\text{A}]$  versus time. 14.43 (a)  $k = 3.0 \times 10^{-8} \text{ s}^{-1}$  (b)  $t_{1/2} = 3.2 \times 10^4 \text{ s}$ 14.45 (a)  $P = 30 \text{ torr}$  (b)  $t = 51 \text{ s}$  14.47 Plot  $(\ln P_{\text{SO}_2\text{Cl}_2})$  versus time,  $k = -\text{slope} = 2.19 \times 10^{-5} \text{ s}^{-1}$  14.49 (a) The plot of  $1/[\text{A}]$  versus time is linear, so the reaction is second order in  $[\text{A}]$ .(b)  $k = 0.040 \text{ M}^{-1}\text{min}^{-1}$  (c)  $t_{1/2} = 38 \text{ min}$  14.51 (a) The plot of  $1/[\text{NO}_2]$  versus time is linear, so the reaction is second order in  $\text{NO}_2$ .(b)  $k = \text{slope} = 10 \text{ M}^{-1}\text{s}^{-1}$  (c) rate at  $0.200 \text{ M} = 0.400 \text{ M/s}$ ; rate at  $0.100 \text{ M} = 0.100 \text{ M/s}$ ; rate at  $0.050 \text{ M} = 0.025 \text{ M/s}$  14.53 (a) The energy of the collision and the orientation of the molecules when they collide determine whether a reaction will occur. (b) At a higher temperature, there are more total collisions and each collision is moreenergetic. (c) The rate constant usually increases with an increase in reaction temperature. 14.55  $f = 4.94 \times 10^{-2}$ . At 400 K approximately 1 out of 20 molecules has this kinetic energy.

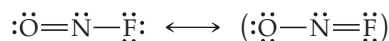
14.57 (a)

(b)  $E_a$  (reverse) = 73 kJ 14.59 (a) False. If you compare two reactions with similar collision factors, the one with the larger activation energy will be slower. (b) False. A reaction that has a small rate constant will have either a small frequency factor, a large activation energy, or both. (c) True. 14.61 Reaction (b) is fastest and reaction (c) is slowest. 14.63 (a)  $k = 1.1 \text{ s}^{-1}$  (b)  $k = 13 \text{ s}^{-1}$  (c) The method in parts (a) and (b) assumes that the collision model and thus the Arrhenius equation describe the kinetics of the reactions. That is, activation energy is constant over the temperature range under consideration.14.65 A plot of  $\ln k$  versus  $1/T$  has a slope of  $-5.71 \times 10^3$ ;  $E_a = -R(\text{slope}) = 47.5 \text{ kJ/mol}$ . 14.67 The reaction will occur 88 times faster at  $50^\circ\text{C}$ , assuming equal initial concentrations.14.69 (a) An elementary reaction is a process that occurs in a single event; the order is given by the coefficients in the balanced equation for the reaction. (b) A unimolecular elementary reaction involves only one reactant molecule; a bimolecular elementary reaction involves two reactant molecules. (c) A reaction mechanism is a series of elementary reactions that describes how an overall reaction occurs and explains the experimentally determined rate law. 14.71 A transition state is a high-energy complex formed when one or more reactants collide and distort in a way that can lead to formation of product(s). An intermediate is the product of an early elementary reaction in a multistep reaction mechanism. 14.73 (a) Unimolecular, rate =  $k[\text{Cl}_2]$  (b) bimolecular, rate =  $k[\text{OCl}^-][\text{H}_2\text{O}]$  (c) bimolecular, rate =  $k[\text{NO}][\text{Cl}_2]$  14.75 (a) Two intermediates, B and C. (b) three transition states (c)  $\text{C} \rightarrow \text{D}$  is fastest. (d) endothermic 14.77 (a)  $\text{H}_2(\text{g}) + 2\text{ICl}(\text{g}) \rightarrow \text{I}_2(\text{g}) + 2\text{HCl}(\text{g})$  (b) HI is the intermediate. (c) If the first step is slow, the observed rate law is rate =  $k[\text{H}_2][\text{ICl}]$ . 14.79 The graph of  $1/[\text{NO}]$  versus time is linear with positive slope, indicating that the reaction is second order in  $[\text{NO}]$ . The rate law obtained by assuming the second step is rate determining is rate =  $[\text{NO}]^2[\text{Cl}_2]$ . The two-step mechanism is consistent with the data. 14.81 (a) A catalyst is a substance that changes (usually increases) the speed of a chemical reaction without undergoing a permanent chemical change itself. (b) A homogeneous catalyst is in the same phase as the reactants, while a heterogeneous catalyst is in a different phase. (c) A catalyst has no effect on the overall enthalpy change for a reaction, but it does affect activation energy. It can also affect the frequency factor. 14.83 (a) 270 Pt atoms in a 2.0-nm sphere (b) 200 Pt atoms on the surface of a 2.0-nm sphere (c) 74% Pt atoms on the surface (d) 4300 Pt atoms in a 5.0-nm sphere; 1300 Pt atoms on the surface; 30% Pt atoms on the surface (e) The 2-nm sphere will definitely be more catalytically active because it has a much greater percentage of its atoms on the surface where they can participate in the chemical reaction. 14.85 (a) Multiply the coefficients in the first reaction by 2 and sum. (b)  $\text{NO}_2(\text{g})$  is a catalyst because it is consumed and then reproduced in the reaction sequence. (c) This is a homogeneous catalysis. 14.87 (a) Use of chemically stable supports makes it possible to obtain very large surface areas per unit mass of the precious metal catalyst because the metal can be deposited in a very thin, even monomolecular, layer on the surface of the support. (b) The greater the surface area of the catalyst, the more reaction sites, the greater the rate of the catalyzed reaction. 14.89 To put

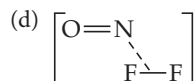
two D atoms on a single carbon, it is necessary that one of the already existing C—H bonds in ethylene be broken while the molecule is adsorbed, so that the H atom moves off as an adsorbed atom and is replaced by a D atom. This requires a larger activation energy than simply adsorbing C<sub>2</sub>H<sub>4</sub> and adding one D atom to each carbon.

**14.91** (a) Living organisms operate efficiently in a very narrow temperature range; the role of enzymes as homogeneous catalysts that speed up desirable reactions, without heating and undesirable side effects, is crucial for biological systems. (b) catalase:  $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$ ; nitrogenase:  $\text{N}_2 \longrightarrow 2\text{NH}_3$  (nitrogen fixation) (c) This model assumes that the rate of the bound substrate being chemically transformed into bound product is slow and rate determining. **14.93** Carbonic anhydrase lowers the activation energy of the reaction by 42 kJ. **14.95** (a) The catalyzed reaction is approximately 10,000,000 times faster at 25 °C. (b) The catalyzed reaction is 180,000 times faster at 125 °C. **14.99** (a) Rate =  $4.7 \times 10^{-5} \text{ M/s}$  (b, c)  $k = 0.84 \text{ M}^{-2}\text{s}^{-1}$  (d) If the [NO] is increased by a factor of 1.8, the rate would increase by a factor of 3.2. **14.101** The reaction is second order in NO<sub>2</sub>. If  $[\text{NO}_2]_0 = 0.100 \text{ M}$  and  $[\text{NO}_2]_t = 0.025 \text{ M}$ , use the integrated form of the second-order rate equation to solve for  $t$ .  $t = 48 \text{ s}$  **14.105** (a) The half-life of <sup>241</sup>Am is  $4.3 \times 10^2 \text{ yr}$ , that of <sup>125</sup>I is 63 days (b) <sup>125</sup>I decays at a much faster rate. (c) 0.13 mg of each isotope remains after 3 half-lives. (d) The amount of <sup>241</sup>Am remaining after 4 days is 1.00 mg. The amount of <sup>125</sup>I remaining after 4 days is 0.957 grams. **14.109** The plot of  $1/[\text{C}_5\text{H}_6]$  versus time is linear and the reaction is second order.  $k = 0.167 \text{ M}^{-1}\text{s}^{-1}$  **14.112** (a) When the two elementary reactions are added, N<sub>2</sub>O<sub>2</sub>(g) appears on both sides and cancels, resulting in the overall reaction.  $2\text{NO}(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{N}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{g})$  (b) First reaction,  $-\frac{[\text{NO}]}{\Delta t} = k[\text{NO}]^2$ ; second reaction,  $-\frac{[\text{H}_2]}{\Delta t} = k[\text{H}_2][\text{N}_2\text{O}_2]$  (c) N<sub>2</sub>O<sub>2</sub> is the intermediate. (d) Since [H<sub>2</sub>] appears in the rate law, the second step must be slow relative to the first. **14.115** (a)  $\text{Cl}_2(\text{g}) + \text{CHCl}_3(\text{g}) \longrightarrow \text{HCl}(\text{g}) + \text{CCl}_4(\text{g})$  (b) Cl(g), CCl<sub>3</sub>(g) (c) reaction 1, unimolecular; reaction 2, bimolecular; reaction 3, bimolecular (d) Reaction 2 is rate determining. (e) Rate =  $k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$ . **14.122** (a)  $k = 8 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$

(b)  $\cdot\dot{\text{N}}=\ddot{\text{O}}:$



(c) NOF is bent with a bond angle of approximately 120°.



(e) The electron-deficient NO molecule is attracted to electron-rich F<sub>2</sub>, so the driving force for formation of the transition state is greater than simple random collisions.

## CHAPTER 15

**15.1**  $k_f > k_r$  (b) The equilibrium constant is greater than 1. **15.7** From the smallest to the largest equilibrium constant, (c) < (b) < (a). **15.11**  $K_c$  decreases as  $T$  increases, so the reaction is exothermic. **15.13** (a)  $K_p = K_c = 8.1 \times 10^{-3}$ . (b) Since  $k_f < k_r$ , in order for the two rates to be equal, [A] must be greater than [B], and the partial pressure of A is greater than the partial pressure of B. **15.15** (a)  $K_c = \frac{[\text{N}_2\text{O}][\text{NO}_2]}{[\text{NO}]^3}$ ; homogeneous (b)  $K_c = \frac{[\text{CS}_2][\text{H}_2]^4}{[\text{CH}_4][\text{H}_2\text{S}]^2}$ ; homogeneous (c)  $K_c = \frac{[\text{CO}]^4}{[\text{Ni}(\text{CO})_4]}$ ; heterogeneous (d)  $K_c = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$ ; homogeneous (e)  $K_c = \frac{[\text{Ag}^+]^2}{[\text{Zn}^{2+}]}$ ; heterogeneous (f)  $K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$ ; homogeneous (g)  $K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$ ; homogeneous **15.17** (a) Mostly reactants (b) mostly products **15.19** No, the equilibrium constant can never be a negative number. The equilibrium constant is a ratio of rate constants (or a ratio of concentrations), which are never negative. **15.21**  $K_p = 1.0 \times 10^{-3}$  **15.23** (a) The equilibrium favors NO and Br<sub>2</sub> at this temperature. (b)  $K_c = 77$  (c)  $K_c = 8.8$  **15.25** (a)  $K_p = 0.541$  (b)  $K_p = 3.42$  (c)  $K_c = 281$  **15.27**  $K_c = 0.14$  **15.29** Pure solids

and liquids are normally excluded from equilibrium-constant expressions because their concentrations, the ratio of moles of a substance to volume occupied by the substance, are constant.

**15.31** (a)  $K_p = P_{\text{O}_2}$  (b)  $K_c = [\text{Hg}(\text{soln})]^4[\text{O}_2(\text{soln})]$  **15.33**  $K_c = 10.5$  **15.35** (a)  $K_p = 51$  (b)  $K_c = 2.1 \times 10^5$  **15.37** (a)  $[\text{H}_2] = 0.012 \text{ M}$ ,  $[\text{N}_2] = 0.019 \text{ M}$ ,  $[\text{H}_2\text{O}] = 0.138 \text{ M}$  (b)  $K_c = 653.7 = 7 \times 10^2$  **15.39** (a)  $P_{\text{CO}_2} = 4.10 \text{ atm}$ ,  $P_{\text{H}_2} = 2.05 \text{ atm}$ ,  $P_{\text{H}_2\text{O}} = 3.28 \text{ atm}$  (b)  $P_{\text{CO}_2} = 3.87 \text{ atm}$ ,  $P_{\text{H}_2} = 1.82 \text{ atm}$ ,  $P_{\text{CO}} = 0.23 \text{ atm}$  (c)  $K_p = 0.11$  **15.41**  $K_c = 2.0 \times 10^4$  **15.43** (a) A reaction quotient is the result of a general set of concentrations whereas the equilibrium constant requires equilibrium concentrations. (b) to the right (c) The concentrations used to calculate  $Q$  must be equilibrium concentrations. **15.45** (a)  $Q = 1.1 \times 10^{-8}$ , the reaction will proceed to the left. (b)  $Q = 5.5 \times 10^{-12}$ , the reaction will proceed to the right. (c)  $Q = 2.19 \times 10^{-10}$ , the mixture is at equilibrium. **15.47**  $P_{\text{Cl}_2} = 5.0 \text{ atm}$  **15.49** (a)  $[\text{Br}_2] = 0.00767 \text{ M}$ ,  $[\text{Br}] = 0.00282 \text{ M}$ ,  $0.0451 \text{ g Br}(\text{g})$  (b)  $[\text{H}_2] = 0.014 \text{ M}$ ,  $[\text{I}_2] = 0.00859 \text{ M}$ ,  $[\text{HI}] = 0.081 \text{ M}$ ,  $21 \text{ g HI}$  **15.51**  $[\text{NO}] = 0.002 \text{ M}$ ,  $[\text{N}_2] = [\text{O}_2] = 0.087 \text{ M}$  **15.53** The equilibrium pressure of Br<sub>2</sub>(g) is 0.416 atm. **15.55** (a)  $[\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = 4.9 \times 10^{-3} \text{ M}$  (b) A bit more than 1.0 g CaSO<sub>4</sub> is needed in order to have some undissolved CaSO<sub>4</sub>(s) in equilibrium with 1.4 L of saturated solution. **15.57**  $[\text{IBr}] = 0.223 \text{ M}$ ,  $[\text{I}_2] = [\text{Br}_2] = 0.0133 \text{ M}$  **15.59** (a)  $P_{\text{CH}_3\text{I}} = P_{\text{HI}} = 0.422 \text{ torr}$ ,  $P_{\text{CH}_4} = 104.7 \text{ torr}$ ,  $P_{\text{I}_2} = 7.54 \text{ torr}$  **15.61** (a) Shift equilibrium to the right (b) decrease the value of  $K$  (c) shift equilibrium to the left (d) no effect (e) no effect (f) shift equilibrium to the right **15.63** (a) No effect (b) no effect (c) no effect (d) increase equilibrium constant (e) no effect **15.65** (a)  $\Delta H^\circ = -155.7 \text{ kJ}$  (b) The reaction is exothermic, so the equilibrium constant will decrease with increasing temperature. (c)  $\Delta n$  does not equal zero, so a change in volume at constant temperature will affect the fraction of products in the equilibrium mixture. **15.67** An increase in pressure favors formation of ozone. **15.71**  $K_p = 24.7$ ;  $K_c = 3.67 \times 10^{-3}$  **15.74** (a)  $P_{\text{Br}_2} = 1.61 \text{ atm}$ ,  $P_{\text{NO}} = 0.628 \text{ atm}$ ,  $P_{\text{NOBr}} = 0.179 \text{ atm}$ ;  $K_c = 0.0643$  (b)  $P_t = 0.968 \text{ atm}$  (c) 10.49 g NOBr **15.77** At equilibrium,  $P_{\text{IBr}} = 0.21 \text{ atm}$ ,  $P_{\text{I}_2} = P_{\text{Br}_2} = 1.9 \times 10^{-3} \text{ atm}$  **15.80**  $K_p = 4.33$ ,  $K_c = 0.0480$  **15.83**  $[\text{CO}_2] = [\text{H}_2] = 0.264 \text{ M}$ ,  $[\text{CO}] = [\text{H}_2\text{O}] = 0.236 \text{ M}$  **15.87** (a) 26% of the CCl<sub>4</sub> is converted to C and Cl<sub>2</sub>. (b)  $P_{\text{CCl}_4} = 1.47 \text{ atm}$ ,  $P_{\text{Cl}_2} = 1.06 \text{ atm}$  **15.91**  $Q = 8 \times 10^{-6}$ .  $Q > K_p$ , so the system is not at equilibrium; it will shift left to attain equilibrium. A catalyst that speeds up the reaction and thereby promotes the attainment of equilibrium would decrease the CO concentration in the exhaust. **15.93** At equilibrium,  $[\text{H}_6\text{IO}_4^-] = 0.0015 \text{ M}$  **15.97** At 850 °C,  $K_p = 14.1$ ; at 950 °C,  $K_p = 73.8$ ; at 1050 °C,  $K_p = 2.7 \times 10^2$ ; at 1200 °C,  $K_p = 1.7 \times 10^3$ . Because  $K$  increases with increasing temperature, the reaction is endothermic.

## CHAPTER 16

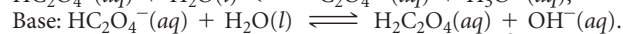
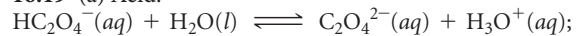
**16.1** (a) HX, the H<sup>+</sup> donor, is the Brønsted–Lowry acid. NH<sub>3</sub>, the H<sup>+</sup> acceptor, is the Brønsted–Lowry base. (b) HX, the electron pair acceptor, is the Lewis acid. NH<sub>3</sub>, the electron pair donor, is the Lewis base. **16.3** (a) HY is a strong acid. There are no neutral HY molecules in solution, only H<sup>+</sup> cations and Y<sup>-</sup> anions. (b) HX has the smallest  $K_a$  value. It has most neutral acid molecules and fewest ions. (c) HX has fewest H<sup>+</sup> and highest pH. **16.5** (a) True. (b) False. Methyl orange turns yellow at a pH slightly greater than 4, so solution B could be at any pH greater than 4. (c) True. **16.7** (a) Molecule A, NH<sub>2</sub>OH (hydroxyl amine), acts as a base. Molecule A is an H<sup>+</sup> acceptor because of the nonbonded electron pair on the N atom of the amine (—NH<sub>2</sub>) group, not because it contains an —OH group. (b) Molecule B, HCOOH (formic acid), acts as an acid. The molecule contains a —COOH group where the H atom bonded to O is ionizable and HCOOH is an H<sup>+</sup> donor. (c) Molecule C, CH<sub>3</sub>OH (methanol), is an organic alcohol. The H atom bonded to O is not ionizable, and the —OH group does not dissociate in aqueous solution; it is neither an acid nor a base. **16.9** (a) Molecule (b) is more acidic because its

conjugate base is resonance-stabilized and the ionization equilibrium favors the more stable products. (b) Increasing the electronegativity of X increases the strength of both acids. As X becomes more electronegative and attracts more electron density, the O—H bond becomes weaker, more polar, and more likely to be ionized. An electronegative X group also stabilizes the anionic conjugate base, causing the ionization equilibrium to favor products and the value of  $K_a$  to increase.

**16.11** Solutions of HCl and  $H_2SO_4$  conduct electricity, taste sour, turn litmus paper red (are acidic), neutralize solutions of bases, and react with active metals to form  $H_2(g)$ . HCl and  $H_2SO_4$  solutions have these properties in common because both compounds are strong acids. That is, they both ionize completely in  $H_2O$  to form  $H^+(aq)$  and an anion. ( $HSO_4^-$  is not completely ionized, but the first ionization step for  $H_2SO_4$  is complete.) The presence of ions enables the solutions to conduct electricity; the presence of  $H^+(aq)$  in excess of  $1 \times 10^{-7} M$  accounts for all other properties listed. **16.13** (a) The Arrhenius definition of an acid is confined to aqueous solution; the Brønsted-Lowry definition applies to any physical state. (b) HCl is the Brønsted-Lowry acid;  $NH_3$  is the Brønsted-Lowry base. **16.15** (a) (i)  $IO_3^-$  (ii)  $NH_3$  (b) (i)  $OH^-$  (ii)  $H_3PO_4$

**16.17**

Acid	+	Base	$\rightleftharpoons$	Conjugate Acid	+	Conjugate Base
(a) $NH_4^+(aq)$		$CN^-(aq)$		$HCN(aq)$		$NH_3(aq)$
(b) $H_2O(l)$		$(CH_3)_3N(aq)$		$(CH_3)_3NH^+(aq)$		$OH^-(aq)$
(c) $HCOOH(aq)$		$PO_4^{3-}(aq)$		$HPO_4^{2-}(aq)$		$HCOO^-(aq)$

**16.19** (a) Acid:

(b)  $H_2C_2O_4$  is the conjugate acid of  $HC_2O_4^-$ .  $C_2O_4^{2-}$  is the conjugate base of  $HC_2O_4^-$ . **16.21** (a)  $CH_3COO^-$ , weak base;  $CH_3COOH$ , weak acid (b)  $HCO_3^-$ , weak base;  $H_2CO_3$ , weak acid (c)  $O_2^{2-}$ , strong base;  $OH^-$ , strong base (d)  $Cl^-$ , negligible base; HCl, strong acid (e)  $NH_3$ , weak base;  $NH_4^+$ , weak acid **16.23** (a) HBr. It is one of the seven strong acids. (b)  $F^-$ . HCl is a stronger acid than HF, so  $F^-$  is the stronger conjugate base. **16.25** (a)  $OH^-(aq) + OH^-(aq)$ , the equilibrium lies to the right. (b)  $H_2S(aq) + CH_3COO^-(aq)$ , the equilibrium lies to the right. (c)  $HNO_3(aq) + OH^-(aq)$ , the equilibrium lies to the left. **16.27** (a) No. In pure water, the only source of  $H^+$  is the autoionization reaction, which produces equal concentrations of  $H^+$  and  $OH^-$ . As the temperature of water changes, the value of  $K_w$  changes, and the pH at which  $[H^+] = [OH^-]$  changes.

**16.29** (a)  $[H^+] = 2.2 \times 10^{-11} M$ , basic (b)  $[H^+] = 1.1 \times 10^{-6} M$ , acidic (c)  $[H^+] = 1.0 \times 10^{-8} M$ , basic **16.31**  $[H^+] = [OH^-] = 3.5 \times 10^{-8} M$  **16.33** (a)  $[H^+]$  changes by a factor of 100. (b)  $[H^+]$  changes by a factor of 3.2 **16.35** (a)  $[H^+]$  decreases, pH increases (b) The pH is between 3 and 4. By calculation, pH = 3.2; the solution is acidic. (c) pH = 5.2 is between pH 5 and pH 6, closer to pH = 5. A good estimate is  $7 \times 10^{-6} M H^+$  and  $3 \times 10^{-9} M OH^-$ . By calculation,  $[H^+] = 6 \times 10^{-6} M$  and  $[OH^-] = 2 \times 10^{-9} M$ .

**16.37**

$[H^+]$	$[OH^-]$	pH	pOH	Acidic or Basic
$7.5 \times 10^{-3} M$	$1.3 \times 10^{-12} M$	2.12	11.88	acidic
$2.8 \times 10^{-5} M$	$3.6 \times 10^{-10} M$	4.56	9.44	acidic
$5.6 \times 10^{-9} M$	$1.8 \times 10^{-6} M$	8.25	5.75	basic
$5.0 \times 10^{-9} M$	$2.0 \times 10^{-6} M$	8.30	5.70	basic

**16.39**  $[H^+] = 4.0 \times 10^{-8} M$ ,  $[OH^-] = 6.0 \times 10^{-7} M$ , pOH = 6.22

**16.41** (a) A strong acid is completely ionized in aqueous solution.

(b)  $[H^+] = 0.500 M$  (c) HCl, HBr, HI **16.43** (a)  $[H^+] = 8.5 \times 10^{-3} M$ , pH = 2.07 (b)  $[H^+] = 0.0419 M$ , pH = 1.377 (c)  $[H^+] = 0.0250 M$ , pH = 1.602 (d)  $[H^+] = 0.167 M$ , pH = 0.778 **16.45** (a)

$[OH^-] = 3.0 \times 10^{-3} M$ , pH = 11.48 (b)  $[OH^-] = 0.3758 M$ , pH = 13.5750 (c)  $[OH^-] = 8.75 \times 10^{-5} M$ , pH = 9.942 (d)

$[OH^-] = 0.17 M$ , pH = 13.23 **16.47**  $3.2 \times 10^{-3} M NaOH$  **16.49**

(a)  $HBrO_2(aq) \rightleftharpoons H^+(aq) + BrO_2^-(aq)$ ,  $K_a = [H^+][BrO_2^-]/[HBrO_2]$ ;

$HBrO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + BrO_2^-(aq)$ ,  $K_a = [H_3O^+][BrO_2^-]/[HBrO_2]$  (b)  $C_2H_5COOH(aq) \rightleftharpoons H^+(aq) + C_2H_5COO^-(aq)$ ,

$K_a = [H^+][C_2H_5COO^-]/[C_2H_5COOH]$ ;

$C_2H_5COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_5COO^-(aq)$ ,  $K_a = [H_3O^+][C_2H_5COO^-]/[C_2H_5COOH]$  **16.51**  $K_a = 1.4 \times 10^{-4}$

**16.53**  $[H^+] = [ClCH_2COO^-] = 0.0110 M$ ,  $[ClCH_2COOH] = 0.089 M$ ,  $K_a = 1.4 \times 10^{-3}$  **16.55**  $0.089 M CH_3COOH$  **16.57**  $[H^+] = [C_6H_5COO^-] = 1.8 \times 10^{-3} M$ ,  $[C_6H_5COOH] = 0.048 M$

**16.59** (a)  $[H^+] = 1.1 \times 10^{-3} M$ , pH = 2.95

(b)  $[H^+] = 1.7 \times 10^{-4} M$ , pH = 3.76 (c)  $[OH^-] = 1.4 \times 10^{-5} M$ , pH = 9.15 **16.61**  $[H^+] = 2.0 \times 10^{-2} M$ , pH = 1.71 **16.63** (a)

$[H^+] = 2.8 \times 10^{-3} M$ , 0.69% ionization (b)  $[H^+] = 1.4 \times 10^{-3} M$ , 1.4% ionization (c)  $[H^+] = 8.7 \times 10^{-4} M$ , 2.2% ionization

**16.65**  $HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$ ;  $K_a = [H^+][X^-]/[HX]$ . Assume that the percent of acid that ionizes is small. Let  $[H^+] = [X^-] = y$ ,  $K_a = y^2/[HX]$ ;  $y = K_a^{1/2}[HX]^{1/2}$ . Percent ionization =  $y/[HX] \times 100$ . Substituting for  $y$ , percent ionization =  $100 K_a^{1/2}[HX]^{1/2}/[HX]$  or  $100 K_a^{1/2}/[HX]^{1/2}$ . That is, percent ionization varies inversely as the square root of the concentration of HX. **16.67**  $[H^+] = 5.1 \times 10^{-3} M$ , pH = 2.29,  $[C_6H_5O_7^{3-}] = 1.3 \times 10^{-9} M$ . The approximation that the first ionization is less than 5% of the total acid concentration is not valid; the quadratic equation must be solved. The  $[H^+]$  produced from the second and third ionizations is small with respect to that present from the first step; the second and third ionizations can be neglected when calculating the  $[H^+]$  and pH.  $[C_6H_5O_7^{3-}]$  is much less than  $[H^+]$ .

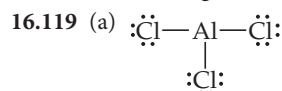
**16.69** (a)  $HONH_3^+$  (b) When hydroxylamine acts as a base, the nitrogen atom accepts a proton. (c) In hydroxylamine, O and N are the atoms with nonbonding electron pairs; in the neutral molecule both have zero formal charges. Nitrogen is less electronegative than oxygen and more likely to share a lone pair of electrons with an incoming (and electron-deficient)  $H^+$ . The resulting cation with the +1 formal charge on N is more stable than the one with the +1 formal charge on O.

**16.71** (a)  $(CH_3)_2NH(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH_2^+(aq) + OH^-(aq)$ ;  $K_b = [(CH_3)_2NH_2^+][OH^-]/[(CH_3)_2NH]$

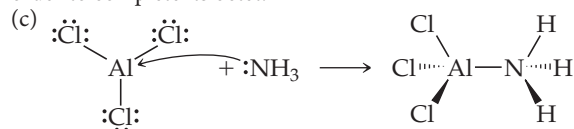
(b)  $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$ ;  $K_b = [HCO_3^-][OH^-]/[CO_3^{2-}]$  (c)  $HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq)$   $K_b = [HCOOH][OH^-]/[HCOO^-]$

**16.73** From the quadratic formula,  $[OH^-] = 6.6 \times 10^{-3} M$ , pH = 11.82. **16.75** (a)  $[C_{10}H_{15}ON] = 0.033 M$ ,  $[C_{10}H_{15}ONH^+] = [OH^-] = 2.1 \times 10^{-3} M$  (b)  $K_b = 1.4 \times 10^{-4}$  **16.77** (a) For a conjugate acid/conjugate base pair such as  $C_6H_5OH/C_6H_5O^-$ ,  $K_b$  for the conjugate base can always be calculated from  $K_a$  for the conjugate acid, so a separate list of  $K_b$  values is not necessary. (b)  $K_b = 7.7 \times 10^{-5}$  (c) Phenolate is a stronger base than  $NH_3$ . **16.79** (a) Acetic acid is stronger. (b) Hypochlorite ion is the stronger base. (c) For  $CH_3COO^-$ ,  $K_b = 5.6 \times 10^{-10}$ ; for  $ClO^-$ ,  $K_b = 3.3 \times 10^{-7}$ . **16.81** (a)  $[OH^-] = 6.3 \times 10^{-4} M$ , pH = 10.80 (b)  $[OH^-] = 9.2 \times 10^{-5} M$ , pH = 9.96 (c)  $[OH^-] = 3.3 \times 10^{-6} M$ , pH = 8.52 **16.83** (a) Acidic (b) acidic (c) basic (d) neutral (e) acidic **16.85**  $K_b$  for the anion of the unknown salt is  $1.4 \times 10^{-11}$ ;  $K_a$  for the conjugate acid is  $7.1 \times 10^{-4}$ . The conju-

gate acid is HF and the salt is NaF. **16.87** (a) As the electronegativity of the central atom (X) increases, the strength of the oxyacid increases. (b) As the number of nonprotonated oxygen atoms in the molecule increases, the strength of the oxyacid increases. **16.89** (a) HNO<sub>3</sub> is a stronger acid because it has one more nonprotonated oxygen atom and thus a higher oxidation number on N. (b) For binary hydrides, acid strength increases going down a family, so H<sub>2</sub>S is a stronger acid than H<sub>2</sub>O. (c) H<sub>2</sub>SO<sub>4</sub> is a stronger acid because H<sup>+</sup> is much more tightly held by the anion HSO<sub>4</sub><sup>-</sup>. (d) For oxyacids, the greater the electronegativity of the central atom, the stronger the acid, so H<sub>2</sub>SO<sub>4</sub> is the stronger acid. (e) CCl<sub>3</sub>COOH is stronger because the electronegative Cl atoms withdraw electron density from other parts of the molecule, which weakens the O—H bond and stabilizes the anionic conjugate base. Both effects favor increased ionization and acid strength. **16.91** (a) BrO<sup>-</sup> (b) BrO<sup>-</sup> (c) HPO<sub>4</sub><sup>2-</sup> **16.93** (a) True (b) False. In a series of acids that have the same central atom, acid strength increases with the number of nonprotonated oxygen atoms bonded to the central atom. (c) False. H<sub>2</sub>Te is a stronger acid than H<sub>2</sub>S because the H—Te bond is longer, weaker, and more easily ionized than the H—S bond. **16.95** Yes. The Arrhenius definition of a base, an OH<sup>-</sup>(aq) donor, is most restrictive; the Brønsted definition, an H<sup>+</sup> acceptor, is more general; and the Lewis definition, an electron-pair donor, is most general. Any substance that fits the narrow Arrhenius definition will fit the broader Brønsted and Lewis definitions. **16.97** (a) Acid, Fe(ClO<sub>4</sub>)<sub>3</sub> or Fe<sup>3+</sup>; base, H<sub>2</sub>O (b) Acid, H<sub>2</sub>O; base, CN<sup>-</sup> (c) Acid, BF<sub>3</sub>; base, (CH<sub>3</sub>)<sub>3</sub>N (d) Acid, HIO; base, NH<sub>2</sub><sup>-</sup> **16.99** (a) Cu<sup>2+</sup>, higher cation charge (b) Fe<sup>3+</sup>, higher cation charge (c) Al<sup>3+</sup>, smaller cation radius, same charge **16.101** (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N is a stronger base than NH<sub>3</sub> by virtue of its smaller pK<sub>b</sub>. **16.104** K = 3.3 × 10<sup>7</sup> **16.107** (a) For solutions with equal concentrations, the weaker acid will have a lower [H<sup>+</sup>] and higher pH. (b) The acid with K<sub>a</sub> = 8 × 10<sup>-5</sup> is the weaker acid, so it has the higher pH. (c) The base with pK<sub>b</sub> = 4.5 is the stronger base, has the greater [OH<sup>-</sup>] and smaller [H<sup>+</sup>], so higher pH. **16.109** K<sub>a</sub> = 1.4 × 10<sup>-5</sup> **16.115** 6.0 × 10<sup>13</sup> H<sup>+</sup> ions **16.118** (a) To the precision of the reported data, the pH of rainwater 40 years ago was 5.4, no different from the pH today. With extra significant figures, [H<sup>+</sup>] = 3.61 × 10<sup>-6</sup> M, pH = 5.443 (b) A 20.0-L bucket of today's rainwater contains 0.02 L (with extra significant figures, 0.0200 L) of dissolved CO<sub>2</sub>.



The electron-domain geometry and molecular structure are trigonal planar. (b) The Al atom is electron deficient. It acts like a Lewis acid in order to complete its octet.

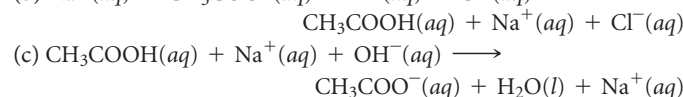


(d) The Lewis theory is most appropriate. H<sup>+</sup> and AlCl<sub>3</sub> are both electron pair acceptors. **16.121** Rx 1, ΔH = 104 kJ; Rx 2, ΔH = -32 kJ. Reaction 2 is exothermic while reaction 1 is endothermic. For binary acids with heavy atoms (X) in the same family, the longer and weaker the H—X bond, the stronger the acid (and the more exothermic the ionization reaction). **16.124** (a) K(i) = 5.6 × 10<sup>3</sup>, K(ii) = 10 (b) Both (i) and (ii) have K > 1, so both could be written with a single arrow.

## CHAPTER 17

**17.1** The middle box has the highest pH. For equal amounts of acid HX, the greater the amount of conjugate base X<sup>-</sup>, the smaller the amount of H<sup>+</sup> and the higher the pH. **17.4** (a) Drawing 3 (b) Drawing 1 (c) Drawing 2 **17.7** (a) The red curve corresponds to the more concentrated acid solution. (b) On the titration curve of a weak acid,

pH = pK<sub>a</sub> at the volume halfway to the equivalence point. At this volume, the red curve has the smaller pK<sub>a</sub> and the larger K<sub>a</sub>. **17.10** (a) Q = 4.67 × 10<sup>-6</sup>; Q < K<sub>sp</sub> and the solution is not saturated. (b) Ca(OH)<sub>2</sub> precipitate forms in beaker (iii). **17.13** (a) The extent of ionization of a weak electrolyte is decreased when a strong electrolyte containing an ion in common with the weak electrolyte is added to it. (b) NaNO<sub>2</sub> **17.15** (a) [H<sup>+</sup>] = 1.8 × 10<sup>-5</sup> M, pH = 4.73 (b) [OH<sup>-</sup>] = 4.8 × 10<sup>-5</sup> M, pH = 9.68 (c) [H<sup>+</sup>] = 1.4 × 10<sup>-5</sup> M, pH = 4.87 **17.17** (a) 4.5% ionization (b) 0.018% ionization **17.19** In a mixture of CH<sub>3</sub>COOH and CH<sub>3</sub>COONa, CH<sub>3</sub>COOH reacts with added base and CH<sub>3</sub>COO<sup>-</sup> combines with added acid, leaving [H<sup>+</sup>] relatively unchanged. Although HCl and Cl<sup>-</sup> are a conjugate acid–base pair, Cl<sup>-</sup> has no tendency to combine with added acid to form undissociated HCl. Any added acid simply increases [H<sup>+</sup>] in an HCl—NaCl mixture. **17.21** (a) pH = 3.82 (b) pH = 3.96 **17.23** (a) pH = 5.26 (b) Na<sup>+</sup>(aq) + CH<sub>3</sub>COO<sup>-</sup>(aq) + H<sup>+</sup>(aq) + Cl<sup>-</sup>(aq) →



(c) CH<sub>3</sub>COOH(aq) + Na<sup>+</sup>(aq) + OH<sup>-</sup>(aq) → CH<sub>3</sub>COO<sup>-</sup>(aq) + H<sub>2</sub>O(l) + Na<sup>+</sup>(aq) **17.25** (a) pH = 1.58 (b) 36 g NaF **17.27** (a) pH = 4.86 (b) pH = 5.0 (c) pH = 4.71 **17.29** (a) [HCO<sub>3</sub><sup>-</sup>]/[H<sub>2</sub>CO<sub>3</sub>] = 11 (b) [HCO<sub>3</sub><sup>-</sup>]/[H<sub>2</sub>CO<sub>3</sub>] = 5.4 **17.31** 360 mL of 0.10 M HCOONa, 640 mL of 0.10 M HCOOH **17.33** (a) Curve B (b) pH at the approximate equivalence point of curve A = 8.0, pH at the approximate equivalence point of curve B = 7.0 (c) For equal volumes of A and B, the concentration of acid B is greater, since it requires a larger volume of base to reach the equivalence point. **17.35** (a) False (b) true (c) true **17.37** (a) Above pH 7 (b) below pH 7 (c) at pH 7 **17.39** The second color change of Thymol blue is in the correct pH range to show the equivalence point of the titration of a weak acid with a strong base. **17.41** (a) 42.4 mL NaOH soln (b) 35.0 mL NaOH soln (c) 29.8 mL NaOH soln **17.43** (a) pH = 1.54 (b) pH = 3.30 (c) pH = 7.00 (d) pH = 10.69 (e) pH = 12.74 **17.45** (a) pH = 2.78 (b) pH = 4.74 (c) pH = 6.58 (d) pH = 8.81 (e) pH = 11.03 (f) pH = 12.42 **17.47** (a) pH = 7.00 (b) [HONH<sub>3</sub><sup>+</sup>] = 0.100 M, pH = 3.52 (c) [C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup>] = 0.100 M, pH = 2.82 **17.49** (a) The concentration of undissolved solid does not appear in the solubility product expression because it is constant. (b) K<sub>sp</sub> = [Ag<sup>+</sup>][I<sup>-</sup>]; K<sub>sp</sub> = [Sr<sup>2+</sup>][SO<sub>4</sub><sup>2-</sup>]; K<sub>sp</sub> = [Fe<sup>2+</sup>][OH<sup>-</sup>]<sup>2</sup>; K<sub>sp</sub> = [Hg<sub>2</sub><sup>2+</sup>][Br<sup>-</sup>]<sup>2</sup> **17.51** (a) K<sub>sp</sub> = 7.63 × 10<sup>-9</sup> (b) K<sub>sp</sub> = 2.7 × 10<sup>-9</sup> (c) 5.3 × 10<sup>-4</sup> mol Ba(IO<sub>3</sub>)<sub>2</sub>/L

**17.53** K<sub>sp</sub> = 2.3 × 10<sup>-9</sup> **17.55** (a) 7.1 × 10<sup>-7</sup> mol AgBr/L (b) 1.7 × 10<sup>-11</sup> mol AgBr/L (c) 5.0 × 10<sup>-12</sup> mol AgBr/L **17.57** (a) The amount of CaF<sub>2</sub>(s) on the bottom of the beaker increases. (b) The [Ca<sup>2+</sup>] in solution increases. (c) The [F<sup>-</sup>] in solution decreases. **17.59** (a) 1.4 × 10<sup>3</sup> g Mn(OH)<sub>2</sub>/L (b) 0.014 g/L (c) 3.6 × 10<sup>-7</sup> g/L **17.61** More soluble in acid: (a) ZnCO<sub>3</sub> (b) ZnS (d) AgCN (e) Ba<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> **17.63** [Ni<sup>2+</sup>] = 1 × 10<sup>-8</sup> M **17.65** (a) 9.1 × 10<sup>-9</sup> mol AgI/L pure water (b) K = K<sub>sp</sub> × K<sub>f</sub> = 8 × 10<sup>4</sup> (c) 0.0500 mol AgI/L 0.100 M NaCN **17.67** (a) Q < K<sub>sp</sub>; no Ca(OH)<sub>2</sub> precipitates (b) Q < K<sub>sp</sub>; no Ag<sub>2</sub>SO<sub>4</sub> precipitates **17.69** pH = 11.5 **17.71** AgI will precipitate first, at [I<sup>-</sup>] = 4.2 × 10<sup>-13</sup> M. **17.73** AgCl will precipitate first. **17.75** The first two experiments eliminate group 1 and 2 ions (Figure 17.23). The absence of insoluble phosphate precipitates in the filtrate from the third experiment rules out group 4 ions. The ions that might be in the sample are those from group 3, Al<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, or Co<sup>2+</sup>, and from group 5, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, or K<sup>+</sup>. **17.77** (a) Make the solution acidic with 0.2 M HCl; saturate with H<sub>2</sub>S. CdS will precipitate; ZnS will not. (b) Add excess base; Fe(OH)<sub>3</sub>(s) precipitates, but Cr<sup>3+</sup> forms the soluble complex Cr(OH)<sub>4</sub><sup>-</sup>. (c) Add (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>; Mg<sup>2+</sup> precipitates as MgNH<sub>4</sub>PO<sub>4</sub>; K<sup>+</sup> remains soluble. (d) Add 6 M HCl; precipitate Ag<sup>+</sup> as AgCl(s); Mn<sup>2+</sup> remains soluble. **17.79** (a) Base is required to increase [PO<sub>4</sub><sup>3-</sup>] so that the solubility product of the metal phosphates of interest is exceeded and the phosphate salts precipitate. (b) K<sub>sp</sub> for the cations in group 3 is much larger, and so to exceed K<sub>sp</sub>, a higher [S<sup>2-</sup>] is required. (c) They should all redissolve in strongly acidic solution.

**17.81**  $\text{pOH} = \text{p}K_b + \log\{\frac{[\text{BH}^-]}{[\text{B}]}\}$  **17.83** (a)  $\text{pH} = 3.171$  (b)  $\text{pH} = 2.938$  (c)  $\text{pH} = 12.862$  **17.86** (a)  $\text{pH}$  of buffer A =  $\text{pH}$  of buffer B = 3.74. For buffers containing the same conjugate acid and base components, the  $\text{pH}$  is determined by the ratio of concentrations of conjugate acid and base. Buffers A and B have the same ratio of concentrations, so their  $\text{pH}$  values are equal. (b) Buffer capacity is determined by the absolute amount of buffer components available to absorb strong acid or strong base. Buffer A has the greater capacity because it contains the greater absolute concentrations of  $\text{HCOOH}$  and  $\text{HCOO}^-$ . (c) Buffer A:  $\text{pH} = 3.74$ ,  $\Delta\text{pH} = 0.00$ ; buffer B:  $\text{pH} = 3.66$ ,  $\Delta\text{pH} = -0.12$  (d) Buffer A:  $\text{pH} = 3.74$ ,  $\Delta\text{pH} = 0.00$ ; buffer B:  $\text{pH} = 2.74$ ,  $\Delta\text{pH} = -1.00$  (e) The results of parts (c) and (d) are quantitative confirmation that buffer A has a significantly greater capacity than buffer B. **17.88** (a) molar mass =  $82.2 \text{ g/mol}$  (b)  $K_a = 3.8 \times 10^{-7}$  **17.90** At the halfway point,  $\text{mol HA} = \text{mol A}^-$  and  $[\text{HA}] = [\text{A}^-]$ .

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

If  $[\text{A}^-]/[\text{HA}] = 1$ ,

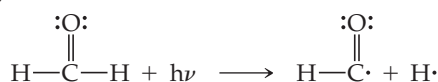
$\log(1) = 0$  and  $\text{pH} = \text{p}K_a$  of the weak acid being titrated. **17.92**  $\text{pH} = 7.75$  **17.93**  $1.6 \text{ L}$  of  $1.0 \text{ M NaOH}$  **17.96** (a)  $\text{CdS}$  (b)  $\text{BaCrO}_4$  (c)  $\text{NiCO}_3$  (d)  $\text{Ag}_2\text{SO}_4$  **17.100** The solubility of  $\text{Mg}(\text{OH})_2$  in  $0.50 \text{ M NH}_4\text{Cl}$  is  $0.11 \text{ mol/L}$  **17.101**  $[\text{KMnO}_4] = [\text{MnO}_4^-] = 0.11 \text{ M}$  **17.104**  $[\text{OH}^-] = 1.7 \times 10^{-11} \text{ M}$ ,  $\text{pH}$  of the buffer =  $3.22$  **17.107** (a) The molar solubility of  $\text{Cd}(\text{OH})_2$  is  $1.8 \times 10^{-5} \text{ mol/L}$ . (b) The initial concentration of  $\text{NaBr}$  required to increase the molar solubility of  $\text{Cd}(\text{OH})_2$  to  $1.0 \times 10^{-3} \text{ mol/L}$  is  $2 \text{ M}$ . **17.108** (a)  $\text{H}^+(\text{aq}) + \text{HCOO}^-(\text{aq}) \longrightarrow \text{HCOOH}(\text{aq})$  (b)  $K = 5.6 \times 10^3$  (c)  $[\text{Na}^+] = [\text{Cl}^-] = 0.075 \text{ M}$ ,  $[\text{H}^+] = [\text{HCOO}^-] = 3.7 \times 10^{-3} \text{ M}$ ,  $[\text{HCOOH}] = 0.071 \text{ M}$  **17.114**  $[\text{Sr}^{2+}] = [\text{SO}_4^{2-}] = 5.7 \times 10^{-4} \text{ M}$ ,  $K_{\text{sp}} = 3.2 \times 10^{-7}$

## CHAPTER 18

**18.1** (a) A greater volume than  $22.4 \text{ L}$  (b) The gas will occupy more volume at  $85 \text{ km}$  than at  $50 \text{ km}$ . (c) We expect gases to behave most ideally in the thermosphere, around the stratopause and in the troposphere at low altitude. **18.6** Salt water contains high concentrations of dissolved salts and solids. It includes the world ocean (97.2% of all water, approximately 35,000 ppm of dissolved salts) and brackish or salty water (0.1% of all water). Freshwater (0.6% of all water on earth) refers to natural waters that have low concentrations (less than 500 ppm) of dissolved salts and solids. It includes the waters of lakes, rivers, ponds, and streams. Groundwater is freshwater that is under the soil. It resides in aquifers, porous rock that holds water, and composes 20% of the world's freshwater. **18.9** The basic goals of green chemistry are to minimize or eliminate solvents and waste, generate nontoxic waste, be energy efficient, employ renewable starting materials, and take advantage of catalysts that enable the use of safe and common reagents. **18.11** (a) Its temperature profile (b) troposphere, 0 to 12 km; stratosphere, 12 to 50 km; mesosphere, 50 to 85 km; thermosphere, 85 to 110 km **18.13** (a) The partial pressure of  $\text{O}_3$  is  $3.0 \times 10^{-7} \text{ atm}$  ( $2.2 \times 10^{-4} \text{ torr}$ ). (b)  $7.3 \times 10^{15} \text{ O}_3$  molecules/ $1.0 \text{ L}$  air **18.15**  $8.6 \times 10^{16} \text{ CO}$  molecules/ $1.0 \text{ L}$  air **18.17** (a)  $570 \text{ nm}$  (b) visible electromagnetic radiation **18.19** (a) Photodissociation is cleavage of a bond such that two neutral species are produced. Photoionization is absorption of a photon with sufficient energy to eject an electron, producing an ion and the ejected electron. (b) Photoionization of  $\text{O}_2$  requires  $1205 \text{ kJ/mol}$ . Photodissociation requires only  $495 \text{ kJ/mol}$ . At lower elevations, high-energy short-wavelength solar radiation has already been absorbed. Below  $90 \text{ km}$ , the increased concentration of  $\text{O}_2$  and the availability of longer-wavelength radiation cause the photodissociation process to dominate. **18.21** Ozone depletion reactions, which involve only  $\text{O}_3$ ,  $\text{O}_2$ , or  $\text{O}$  (oxidation state = 0), do not involve a change in oxidation state for oxygen atoms. Reactions involving  $\text{ClO}$  and one of the oxygen species with a zero oxidation state do involve a change in the oxidation state of oxygen atoms. **18.23** (a) A chlorofluorocarbon is a compound that contains chlorine, fluorine, and

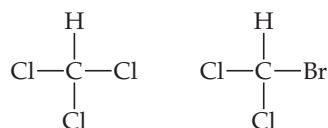
carbon, while a hydrofluorocarbon is a compound that contains hydrogen, fluorine, and carbon. An HFC contains hydrogen in place of the chlorine present in a CFC. (b) HFCs are potentially less harmful than CFCs because their photodissociation does not produce  $\text{Cl}$  atoms, which catalyze the destruction of ozone. **18.25** (a) The  $\text{C}-\text{F}$  bond requires more energy for dissociation than the  $\text{C}-\text{Cl}$  bond and is not readily cleaved by the available wavelengths of UV light. (b) Chlorine is present as chlorine atoms and chlorine oxide molecules,  $\text{Cl}$  and  $\text{ClO}$ , respectively. **18.27** (a) Methane,  $\text{CH}_4$ , arises from decomposition of organic matter by certain microorganisms; it also escapes from underground gas deposits. (b)  $\text{SO}_2$  is released in volcanic gases and also is produced by bacterial action on decomposing vegetable and animal matter. (c) Nitric oxide,  $\text{NO}$ , results from oxidation of decomposing organic matter and is formed in lightning flashes. **18.29** (a)  $\text{H}_2\text{SO}_4(\text{aq}) + \text{CaCO}_3(\text{s}) \longrightarrow \text{CaSO}_4(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$  (b) The  $\text{CaSO}_4(\text{s})$  would be much less reactive with acidic solution, since it would require a strongly acidic solution to shift the relevant equilibrium to the right:  $\text{CaSO}_4(\text{s}) + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{HSO}_4^-(\text{aq})$ .  $\text{CaSO}_4$  would protect  $\text{CaCO}_3$  from attack by acid rain, but it would not provide the structural strength of limestone. **18.31** (a) Ultraviolet (b)  $357 \text{ kJ/mol}$  (c) The average  $\text{C}-\text{H}$  bond energy from Table 8.4 is  $413 \text{ kJ/mol}$ . The  $\text{C}-\text{H}$  bond energy in  $\text{CH}_2\text{O}$ ,  $357 \text{ kJ/mol}$ , is less than the "average"  $\text{C}-\text{H}$  bond energy.

(d)



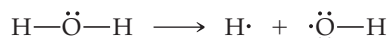
**18.33** Incoming and outgoing energies are in different regions of the electromagnetic spectrum.  $\text{CO}_2$  is transparent to incoming visible radiation but absorbs outgoing infrared radiation. **18.35**  $0.099 \text{ M Na}^+$  **18.37** (a)  $3.22 \times 10^3 \text{ g H}_2\text{O}$  (b) The final temperature is  $43.4^\circ\text{C}$ . **18.39**  $4.361 \times 10^5 \text{ g CaO}$  **18.41** (a) Groundwater is freshwater (less than 500 ppm total salt content) that is under the soil; it composes 20% of the world's freshwater. (b) An aquifer is a layer of porous rock that holds groundwater. **18.43** The minimum pressure required to initiate reverse osmosis is greater than  $5.1 \text{ atm}$ . **18.45** (a)  $\text{CO}_2(\text{g})$ ,  $\text{HCO}_3^-$ ,  $\text{H}_2\text{O}(\text{l})$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$  (b)  $\text{CH}_4(\text{g})$ ,  $\text{H}_2\text{S}(\text{g})$ ,  $\text{NH}_3(\text{g})$ ,  $\text{PH}_3(\text{g})$  **18.47**  $25.1 \text{ g O}_2$  **18.49**  $\text{Mg}^{2+}(\text{aq}) + \text{Ca}(\text{OH})_2(\text{s}) \longrightarrow \text{Mg}(\text{OH})_2(\text{s}) + \text{Ca}^{2+}(\text{aq})$  **18.51**  $0.42 \text{ mol Ca}(\text{OH})_2$ ,  $0.18 \text{ mol Na}_2\text{CO}_3$  **18.53**  $4 \text{ FeSO}_4(\text{aq}) + \text{O}_2(\text{aq}) + 2 \text{ H}_2\text{O}(\text{l}) \longrightarrow 4 \text{ Fe}^{3+}(\text{aq}) + 4 \text{ OH}^-(\text{aq}) + 4 \text{ SO}_4^{2-}(\text{aq})$ ;  $\text{Fe}^{3+}(\text{aq}) + 3 \text{ HCO}_3^-(\text{aq}) \longrightarrow \text{Fe}(\text{OH})_3(\text{s}) + 3 \text{ CO}_2(\text{g})$  **18.55** (a) Trihalomethanes are the by-products of water chlorination; they contain one central carbon atom bound to one hydrogen and three halogen atoms.

(b)



**18.57** The fewer steps in a process, the less waste is generated. Processes with fewer steps require less energy at the site of the process and for subsequent cleanup or disposal of waste. **18.59** (a)  $\text{H}_2\text{O}$  (b) It is better to prevent waste than to treat it. Atom economy. Less hazardous chemical synthesis and inherently safer for accident prevention. Catalysis and design for energy efficiency. Raw materials should be renewable. **18.61** (a) Water as a solvent, by criteria 5, 7, and 12. (b) Reaction temperature of  $500 \text{ K}$ , by criteria 6, 12, and 1. (c) Sodium chloride as a by-product, according to criteria 1, 3, and 12. **18.66** Multiply Equation 18.7 by a factor of 2; then add it to Equation 18.9.  $2 \text{ Cl}(\text{g})$  and  $2 \text{ ClO}(\text{g})$  cancel from each side of the resulting equation to produce Equation 18.10. **18.69** Although HFCs have long lifetimes in the stratosphere, it is infrequent that light with energy sufficient to dissociate a  $\text{C}-\text{F}$  bond will reach an HFC molecule. F atoms, the bad actors in ozone destruction, are much less likely than Cl atoms to be produced by photodissociation in the stratosphere. **18.71** The formation of  $\text{NO}(\text{g})$  is endothermic, so  $K$  increases with increasing

temperature. The oxidation of  $\text{NO}(g)$  to  $\text{NO}_2(g)$  is exothermic, so the value of  $K$  decreases with increasing temperature. **18.75**  $7.1 \times 10^8 \text{ m}^2$  **18.77** (a)  $\text{CO}_3^{2-}$  is a relatively strong Brønsted-Lowry base and produces  $\text{OH}^-$  in aqueous solution. If  $[\text{OH}^-(aq)]$  is sufficient for the reaction quotient to exceed  $K_{sp}$  for  $\text{Mg}(\text{OH})_2$ , the solid will precipitate. (b) At these ion concentrations,  $Q > K_{sp}$  and  $\text{Mg}(\text{OH})_2$  will precipitate. **18.81** (a)  $2.5 \times 10^7 \text{ ton CO}_2$ ,  $4.2 \times 10^5 \text{ ton SO}_2$  (b)  $4.3 \times 10^5 \text{ ton CaSO}_3$  **18.84** (a)



(b) 258 nm (c) The overall reaction is  $\text{O}_3(g) + \text{O}(g) \longrightarrow 2 \text{O}_2(g)$ .  $\text{OH}(g)$  is the catalyst in the overall reaction because it is consumed and then reproduced. **18.86** The enthalpy change for the first step is  $-141 \text{ kJ}$ , for the second step,  $-249 \text{ kJ}$ , for the overall reaction,  $-390 \text{ kJ}$ . **18.90** (a)  $\text{Rate} = k[\text{O}_3][\text{H}]$  (b)  $k_{\text{avg}} = 1.13 \times 10^{44} \text{ M}^{-1} \text{ s}^{-1}$  **18.95** (a) Process (i) is greener because it involves neither the toxic reactant phosgene nor the by-product HCl. (b) Reaction (i): C in  $\text{CO}_2$  is linear with  $sp$  hybridization; C in  $\text{R}-\text{N}=\text{C}=\text{O}$  is linear with  $sp$  hybridization; C in the urethane monomer is trigonal planar with  $sp^2$  hybridization. Reaction (ii): C in  $\text{COCl}_2$  is linear with  $sp^2$  hybridization; C in  $\text{R}-\text{N}=\text{C}=\text{O}$  is linear with  $sp$  hybridization; C in the urethane monomer is trigonal planar with  $sp^2$  hybridization. (c) The greenest way to promote formation of the isocyanate is to remove by-product, either water or HCl, from the reaction mixture.

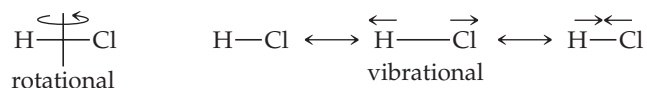
## CHAPTER 19

**19.1** (a)

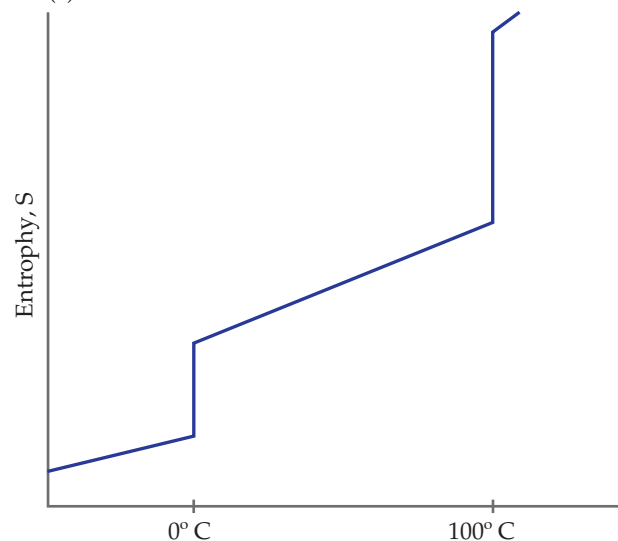


(b)  $\Delta H = 0$  for mixing ideal gases.  $\Delta S$  is positive because the disorder of the system increases. (c) The process is spontaneous and therefore irreversible. (d) Since  $\Delta H = 0$ , the process does not affect the entropy of the surroundings. **19.4**  $\Delta S$  is positive. **19.7** (a) At 300 K,  $\Delta G = 0$ , and the system is at equilibrium. (b) The reaction is spontaneous at temperatures above 300 K. **19.10** (a) The minimum in the plot is the equilibrium position of the reaction. (b) The quantity  $x$  is  $\Delta G^\circ$ . **19.11** Spontaneous: a, b, c, d; nonspontaneous: e **19.13** (a)  $\text{NH}_4\text{NO}_3(s)$  dissolves in water, as in a chemical cold pack. Naphthalene (moth balls) sublimates at room temperature. (b) Melting of a solid is spontaneous above its melting point but nonspontaneous below its melting point. **19.15** (a) Endothermic (b) above  $100^\circ\text{C}$  (c) below  $100^\circ\text{C}$  (d) at  $100^\circ\text{C}$  **19.17** (a) For a reversible process, the forward and reverse changes occur by the same path. In a reversible process, both the system and the surroundings are restored to their original condition by exactly reversing the change. A reversible change produces the maximum amount of work. (b) There is no net change in the surroundings. (c) The vaporization of water to steam is reversible if it occurs at the boiling temperature of water for a specified external (atmospheric) pressure and if the required heat is added infinitely slowly. (d) No. Natural processes are spontaneous in the direction they occur and nonspontaneous in the opposite direction. By definition they are irreversible. **19.19** (a) If the ideal gas is contained in a closed system at constant volume, a decrease in external temperature leads to a decrease in both temperature and pressure of the gas. (b) If the ideal gas is contained in a closed system at constant pressure, a decrease in external temperature leads to a decrease in both temperature and volume of the gas. (c) No.  $\Delta E$  is a state function.  $\Delta E = q + w$ ;  $q$  and  $w$  are not state functions. Their values do depend on path, but their sum,  $\Delta E$ , does not. **19.21** (a) An ice cube can melt reversibly at the conditions of temperature and pressure where the solid and liquid are in equilibrium. (b) We know that melting is a process that increases the energy of the system even though there is no change in temper-

ature.  $\Delta E$  is not zero for the process. **19.23** (a) At constant temperature,  $\Delta S = q_{\text{rev}}/T$ , where  $q_{\text{rev}}$  is the heat that would be transferred if the process were reversible. (b) No.  $\Delta S$  is a state function, so it is independent of path. **19.25** (a) Entropy increases. (b)  $89.2 \text{ J/K}$  **19.27** (a) For a spontaneous process, the entropy of the universe increases; for a reversible process, the entropy of the universe does not change. (b) For a reversible process, if the entropy of the system increases, the entropy of the surroundings must decrease by the same amount. (c) For a spontaneous process, the entropy of the universe must increase, so the entropy of the surroundings must decrease by less than  $42 \text{ J/K}$ . **19.29** (a) Positive  $\Delta S$  (b)  $\Delta S = 1.02 \text{ J/K}$  (c) Temperature need not be specified to calculate  $\Delta S$ , as long as the expansion is isothermal. **19.31** (a) Yes, the expansion is spontaneous. (b) As the ideal gas expands into the vacuum, there is nothing for it to “push back,” so no work is done. Mathematically,  $w = -P_{\text{ext}}\Delta V$ . Since the gas expands into a vacuum,  $P_{\text{ext}} = 0$  and  $w = 0$ . (c) The “driving force” for the expansion of the gas is the increase in entropy. **19.33** (a) An increase in temperature produces more available microstates for a system. (b) A decrease in volume produces fewer available microstates for a system. (c) Going from liquid to gas, the number of available microstates increases. **19.35** (a)  $\Delta S$  is positive. (b)  $S$  of the system clearly increases in 19.11 (b) and (e); it clearly decreases in 19.9 (c). The entropy change is difficult to judge in 19.9 (a) and definition of the system in (d) is problematic. **19.37**  $S$  increases in (a) and (c);  $S$  decreases in (b). **19.39** (a) The entropy of a pure crystalline substance at absolute zero is zero. (b) In translational motion the entire molecule moves in a single direction; in rotational motion the molecule rotates or spins around a fixed axis. In vibrational motion the bonds within a molecule stretch and bend, but the average position of the atoms does not change.



**19.41** (a)  $\text{Ar}(g)$  (b)  $\text{He}(g)$  at 1.5 atm (c) 1 mol of  $\text{Ne}(g)$  in 15.0 L (d)  $\text{CO}_2(g)$  **19.43** (a)  $\Delta S < 0$  (b)  $\Delta S > 0$  (c)  $\Delta S < 0$  (d)  $\Delta S \approx 0$  **19.45** (a)



(b) Boiling water, at  $100^\circ\text{C}$ , has a much larger entropy change than melting ice at  $0^\circ\text{C}$ . **19.47** (a)  $\text{C}_2\text{H}_6(g)$  (b)  $\text{CO}_2(g)$  **19.49** (a)  $\text{Sc}(s)$ ,  $34.6 \text{ J/mol}\cdot\text{K}$ ;  $\text{Sc}(g)$ ,  $174.7 \text{ J/mol}\cdot\text{K}$ . In general, the gas phase of a substance has a larger  $S^\circ$  than the solid phase because of the greater volume and motional freedom of the molecules. (b)  $\text{NH}_3(g)$ ,  $192.5 \text{ J/mol}\cdot\text{K}$ ;  $\text{NH}_3(aq)$ ,  $111.3 \text{ J/mol}\cdot\text{K}$ . Molecules in the gas phase have more motional freedom than molecules in solution. (c) 1 mol of

$P_4(g)$ , 280 J/K; 2 mol of  $P_2(g)$ ,  $2(218.1) = 436.2$  J/K. More particles have a greater motional energy (more available microstates). (d) C (diamond), 2.43 J/mol-K; C (graphite), 5.69 J/mol-K. The internal entropy in graphite is greater because there is translational freedom among planar sheets of C atoms, while there is very little freedom within the covalent-network diamond lattice. **19.51** For elements with similar structures, the heavier the atoms, the lower the vibrational frequencies at a given temperature. This means that more vibrations can be accessed at a particular temperature, resulting in greater absolute entropy for the heavier elements. **19.53** (a)  $\Delta S^\circ = -120.5$  J/K.  $\Delta S^\circ$  is negative because there are fewer moles of gas in the products. (b)  $\Delta S^\circ = +176.6$  J/K.  $\Delta S^\circ$  is positive because there are more moles of gas in the products. (c)  $\Delta S^\circ = +152.39$  J/K.  $\Delta S^\circ$  is positive because the product contains more total particles and more moles of gas. (d)  $\Delta S^\circ = +92.3$  J/K.  $\Delta S^\circ$  is positive because there are more moles of gas in the products. **19.55** (a)  $\Delta G = \Delta H - T\Delta S$  (b) If  $\Delta G$  is positive, the process is nonspontaneous, but the reverse process is spontaneous. (c) There is no relationship between  $\Delta G$  and rate of reaction. **19.57** (a) Exothermic (b)  $\Delta S^\circ$  is negative; the reaction leads to a decrease in disorder. (c)  $\Delta G^\circ = -9.9$  kJ (d) If all reactants and products are present in their standard states, the reaction is spontaneous in the forward direction at this temperature. **19.59** (a)  $\Delta H^\circ = -537.22$  kJ,  $\Delta S^\circ = 13.7$  J/K,  $\Delta G^\circ = -541.40$  kJ,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -541.31$  kJ (b)  $\Delta H^\circ = -106.7$  kJ,  $\Delta S^\circ = -142.2$  kJ,  $\Delta G^\circ = -64.0$  kJ,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -64.3$  kJ (c)  $\Delta H^\circ = -508.3$  kJ,  $\Delta S^\circ = -178$  kJ,  $\Delta G^\circ = -465.8$  kJ,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -455.1$  kJ. The discrepancy in  $\Delta G^\circ$  values is due to experimental uncertainties in the tabulated thermodynamic data. (d)  $\Delta H^\circ = -165.9$  kJ,  $\Delta S^\circ = 1.4$  kJ,  $\Delta G^\circ = -166.2$  kJ,  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -166.3$  kJ **19.61** (a)  $\Delta G^\circ = -140.0$  kJ, spontaneous (b)  $\Delta G^\circ = +104.70$  kJ, nonspontaneous (c)  $\Delta G^\circ = +146$  kJ, nonspontaneous (d)  $\Delta G^\circ = -156.7$  kJ, spontaneous **19.63** (a)  $2C_8H_{18}(l) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(l)$  (b) Because  $\Delta S^\circ$  is positive,  $\Delta G^\circ$  is more negative than  $\Delta H^\circ$ . **19.65** (a) The forward reaction is spontaneous at low temperatures but becomes nonspontaneous at higher temperatures. (b) The reaction is nonspontaneous in the forward direction at all temperatures. (c) The forward reaction is nonspontaneous at low temperatures but becomes spontaneous at higher temperatures. **19.67**  $\Delta S > 60.8$  J/K **19.69** (a)  $T = 330$  K (b) nonspontaneous **19.71** (a)  $\Delta H^\circ = 155.7$  kJ,  $\Delta S^\circ = 171.4$  kJ. Since  $\Delta S^\circ$  is positive,  $\Delta G^\circ$  becomes more negative with increasing temperature. (b)  $\Delta G^\circ = 19$  kJ. The reaction is not spontaneous under standard conditions at 800 K (c)  $\Delta G^\circ = -15.7$  kJ. The reaction is spontaneous under standard conditions at 1000 K. **19.73** (a)  $T_b = 79^\circ\text{C}$  (b) From the *Handbook of Chemistry and Physics*, 74th Edition,  $T_b = 80.1^\circ\text{C}$ . The values are remarkably close; the small difference is due to deviation from ideal behavior by  $C_6H_6(g)$  and experimental uncertainty in the boiling point measurement and the thermodynamic data. **19.75** (a)  $C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$  (b)  $-1299.5$  kJ of heat produced/mol  $C_2H_2$  burned (c)  $w_{\max} = -1235.1$  kJ/mol  $C_2H_2$  **19.77** (a)  $\Delta G$  becomes more negative. (b)  $\Delta G$  becomes more positive. (c)  $\Delta G$  becomes more positive. **19.79** (a)  $\Delta G^\circ = -5.40$  kJ (b)  $\Delta G = 0.30$  kJ **19.81** (a)  $\Delta G^\circ = -16.77$  kJ,  $K = 870$  (b)  $\Delta G^\circ = 8.0$  kJ,  $K = 0.039$  (c)  $\Delta G^\circ = -497.9$  kJ,  $K = 2 \times 10^{87}$  **19.83**  $\Delta H^\circ = 269.3$  kJ,  $\Delta S^\circ = 0.1719$  kJ/K (a)  $P_{CO_2} = 6.0 \times 10^{-39}$  atm (b)  $P_{CO_2} = 1.6 \times 10^{-4}$  atm **19.85** (a)  $HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$  (b)  $\Delta G^\circ = 19.1$  kJ (c)  $\Delta G = 0$  at equilibrium (d)  $\Delta G = -2.7$  kJ **19.87** (a) The thermodynamic quantities  $T$ ,  $E$ , and  $S$  are state functions. (b) The quantities  $q$  and  $w$  depend on the path taken. (c) There is only one reversible path between states. (d)  $\Delta E = q_{rev} + w_{max}$ ,  $\Delta S = q_{rev}/T$ . **19.91** (a) 16 arrangements (b) 1 arrangement (c) The gas will spontaneously adopt the state with the most possible arrangements for the molecules, the state with maximum disorder. **19.96** (a) For all three compounds listed, there are fewer moles of gaseous products than reactants in the formation reaction, so we expect  $\Delta S_f^\circ$  to be negative. If  $\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ$  and  $\Delta S_f^\circ$  is negative,  $-T\Delta S_f^\circ$  is positive and  $\Delta G_f^\circ$  is more positive than

$\Delta H_f^\circ$ . (b) In this reaction, there are more moles of gas in products,  $\Delta S_f^\circ$  is positive,  $-T\Delta S_f^\circ$  is negative and  $\Delta G_f^\circ$  is more negative than  $\Delta H_f^\circ$ .

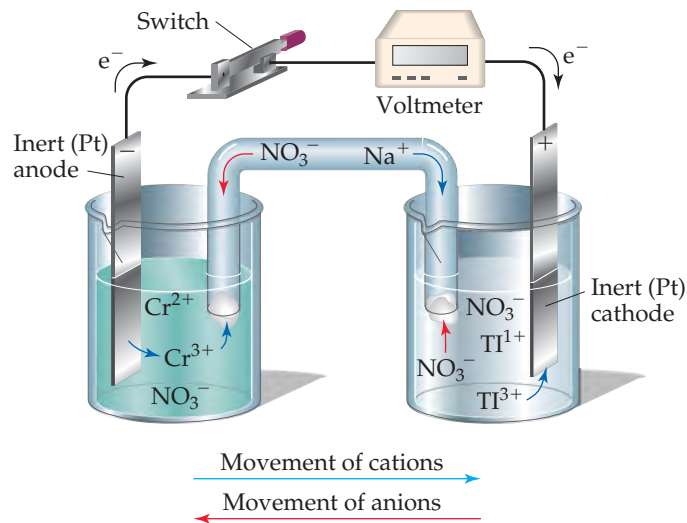
**19.100** (a)  $K = 4 \times 10^{15}$  (b) An increase in temperature will decrease the mole fraction of  $CH_3COOH$  at equilibrium. Elevated temperatures must be used to increase the speed of the reaction. (c)  $K = 1$  at 836 K or  $563^\circ\text{C}$ . **19.104** (a)  $\Delta G = 8.77$  kJ (b)  $w_{\min} = 8.77$  kJ. In practice, a larger than minimum amount of work is required. **19.108** (a) Acetone,  $\Delta S_{\text{vap}}^\circ = 88.4$  J/mol-K; dimethyl ether,  $\Delta S_{\text{vap}}^\circ = 86.6$  J/mol-K; ethanol,  $\Delta S_{\text{vap}}^\circ = 110$  J/mol-K; octane,  $\Delta S_{\text{vap}}^\circ = 86.3$  J/mol-K; pyridine,  $\Delta S_{\text{vap}}^\circ = 90.4$  J/mol-K. Ethanol does not obey Trouton's rule. (b) Hydrogen bonding (in ethanol and other liquids) leads to more ordering in the liquid state and a greater than usual increase in entropy upon vaporization. Liquids that experience hydrogen bonding are probably exceptions to Trouton's rule. (c) Owing to strong hydrogen bonding interactions, water probably does not obey Trouton's rule.  $\Delta S_{\text{vap}}^\circ = 109.0$  J/mol-K. (d)  $\Delta H_{\text{vap}}$  for  $C_6H_5Cl \approx 36$  kJ/mol **19.113** (a) For any given total pressure, the condition of equal moles of the two gases can be achieved at some temperature. For individual gas pressures of 1 atm and a total pressure of 2 atm, the mixture is at equilibrium at 328.5 K or  $55.5^\circ\text{C}$ . (b) 333.0 K or  $60^\circ\text{C}$  (c) 374.2 K or  $101.2^\circ\text{C}$  (d) The reaction is endothermic, so an increase in the value of  $K$  as calculated in parts (a)–(c) should be accompanied by an increase in  $T$ .

## CHAPTER 20

**20.1** In a Brønsted–Lowry acid–base reaction,  $H^+$  is transferred from the acid to the base. In a redox reaction, one or more electrons are transferred from the reductant to the oxidant. The greater the tendency of an acid to donate  $H^+$ , the lesser the tendency of its conjugate base to accept  $H^+$ . The stronger the acid, the weaker its conjugate base. Similarly, the greater the tendency of a reduced species to donate electrons, the lesser the tendency of the corresponding oxidized species to accept electrons. The stronger the reducing agent, the weaker the corresponding oxidizing agent. **20.4** (a) Add 1 M  $A^{2+}(aq)$  to the beaker with the A(s) electrode. Add 1 M  $B^{2+}(aq)$  to the beaker with the B(s) electrode. Add a salt bridge to enable the flow of ions from one compartment to the other. (b) The A electrode functions as the cathode. (c) Electrons flow through the external circuit from the anode to the cathode, from B to A in this cell. (d)  $E_{\text{cell}}^\circ = 1.00$  V. **20.7** (a) The sign of  $\Delta G^\circ$  is positive. (b) The equilibrium constant is less than one. (c) No. An electrochemical cell based on this reaction cannot accomplish work on its surroundings. **20.9** (a) Line 1 (b)  $E_{\text{red}} = E_{\text{red}}^\circ = 0.799$  V. **20.13** (a) Oxidation is the loss of electrons. (b) Electrons appear on the products' side (right side). (c) The oxidant is the reactant that is reduced. (d) An oxidizing agent is the substance that promotes oxidation; it is the oxidant. **20.15** (a) True (b) false (c) true **20.17** (a) I, +5 to 0; C, +2 to +4 (b) Hg, +2 to 0; N, -2 to 0 (c) N, +5 to +2; S, -2 to 0 (d) Cl, +4 to +3; O, -1 to 0 **20.19** (a)  $TiCl_4(g) + 2Mg(l) \longrightarrow Ti(s) + 2MgCl_2(l)$  (b)  $Mg(l)$  is oxidized;  $TiCl_4(g)$  is reduced. (c)  $Mg(l)$  is the reductant;  $TiCl_4(g)$  is the oxidant. **20.21** (a)  $Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2e^-$ , oxidation (b)  $TiO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Ti^{2+}(aq) + 2H_2O(l)$ , reduction (c)  $ClO_3^-(aq) + 6H^+(aq) + 6e^- \longrightarrow Cl^-(aq) + 3H_2O(l)$ , reduction (d)  $N_2(g) + 8H^+(aq) + 6e^- \longrightarrow 2NH_4^+(aq)$ , reduction (e)  $4OH^-(aq) \longrightarrow O_2(g) + 2H_2O(l) + 4e^-$ , oxidation (f)  $SO_3^{2-}(aq) + 2OH^-(aq) \longrightarrow SO_4^{2-}(aq) + H_2O(l) + 2e^-$ , oxidation (g)  $N_2(g) + 6H_2O(l) + 6e^- \longrightarrow 2NH_3(g) + 6OH^-(aq)$ , reduction **20.23** (a)  $Cr_2O_7^{2-}(aq) + I^-(aq) + 8H^+(aq) \longrightarrow 2Cr^{3+}(aq) + IO_3^-(aq) + 4H_2O(l)$ ; oxidizing agent,  $Cr_2O_7^{2-}$ ; reducing agent,  $I^-$  (b)  $4MnO_4^-(aq) + 5CH_3OH(aq) + 12H^+(aq) \longrightarrow 4Mn^{2+}(aq) + 5HCO_2H(aq) + 12H_2O(aq)$ ; oxidizing agent,  $MnO_4^-$ ; reducing agent,  $CH_3OH$  (c)  $I_2(s) + 5OCl^-(aq) + H_2O(l) \longrightarrow 2IO_3^-(aq) + 5Cl^-(aq) + 2H^+(aq)$ ; oxidizing agent,  $OCl^-$ ; reducing agent,  $I_2$  (d)  $As_2O_3(s) +$



$2 \text{NO}_3^-(aq) + 2 \text{H}_2\text{O}(l) + 2 \text{H}^+(aq) \longrightarrow 2 \text{H}_3\text{AsO}_4(aq) + \text{N}_2\text{O}_3(aq)$ ; oxidizing agent,  $\text{NO}_3^-$ ; reducing agent,  $\text{As}_2\text{O}_3$   
 (e)  $2 \text{MnO}_4^-(aq) + \text{Br}^-(aq) + \text{H}_2\text{O}(l) \longrightarrow 2 \text{MnO}_2(s) + \text{BrO}_3^-(aq) + 2 \text{OH}^-(aq)$ ; oxidizing agent,  $\text{MnO}_4^-$ ; reducing agent,  $\text{Br}^-$  (f)  $\text{Pb}(\text{OH})_4^{2-}(aq) + \text{ClO}^-(aq) \longrightarrow \text{PbO}_2(s) + \text{Cl}^-(aq) + 2 \text{OH}^-(aq) + \text{H}_2\text{O}(l)$ ; oxidizing agent,  $\text{ClO}^-$ ; reducing agent,  $\text{Pb}(\text{OH})_4^{2-}$   
**20.25** (a) The reaction  $\text{Cu}^{2+}(aq) + \text{Zn}(s) \longrightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq)$  is occurring in both figures. In Figure 20.3 the reactants are in contact, while in Figure 20.4 the oxidation half-reaction and reduction half-reaction are occurring in separate compartments. In Figure 20.3 the flow of electrons cannot be isolated or utilized; in Figure 20.4 electrical current is isolated and flows through the voltmeter. (b)  $\text{Na}^+$  cations are drawn into the cathode compartment to maintain charge balance as  $\text{Cu}^{2+}$  ions are removed. **20.27** (a)  $\text{Fe}(s)$  is oxidized,  $\text{Ag}^+(aq)$  is reduced. (b)  $\text{Ag}^+(aq) + e^- \longrightarrow \text{Ag}(s)$ ;  $\text{Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 2e^-$  (c)  $\text{Fe}(s)$  is the anode,  $\text{Ag}(s)$  is the cathode. (d)  $\text{Fe}(s)$  is negative;  $\text{Ag}(s)$  is positive. (e) Electrons flow from the Fe electrode (-) toward the Ag electrode (+). (f) Cations migrate toward the  $\text{Ag}(s)$  cathode; anions migrate toward the  $\text{Fe}(s)$  anode. **20.29** *Electromotive force*, emf, is the potential energy difference between an electron at the anode and an electron at the cathode of a voltaic cell. (b) One volt is the potential energy difference required to impart 1 J of energy to a charge of 1 coulomb. (c) *Cell potential*,  $E_{\text{cell}}$ , is the emf of an electrochemical cell.  
**20.31** (a)  $2 \text{H}^+(aq) + 2e^- \longrightarrow \text{H}_2(g)$  (b) A standard hydrogen electrode, SHE, has components that are at standard conditions, 1 M  $\text{H}^+(aq)$  and  $\text{H}_2(g)$  at 1 atm. (c) The platinum foil in a SHE serves as an inert electron carrier and a solid reaction surface. **20.33** (a) A *standard reduction potential* is the relative potential of a reduction half-reaction measured at standard conditions. (b)  $E_{\text{red}}^\circ = 0 \text{ V}$  **20.35** (a)  $\text{Cr}^{2+}(aq) \longrightarrow \text{Cr}^{3+}(aq) + e^-$ ;  $\text{Tl}^{3+}(aq) + 2e^- \longrightarrow \text{Tl}^+(aq)$  (b)  $E_{\text{red}}^\circ = 0.78 \text{ V}$  (c)



**20.37** (a)  $E^\circ = 0.823 \text{ V}$  (b)  $E^\circ = 1.89 \text{ V}$  (c)  $E^\circ = 1.211 \text{ V}$  (d)  $E^\circ = 0.62 \text{ V}$  **20.39** (a)  $3 \text{Ag}^+(aq) + \text{Cr}(s) \longrightarrow 3 \text{Ag}(s) + \text{Cr}^{3+}(aq)$ ,  $E^\circ = 1.54 \text{ V}$  (b) Two of the combinations have essentially equal  $E^\circ$  values:  $2 \text{Ag}^+(aq) + \text{Cu}(s) \longrightarrow 2 \text{Ag}(s) + \text{Cu}^{2+}(aq)$ ,  $E^\circ = 0.462 \text{ V}$ ;  $3 \text{Ni}^{2+}(aq) + 2 \text{Cr}(s) \longrightarrow 3 \text{Ni}(s) + 2 \text{Cr}^{3+}(aq)$ ,  $E^\circ = 0.46 \text{ V}$  **20.41** (a) Anode,  $\text{Sn}(s)$ ; cathode,  $\text{Cu}(s)$ . (b) The copper electrode gains mass as  $\text{Cu}$  is plated out, and the tin electrode loses mass as  $\text{Sn}$  is oxidized. (c)  $\text{Cu}^{2+}(aq) + \text{Sn}(s) \longrightarrow \text{Cu}(s) + \text{Sn}^{2+}(aq)$ . (d)  $E^\circ = 0.473 \text{ V}$ . **20.43** (a)  $\text{Mg}(s)$  (b)  $\text{Ca}(s)$  (c)  $\text{H}_2(g)$  (d)  $\text{BrO}_3^-(aq)$   
**20.45** (a)  $\text{Cl}_2(aq)$ , strong oxidant (b)  $\text{MnO}_4^-(aq)$ , acidic, strong oxidant (c)  $\text{Ba}(s)$  strong reductant (d)  $\text{Zn}(s)$ , reductant  
**20.47** (a)  $\text{Cu}^{2+}(aq) < \text{O}_2(g) < \text{Cr}_2\text{O}_7^{2-}(aq) < \text{Cl}_2(g) < \text{H}_2\text{O}_2(aq)$

(b)  $\text{H}_2\text{O}_2(aq) < \text{I}^-(aq) < \text{Sn}^{2+}(aq) < \text{Zn}(s) < \text{Al}(s)$  **20.49**  $\text{Al}$  and  $\text{H}_2\text{C}_2\text{O}_4$  **20.51** (a)  $2 \text{Fe}^{2+}(aq) + \text{S}_2\text{O}_6^{2-}(aq) + 4 \text{H}^+(aq) \longrightarrow 2 \text{Fe}^{3+}(aq) + 2 \text{H}_2\text{SO}_3(aq)$ ;  $2 \text{Fe}^{2+}(aq) + \text{N}_2\text{O}(aq) + 2 \text{H}^+(aq) \longrightarrow 2 \text{Fe}^{3+}(aq) + \text{N}_2(g) + \text{H}_2\text{O}(l)$ ;  $\text{Fe}^{2+}(aq) + \text{VO}_2^+(aq) + 2 \text{H}^+(aq) \longrightarrow \text{Fe}^{3+}(aq) + \text{VO}^{2+}(aq) + \text{H}_2\text{O}(l)$  (b)  $E^\circ = -0.17 \text{ V}$ ,  $\Delta G^\circ = 33 \text{ kJ}$ ;  $E^\circ = -2.54 \text{ V}$ ,  $\Delta G^\circ = 4.90 \times 10^2 \text{ kJ}$ ;  $E^\circ = 0.23 \text{ V}$ ,  $\Delta G^\circ = -22 \text{ kJ}$   
 (c)  $K = 1.8 \times 10^{-6} = 10^{-6}$ ;  $K = 1.2 \times 10^{-86} = 10^{-86}$ ;  
 $K = 7.8 \times 10^3 = 8 \times 10^3$  **20.53**  $\Delta G^\circ = 21.8 \text{ kJ}$ ,  $E_{\text{cell}}^\circ = -0.113 \text{ V}$   
**20.55** (a)  $E^\circ = 0.16 \text{ V}$ ,  $K = 2.54 \times 10^5 = 3 \times 10^5$  (b)  $E^\circ = 0.277 \text{ V}$ ,  $K = 2.3 \times 10^9$  (c)  $E^\circ = 0.45 \text{ V}$ ,  $K = 1.5 \times 10^{75} = 10^{75}$   
**20.57** (a)  $K = 9.8 \times 10^2$  (b)  $K = 9.5 \times 10^5$  (c)  $K = 9.3 \times 10^8$   
**20.59** (a)  $w_{\text{max}} = -130 \text{ kJ/mol Sn}$  **20.61** (a) The Nernst equation is applicable when the components of an electrochemical cell are at nonstandard conditions. (b)  $Q = 1$  (c)  $Q$  decreases and  $E$  increases **20.63** (a)  $E$  decreases (b)  $E$  decreases (c)  $E$  decreases (d) no effect  
**20.65** (a)  $E^\circ = 0.48 \text{ V}$  (b)  $E = 0.53 \text{ V}$  (c)  $E = 0.46 \text{ V}$   
**20.67** (a)  $E^\circ = 0.46 \text{ V}$  (b)  $E = 0.37 \text{ V}$  **20.69** (a) The compartment with  $[\text{Zn}^{2+}] = 1.00 \times 10^{-2} \text{ M}$  is the anode. (b)  $E^\circ = 0$  (c)  $E = 0.0668 \text{ V}$  (d) In the anode compartment  $[\text{Zn}^{2+}]$  increases; in the cathode compartment  $[\text{Zn}^{2+}]$  decreases **20.71**  $E^\circ = 0.763 \text{ V}$ ,  $\text{pH} = 1.6$  **20.73** (a) The emf of a battery decreases as it is used. The concentrations of products increase and the concentrations of reactants decrease, causing  $Q$  to increase and  $E_{\text{cell}}$  to decrease. (b) A D-size battery contains more reactants than a AA, enabling the D to provide power for a longer time.  
**20.75** (a) 464 g  $\text{PbO}_2$  (b)  $3.74 \times 10^5 \text{ C}$  of charge transferred  
**20.77** (a) The anode (b)  $E^\circ = 0.50 \text{ V}$  (c) The emf of the battery, 3.5 V, is exactly the standard cell potential calculated in part (b). (d) At ambient conditions,  $E \approx E^\circ$ , so  $\log Q \approx 1$ . Assuming that the value of  $E^\circ$  is relatively constant with temperature, the value of the second term in the Nernst equation is approximately zero at  $37^\circ\text{C}$ , and  $E \approx 3.5 \text{ V}$ .  
**20.79** (a) The cell emf will have a smaller value. (b) NiMH batteries use an alloy such as  $\text{ZrNi}_2$  as the anode material. This eliminates the use and disposal problems associated with  $\text{Cd}$ , a toxic heavy metal.  
**20.81** The main advantage of a fuel cell is that fuel is continuously supplied, so that it can produce electrical current for a time limited only by the amount of available fuel. For the hydrogen-oxygen fuel cell, this is also a disadvantage because volatile and explosive hydrogen must be acquired and stored. Alkaline batteries are convenient, but they have a short lifetime, and the disposal of their zinc and manganese solids is more problematic than disposal of water produced by the hydrogen-oxygen fuel cell. **20.83** (a) anode:  $\text{Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 2e^-$ ; cathode:  $\text{O}_2(g) + 4 \text{H}^+(aq) + 4e^- \longrightarrow 2 \text{H}_2\text{O}(l)$  (b)  $2 \text{Fe}^{2+}(aq) + 3 \text{H}_2\text{O}(l) + 3 \text{H}_2\text{O}(l) \longrightarrow \text{Fe}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}(s) + 6 \text{H}^+(aq) + 2e^-$ ;  $\text{O}_2(g) + 4 \text{H}^+(aq) + 4e^- \longrightarrow 2 \text{H}_2\text{O}(l)$  **20.85** (a)  $\text{Mg}$  is called a "sacrificial anode" because it has a more negative  $E_{\text{red}}^\circ$  than the pipe metal and is preferentially oxidized when the two are coupled. It is sacrificed to preserve the pipe. (b)  $E_{\text{red}}^\circ$  for  $\text{Mg}^{2+}$  is  $-2.37 \text{ V}$ , more negative than most metals present in pipes, including  $\text{Fe}$  and  $\text{Zn}$ . **20.87** Under acidic conditions, air ( $\text{O}_2$ ) oxidation of  $\text{Zn}(s)$ , 1.99 V;  $\text{Fe}(s)$ , 1.67 V; and  $\text{Cu}(s)$ , 0.893 V are all spontaneous. When the three metals are in contact,  $\text{Zn}$  will act as a sacrificial anode for both  $\text{Fe}$  and  $\text{Cu}$ , but after the  $\text{Zn}$  is depleted,  $\text{Fe}$  will be oxidized (corroded). **20.89** (a) *Electrolysis* is an electrochemical process driven by an outside energy source. (b) By definition, electrolysis reactions are nonspontaneous. (c)  $2 \text{Cl}^-(l) \longrightarrow \text{Cl}_2(g) + 2e^-$  (d) When an aqueous solution of  $\text{NaCl}$  undergoes electrolysis, sodium metal is not formed because  $\text{H}_2\text{O}$  is preferentially reduced to form  $\text{H}_2(g)$ .  
**20.91** (a) 236 g  $\text{Cr}(s)$  (b) 2.51 A **20.93** (a)  $4.0 \times 10^5 \text{ g Li}$  (b) The minimum voltage required to drive the electrolysis is +4.41 V.  
**20.95** Gold is less active than copper and thus more difficult to oxidize. When crude copper is refined by electrolysis,  $\text{Cu}$  is oxidized from the crude anode, but any metallic gold present in the crude copper is not oxidized, so it accumulates near the anode, available for collection.  
**20.97** (a)  $2 \text{Ni}^+(aq) \longrightarrow \text{Ni}(s) + \text{Ni}^{2+}(aq)$  (b)  $3 \text{MnO}_4^{2-}(aq) + 4 \text{H}^+(aq) \longrightarrow 2 \text{MnO}_4^-(aq) + \text{MnO}_2(s) + 2 \text{H}_2\text{O}(l)$

(c)  $3\text{H}_2\text{SO}_3(aq) \longrightarrow \text{S}(s) + 2\text{HSO}_4^-(aq) + 2\text{H}^+(aq) + \text{H}_2\text{O}(l)$   
 (d)  $\text{Cl}_2(aq) + 2\text{OH}^-(aq) \longrightarrow \text{Cl}^-(aq) + \text{ClO}^-(aq) + \text{H}_2\text{O}(l)$   
**20.100** (a)  $E^\circ = 0.627\text{V}$ , spontaneous (b)  $E^\circ = -0.82\text{V}$ , nonspontaneous (c)  $E^\circ = 0.93\text{V}$ , spontaneous (d)  $E^\circ = 0.183\text{V}$ , spontaneous  
**20.104**  $K = 1.6 \times 10^6$  **20.107** The ship's hull should be made negative. The ship, as a negatively charged "electrode," becomes the site of reduction, rather than oxidation, in an electrolytic process.  
**20.110**  $3.0 \times 10^4\text{ kWh}$  required **20.112** (a)  $\text{H}_2$  is being oxidized and  $\text{N}_2$  is being reduced. (b)  $K = 6.9 \times 10^5$  (c)  $E^\circ = 0.05755\text{V}$   
**20.115** (a)  $E^\circ = 0.028\text{V}$  (b) cathode:  $\text{Ag}^+(aq) + e^- \longrightarrow \text{Ag}(s)$ ; anode:  $\text{Fe}^{2+}(aq) \longrightarrow \text{Fe}^{3+}(aq) + e^-$  (c)  $\Delta S^\circ = 148.5\text{J}$ . Since  $\Delta S^\circ$  is positive,  $\Delta G^\circ$  will become more negative and  $E^\circ$  will become more positive as temperature is increased. **20.118**  $K_{sp}$  for  $\text{AgSCN}$  is  $1.0 \times 10^{-12}$ .

## CHAPTER 21

**21.1** (a)  $^{24}\text{Ne}$ ; outside; reduce neutron-to-proton ratio via  $\beta$  decay (b)  $^{32}\text{Cl}$ ; outside; increase neutron-to-proton ratio via positron emission or orbital electron capture (c)  $^{108}\text{Sn}$ ; outside; increase neutron-to-proton ratio via positron emission or orbital electron capture (d)  $^{216}\text{Po}$ ; outside; nuclei with  $Z \geq 84$  usually decay via  $\alpha$  emission. **21.4** (a) 7 min (b)  $0.1\text{ min}^{-1}$  (c) 30% (3/10) of the sample remains after 12 min. (d)  $^{88}_{41}\text{Nb}$  **21.5** (a)  $^{10}_5\text{B}$ ,  $^{11}_5\text{B}$ ;  $^{12}_6\text{C}$ ,  $^{13}_6\text{C}$ ;  $^{14}_7\text{N}$ ,  $^{15}_7\text{N}$ ;  $^{16}_8\text{O}$ ,  $^{17}_8\text{O}$ ;  $^{19}_9\text{F}$  (b)  $^{14}_6\text{C}$  (c)  $^{11}_6\text{C}$ ,  $^{13}_7\text{N}$ ,  $^{15}_8\text{O}$ ,  $^{18}_9\text{F}$  (d)  $^{11}_6\text{C}$  **21.7** (a) 25 protons, 30 neutrons (b) 80 protons, 121 neutrons (c) 19 protons, 20 neutrons  
**21.9** (a)  $^1_0\text{n}$  (b)  $^4_2\text{He}$  or  $\alpha$  (c)  $^0_0\gamma$  or  $\gamma$  **21.11** (a)  $^{90}_{37}\text{Rb} \longrightarrow ^{90}_{38}\text{Sr} + ^0_{-1}\text{e}$  (b)  $^{72}_{34}\text{Se} + ^0_{-1}\text{e}$  (orbital electron)  $\longrightarrow ^{72}_{33}\text{As}$  (c)  $^{76}_{36}\text{Kr} \longrightarrow ^{76}_{35}\text{Br} + ^0_{-1}\text{e}$  (d)  $^{226}_{88}\text{Ra} \longrightarrow ^{222}_{86}\text{Rn} + ^4_2\text{He}$  **21.13** (a)  $^{211}_{82}\text{Pb} \longrightarrow ^{211}_{83}\text{Bi} + ^0_{-1}\beta$  (b)  $^{50}_{25}\text{Mn} \longrightarrow ^{50}_{24}\text{Cr} + ^0_{-1}\text{e}$  (c)  $^{179}_{74}\text{W} + ^0_{-1}\text{e} \longrightarrow ^{179}_{73}\text{Ta}$  (d)  $^{230}_{90}\text{Th} \longrightarrow ^{226}_{88}\text{Ra} + ^4_2\text{He}$  **21.15** 7 alpha emissions, 4 beta emissions **21.17** (a) Positron emission (for low atomic numbers, positron emission is more common than electron capture) (b) beta emission (c) beta emission (d) beta emission **21.19** (a) Stable:  $^{39}_{19}\text{K}$ , 20 neutrons is a magic number (b) stable:  $^{83}_{33}\text{Bi}$ , 126 neutrons is a magic number (c) stable:  $^{58}_{28}\text{Ni}$  even proton, even neutron more likely to be stable;  $^{65}_{28}\text{Ni}$  has high neutron-to-proton ratio **21.21** (a)  $^4_2\text{He}$  (c)  $^{40}_{20}\text{Ca}$  (e)  $^{126}_{82}\text{Pb}$   
**21.23** The alpha particle,  $^4_2\text{He}$ , has a magic number of both protons and neutrons, while the proton is an odd proton, even neutron particle. Alpha is a very stable emitted particle, which makes alpha emission a favorable process. The proton is not a stable emitted particle, and its formation does not encourage proton emission as a process.  
**21.25** Protons and alpha particles are positively charged and must be moving very fast to overcome electrostatic forces that would repel them from the target nucleus. Neutrons are electrically neutral and not repelled by the nucleus. **21.27** (a)  $^{252}_{98}\text{Cf} + ^{10}_5\text{B} \longrightarrow 3^1_0\text{n} + ^{259}_{103}\text{Lr}$  (b)  $^2_1\text{H} + ^4_2\text{He} \longrightarrow ^4_2\text{He} + ^1_1\text{H}$  (c)  $^1_1\text{H} + ^{11}_5\text{B} \longrightarrow 3^4_2\text{He}$  (d)  $^{122}_{53}\text{I} \longrightarrow ^{122}_{54}\text{Xe} + ^0_{-1}\text{e}$  (e)  $^{59}_{26}\text{Fe} \longrightarrow ^0_{-1}\text{e} + ^{59}_{27}\text{Co}$   
**21.29** (a)  $^{238}_{92}\text{U} + ^4_2\text{He} \longrightarrow ^{241}_{94}\text{Pu} + ^1_0\text{n}$  (b)  $^{14}_7\text{N} + ^4_2\text{He} \longrightarrow ^{17}_8\text{O} + ^1_1\text{H}$  (c)  $^{56}_{26}\text{Fe} + ^4_2\text{He} \longrightarrow ^{60}_{29}\text{Cu} + ^0_{-1}\text{e}$  **21.31** (a) True. The decay rate constant and half-life are inversely related. (b) False. If X is not radioactive, its half-life is essentially infinity. (c) True. Changes in the amount of A would be substantial and measurable over the 40-year time frame, while changes in the amount of X would be very small and difficult to detect. **21.33** When the watch is 50 years old, only 6% of the tritium remains. The dial will be dimmed by 94%. **21.35** The source must be replaced after 2.18 yr or 26.2 months; this corresponds to August 2012. **21.37** (a)  $1.1 \times 10^{11}$  alpha particles emitted in 5.0 min (b) 9.9 mCi **21.39**  $k = 1.21 \times 10^{-4}\text{ yr}^{-1}$ ;  $t = 4.3 \times 10^3\text{ yr}$  **21.41**  $k = 5.46 \times 10^{-10}\text{ yr}^{-1}$ ;  $t = 3.0 \times 10^9\text{ yr}$  **21.43** The energy released when one mole of  $\text{Fe}_2\text{O}_3$  reacts is  $8.515 \times 10^3\text{ J}$ . The energy released when one mole of  $^4_2\text{He}$  is formed from protons and neutrons is

$2.73 \times 10^{12}\text{ J}$ . This is  $3 \times 10^8$  or 300 million times as much energy as the thermite reaction. **21.45**  $\Delta m = 0.2414960\text{ amu}$ ,  $\Delta E = 3.604129 \times 10^{-11}\text{ J}/^{27}\text{Al}$  nucleus required,  $8.044234 \times 10^{13}\text{ J}/100\text{ g }^{27}\text{Al}$  **21.47** (a) Nuclear mass:  $^2\text{H}$ , 2.013553 amu;  $^4\text{He}$ , 4.001505 amu;  $^6\text{Li}$ , 6.0134771 amu (b) nuclear binding energy:  $^2\text{H}$ ,  $3.564 \times 10^{-13}\text{ J}$ ;  $^4\text{He}$ ,  $4.5336 \times 10^{-12}\text{ J}$ ;  $^6\text{Li}$ ,  $5.12602 \times 10^{-12}\text{ J}$  (c) binding energy/nucleon:  $^2\text{H}$ ,  $1.782 \times 10^{-13}\text{ J/nucleon}$ ;  $^4\text{He}$ ,  $1.1334 \times 10^{-12}\text{ J/nucleon}$ ;  $^6\text{Li}$ ,  $8.54337 \times 10^{-13}\text{ J/nucleon}$ . This trend in binding energy/nucleon agrees with the curve in Figure 21.12. The anomalously high calculated value for  $^4\text{He}$  is also apparent on the figure. **21.49** (a)  $1.71 \times 10^5\text{ kg/d}$  (b)  $2.1 \times 10^8\text{ g }^{235}\text{U}$  **21.51** (a)  $^{59}\text{Co}$ ; it has the largest binding energy per nucleon, and binding energy gives rise to mass defect. **21.53** (a)  $\text{NaI}$  is a good source of iodine because iodine is a large percentage of its mass; it is completely dissociated into ions in aqueous solution, and iodine in the form of  $\text{I}^-$  is mobile and immediately available for biouptake. (b) A Geiger counter placed near the thyroid immediately after ingestion will register background, then gradually increase in signal until the concentration of iodine in the thyroid reaches a maximum. Over time, iodine-131 decays, and the signal decreases. (c) The radioactive iodine will decay to 0.01% of the original amount in approximately 82 days. **21.55**  $^{235}\text{U}$  **21.57** The control rods in a nuclear reactor regulate the flux of neutrons to keep the reaction chain self-sustaining and also prevent the reactor core from overheating. They are composed of materials such as boron or cadmium that absorb neutrons. **21.59** (a)  $^1_1\text{H} + ^1_1\text{H} \longrightarrow ^3_2\text{He} + ^1_0\text{n}$  (b)  $^{239}_{92}\text{U} + ^1_0\text{n} \longrightarrow ^{133}_{51}\text{Sb} + ^{98}_{41}\text{Nb} + 9^1_0\text{n}$  **21.61** (a)  $\Delta m = 0.006627\text{ g/mol}$ ;  $\Delta E = 5.956 \times 10^{11}\text{ J} = 5.956 \times 10^8\text{ kJ/mol } ^1_1\text{H}$  (b) The extremely high temperature is required to overcome electrostatic charge repulsions between the nuclei so that they can come together to react. **21.63** (a) Boiling water reactor (b) fast breeder reactor (c) gas-cooled reactor **21.65** Hydrogen abstraction:  $\text{RCOOH} + \cdot\text{OH} \longrightarrow \text{RCOO}\cdot + \text{H}_2\text{O}$ ; deprotonation:  $\text{RCOOH} + \text{OH}^- \longrightarrow \text{RCOO}^- + \text{H}_2\text{O}$ . Hydroxyl radical is more toxic to living systems because it produces other radicals when it reacts with molecules in the organism. Hydroxide ion,  $\text{OH}^-$ , on the other hand, will be readily neutralized in the buffered cell environment. The acid-base reactions of  $\text{OH}^-$  are usually much less disruptive to the organism than the chain of redox reactions initiated by  $\cdot\text{OH}$  radical. **21.67** (a)  $5.3 \times 10^8\text{ dis/s}$ ,  $5.3 \times 10^8\text{ Bq}$  (b)  $6.1 \times 10^2\text{ mrad}$ ,  $6.1 \times 10^{-3}\text{ Gy}$  (c)  $5.8 \times 10^3\text{ mrem}$ ,  $5.8 \times 10^{-2}\text{ Sv}$  **21.69**  $^{210}_{82}\text{Pb}$  **21.71** (a)  $^{36}_{17}\text{Cl} \longrightarrow ^{36}_{18}\text{Ar} + ^0_{-1}\text{e}$  (b)  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  both have an odd number of protons but an even number of neutrons.  $^{36}\text{Cl}$  has an odd number of protons and neutrons, so it is less stable than the other two isotopes. **21.73** (a)  $^6_3\text{Li} + ^{56}_{28}\text{Ni} \longrightarrow ^{62}_{31}\text{Ga}$  (b)  $^{40}_{20}\text{Ca} + ^{248}_{96}\text{Cm} \longrightarrow ^{147}_{62}\text{Sm} + ^{141}_{54}\text{Xe}$  (c)  $^{88}_{38}\text{Sr} + ^{84}_{36}\text{Kr} \longrightarrow ^{116}_{46}\text{Pd} + ^{56}_{28}\text{Ni}$  (d)  $^{40}_{20}\text{Ca} + ^{238}_{92}\text{U} \longrightarrow ^{70}_{20}\text{Zn} + 4^1_0\text{n} + 2^{102}_{41}\text{Nb}$   
**21.77** The C—OH bond of the acid and the O—H bond of the alcohol break in this reaction. Initially,  $^{18}\text{O}$  is present in the C— $^{18}\text{OH}$  group of the alcohol. In order for  $^{18}\text{O}$  to end up in the ester, the  $^{18}\text{O}$ —H bond of the alcohol must break. This requires that the C—OH bond in the acid also breaks. The unlabeled O from the acid ends up in the  $\text{H}_2\text{O}$  product. **21.79**  $^7\text{Be}$ ,  $8.612 \times 10^{-13}\text{ J/nucleon}$ ;  $^9\text{Be}$ ,  $1.035 \times 10^{-12}\text{ J/nucleon}$ ;  $^{10}\text{Be}$ ,  $1.042 \times 10^{-12}\text{ J/nucleon}$ . The binding energies/nucleon for  $^9\text{Be}$  and  $^{10}\text{Be}$  are very similar; that for  $^{10}\text{Be}$  is slightly higher. **21.85**  $1.4 \times 10^4\text{ kg C}_8\text{H}_{18}$

## CHAPTER 22

**22.1** (a)  $\text{C}_2\text{H}_4$ , the structure on the left, is the stable compound. Carbon can form strong multiple bonds to satisfy the octet rule, while silicon cannot. (b) The geometry about the central atoms in  $\text{C}_2\text{H}_4$  is trigonal planar. **22.3** Molecules (b) and (d) will have the seesaw structure shown in the figure. **22.6** (c) Density, the ratio of mass to volume, increases going down the family; only this trend is consistent with the data in the figure. Other properties do not match the trend because (a) electronegativity and (b) first ionization energy both decrease rather than increase going down the family. Trends for both (d) X—X single bond enthalpy and (e) electron affinity are