

Questions and Problems

Spontaneous Processes and Entropy

Review Questions

- 18.1 Explain what is meant by a spontaneous process. Give two examples each of spontaneous and non-spontaneous processes.
- 18.2 Which of the following processes are spontaneous and which are nonspontaneous? (a) dissolving table salt (NaCl) in hot soup; (b) climbing Mt. Everest; (c) spreading fragrance in a room by removing the cap from a perfume bottle; (d) separating helium and neon from a mixture of the gases
- 18.3 Which of the following processes are spontaneous and which are nonspontaneous at a given temperature?
- (a)  $\text{NaNO}_3(s) \xrightarrow{\text{H}_2\text{O}} \text{NaNO}_3(aq)$  saturated soln  
 (b)  $\text{NaNO}_3(s) \xrightarrow{\text{H}_2\text{O}} \text{NaNO}_3(aq)$  unsaturated soln  
 (c)  $\text{NaNO}_3(s) \xrightarrow{\text{H}_2\text{O}} \text{NaNO}_3(aq)$  supersaturated soln
- 18.4 Define entropy. What are the units of entropy?

Problems

- 18.5 How does the entropy of a system change for each of the following processes?
- (a) A solid melts.  
 (b) A liquid freezes.  
 (c) A liquid boils.  
 (d) A vapor is converted to a solid.  
 (e) A vapor condenses to a liquid.  
 (f) A solid sublimes.  
 (g) Urea dissolves in water.
- 18.6 Consider the arrangement in Figure 18.1. Because the volume of the two bulbs is the same, the probability of finding a molecule in either bulb is  $\frac{1}{2}$ . Calculate the probability of all the molecules ending up in the same bulb if the number is (a) 2, (b) 100, and (c)  $6 \times 10^{23}$ . Based on your results, explain why the situation shown in Figure 18.1(b) will not be observed for a macroscopic system.

Second Law of Thermodynamics

Review Questions

- 18.7 State the second law of thermodynamics in words and express it mathematically.
- 18.8 State the third law of thermodynamics and explain its usefulness in calculating entropy values.

Problems

- 18.9 For each pair of substances listed here, choose the one having the larger standard entropy value at 25°C. The

same molar amount is used in the comparison. Explain the basis for your choice. (a) Li(s) or Li(l); (b)  $\text{C}_2\text{H}_5\text{OH}(l)$  or  $\text{CH}_3\text{OCH}_3(l)$  (Hint: Which molecule can hydrogen-bond?); (c) Ar(g) or Xe(g); (d) CO(g) or  $\text{CO}_2(g)$ ; (e)  $\text{O}_2(g)$  or  $\text{O}_3(g)$ ; (f)  $\text{NO}_2(g)$  or  $\text{N}_2\text{O}_4(g)$

- 18.10 Arrange the following substances (1 mole each) in order of increasing entropy at 25°C: (a) Ne(g), (b)  $\text{SO}_2(g)$ , (c) Na(s), (d) NaCl(s), (e)  $\text{H}_2(g)$ . Give the reasons for your arrangement.

- 18.11 Using the data in Appendix 3, calculate the standard entropy changes for the following reactions at 25°C:
- (a)  $\text{S}(s) + \text{O}_2(g) \longrightarrow \text{SO}_2(g)$   
 (b)  $\text{MgCO}_3(s) \longrightarrow \text{MgO}(s) + \text{CO}_2(g)$

- 18.12 Using the data in Appendix 3, calculate the standard entropy changes for the following reactions at 25°C:
- (a)  $\text{H}_2(g) + \text{CuO}(s) \longrightarrow \text{Cu}(s) + \text{H}_2\text{O}(g)$   
 (b)  $2\text{Al}(s) + 3\text{ZnO}(s) \longrightarrow \text{Al}_2\text{O}_3(s) + 3\text{Zn}(s)$   
 (c)  $\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$

- 18.13 Without consulting Appendix 3, predict whether the entropy change is positive or negative for each of the following reactions. Give reasons for your predictions.
- (a)  $2\text{KClO}_4(s) \longrightarrow 2\text{KClO}_3(s) + \text{O}_2(g)$   
 (b)  $\text{H}_2\text{O}(g) \longrightarrow \text{H}_2\text{O}(l)$   
 (c)  $2\text{Na}(s) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{NaOH}(aq) + \text{H}_2(g)$   
 (d)  $\text{N}_2(g) \longrightarrow 2\text{N}(g)$

- 18.14 State whether the sign of the entropy change expected for each of the following processes will be positive or negative, and explain your predictions.
- (a)  $\text{PCl}_3(l) + \text{Cl}_2(g) \longrightarrow \text{PCl}_5(s)$   
 (b)  $2\text{HgO}(s) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$   
 (c)  $\text{H}_2(g) \longrightarrow 2\text{H}(g)$   
 (d)  $\text{U}(s) + 3\text{F}_2(g) \longrightarrow \text{UF}_6(s)$

Gibbs Free Energy

Review Questions

- 18.15 Define free energy. What are its units?
- 18.16 Why is it more convenient to predict the direction of a reaction in terms of  $\Delta G_{\text{sys}}$  instead of  $\Delta S_{\text{univ}}$ ? Under what conditions can  $\Delta G_{\text{sys}}$  be used to predict the spontaneity of a reaction?

Problems

- 18.17 Calculate  $\Delta G^\circ$  for the following reactions at 25°C:
- (a)  $\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2\text{NO}(g)$   
 (b)  $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$   
 (c)  $2\text{C}_2\text{H}_2(g) + 5\text{O}_2(g) \longrightarrow 4\text{CO}_2(g) + 2\text{H}_2\text{O}(l)$

(Hint: Look up the standard free energies of formation of the reactants and products in Appendix 3.)

18.18 Calculate  $\Delta G^\circ$  for the following reactions at 25°C:

- ARIS
- (a)  $2\text{Mg}(s) + \text{O}_2(g) \longrightarrow 2\text{MgO}(s)$   
 (b)  $2\text{SO}_2(g) + \text{O}_2(g) \longrightarrow 2\text{SO}_3(g)$   
 (c)  $2\text{C}_2\text{H}_6(g) + 7\text{O}_2(g) \longrightarrow 4\text{CO}_2(g) + 6\text{H}_2\text{O}(l)$

See Appendix 3 for thermodynamic data.

18.19 From the values of  $\Delta H$  and  $\Delta S$ , predict which of the following reactions would be spontaneous at 25°C: Reaction A:  $\Delta H = 10.5 \text{ kJ/mol}$ ,  $\Delta S = 30 \text{ J/K} \cdot \text{mol}$ ; reaction B:  $\Delta H = 1.8 \text{ kJ/mol}$ ,  $\Delta S = -113 \text{ J/K} \cdot \text{mol}$ . If either of the reactions is nonspontaneous at 25°C, at what temperature might it become spontaneous?

18.20 Find the temperatures at which reactions with the following  $\Delta H$  and  $\Delta S$  values would become spontaneous: (a)  $\Delta H = -126 \text{ kJ/mol}$ ,  $\Delta S = 84 \text{ J/K} \cdot \text{mol}$ ; (b)  $\Delta H = -11.7 \text{ kJ/mol}$ ,  $\Delta S = -105 \text{ J/K} \cdot \text{mol}$ .

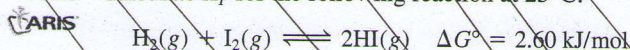
## Free Energy and Chemical Equilibrium

### Review Questions

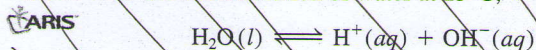
- 18.21 Explain the difference between  $\Delta G$  and  $\Delta G^\circ$ .  
 18.22 Explain why Equation (18.14) is of great importance in chemistry.

### Problems

18.23 Calculate  $K_p$  for the following reaction at 25°C:

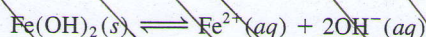


18.24 For the autoionization of water at 25°C,



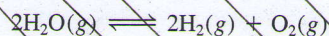
$K_w$  is  $1.0 \times 10^{-14}$ . What is  $\Delta G^\circ$  for the process?

18.25 Consider the following reaction at 25°C:

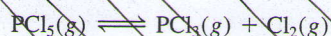


Calculate  $\Delta G^\circ$  for the reaction.  $K_{sp}$  for  $\text{Fe}(\text{OH})_2$  is  $1.6 \times 10^{-14}$ .

18.26 Calculate  $\Delta G^\circ$  and  $K_p$  for the following equilibrium reaction at 25°C.

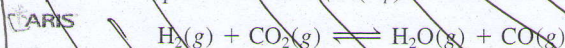


18.27 (a) Calculate  $\Delta G^\circ$  and  $K_p$  for the following equilibrium reaction at 25°C. The  $\Delta G_f^\circ$  values are 0 for  $\text{Cl}_2(g)$ ,  $-286 \text{ kJ/mol}$  for  $\text{PCl}_3(g)$ , and  $-325 \text{ kJ/mol}$  for  $\text{PCl}_5(g)$ .



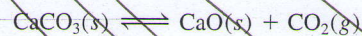
(b) Calculate  $\Delta G$  for the reaction if the partial pressures of the initial mixture are  $P_{\text{PCl}_5} = 0.0029 \text{ atm}$ ,  $P_{\text{PCl}_3} = 0.27 \text{ atm}$ , and  $P_{\text{Cl}_2} = 0.40 \text{ atm}$ .

18.28 The equilibrium constant ( $K_p$ ) for the reaction



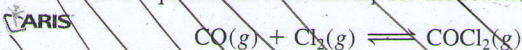
is 4.40 at 2000 K. (a) Calculate  $\Delta G^\circ$  for the reaction. (b) Calculate  $\Delta G$  for the reaction when the partial pressures are  $P_{\text{H}_2} = 0.25 \text{ atm}$ ,  $P_{\text{CO}_2} = 0.78 \text{ atm}$ ,  $P_{\text{H}_2\text{O}} = 0.66 \text{ atm}$ , and  $P_{\text{CO}} = 1.20 \text{ atm}$ .

18.29 Consider the decomposition of calcium carbonate:



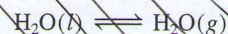
Calculate the pressure in atm of  $\text{CO}_2$  in an equilibrium process (a) at 25°C and (b) at 800°C. Assume that  $\Delta H^\circ = 177.8 \text{ kJ/mol}$  and  $\Delta S^\circ = 160.5 \text{ J/K} \cdot \text{mol}$  for the temperature range.

18.30 The equilibrium constant  $K_p$  for the reaction



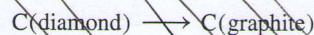
is  $5.62 \times 10^{-35}$  at 25°C. Calculate  $\Delta G_f^\circ$  for  $\text{COCl}_2$  at 25°C.

18.31 At 25°C,  $\Delta G^\circ$  for the process



is 8.6 kJ/mol. Calculate the vapor pressure of water at this temperature.

18.32 Calculate  $\Delta G^\circ$  for the process



Is the formation of graphite from diamond favored at 25°C? If so, why is it that diamonds do not become graphite on standing?

## Thermodynamics in Living Systems

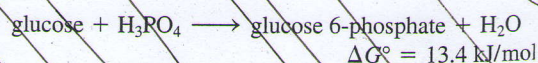
### Review Questions

- 18.33 What is a coupled reaction? What is its importance in biological reactions?  
 18.34 What is the role of ATP in biological reactions?

### Problems

18.35 Referring to the metabolic process involving glucose on p. 826, calculate the maximum number of moles of ATP that can be synthesized from ADP from the breakdown of one mole of glucose.

18.36 In the metabolism of glucose, the first step is the conversion of glucose to glucose 6-phosphate:



Because  $\Delta G^\circ$  is positive, this reaction does not favor the formation of products. Show how this reaction can be made to proceed by coupling it with the hydrolysis of ATP. Write an equation for the coupled reaction and estimate the equilibrium constant for the coupled process.

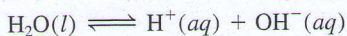
Do Not Worry About Problems  
on Equilibrium... yet!

**Additional Problems**

18.37 Explain the following nursery rhyme in terms of the second law of thermodynamics.

Humpty Dumpty sat on a wall;  
Humpty Dumpty had a great fall.  
All the King's horses and all the King's men  
Couldn't put Humpty together again.

18.38 Calculate  $\Delta G$  for the reaction



at 25°C for the following conditions:

- (a)  $[\text{H}^+] = 1.0 \times 10^{-7} \text{ M}$ ,  $[\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$
- (b)  $[\text{H}^+] = 1.0 \times 10^{-3} \text{ M}$ ,  $[\text{OH}^-] = 1.0 \times 10^{-4} \text{ M}$
- (c)  $[\text{H}^+] = 1.0 \times 10^{-12} \text{ M}$ ,  $[\text{OH}^-] = 2.0 \times 10^{-8} \text{ M}$
- (d)  $[\text{H}^+] = 3.5 \text{ M}$ ,  $[\text{OH}^-] = 4.8 \times 10^{-4} \text{ M}$

18.39 Which of the following thermodynamic functions are associated only with the first law of thermodynamics:  $S$ ,  $E$ ,  $G$ , and  $H$ ?

18.40 A student placed 1 g of each of three compounds A, B, and C in a container and found that after 1 week no change had occurred. Offer some possible explanations for the fact that no reactions took place. Assume that A, B, and C are totally miscible liquids.

18.41 Use the data in Appendix 3 to calculate the equilibrium constant for the reaction  $\text{AgI}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{I}^-(aq)$  at 25°C. Compare your result with the  $K_{sp}$  value in Table 16.2.

18.42 Predict the signs of  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  of the system for the following processes at 1 atm: (a) ammonia melts at  $-60^\circ\text{C}$ , (b) ammonia melts at  $-77.7^\circ\text{C}$ , (c) ammonia melts at  $-100^\circ\text{C}$ . (The normal melting point of ammonia is  $-77.7^\circ\text{C}$ .)

18.43 Consider the following facts: Water freezes spontaneously at  $-5^\circ\text{C}$  and 1 atm, and ice has a more ordered structure than liquid water. Explain how a spontaneous process can lead to a decrease in entropy.

18.44 Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) dissolves spontaneously and endothermically in water. What can you deduce about the sign of  $\Delta S$  for the solution process?

18.45 Calculate the equilibrium pressure of  $\text{CO}_2$  due to the decomposition of barium carbonate ( $\text{BaCO}_3$ ) at 25°C.

18.46 (a) Trouton's rule states that the ratio of the molar heat of vaporization of a liquid ( $\Delta H_{\text{vap}}$ ) to its boiling point in kelvins is approximately  $90 \text{ J/K} \cdot \text{mol}$ . Use the following data to show that this is the case and explain why Trouton's rule holds true:

	$t_{\text{bp}}(^{\circ}\text{C})$	$\Delta H_{\text{vap}}(\text{kJ/mol})$
Benzene	80.1	31.0
Hexane	68.7	30.8
Mercury	357	59.0
Toluene	110.6	35.2

(b) Use the values in Table 11.6 to calculate the same ratio for ethanol and water. Explain why Trouton's rule does not apply to these two substances as well as it does to other liquids.

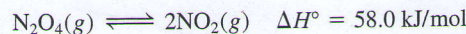
18.47 Referring to Problem 18.46, explain why the ratio is considerably smaller than  $90 \text{ J/K} \cdot \text{mol}$  for liquid HF.

18.48 Carbon monoxide (CO) and nitric oxide (NO) are polluting gases contained in automobile exhaust. Under suitable conditions, these gases can be made to react to form nitrogen ( $\text{N}_2$ ) and the less harmful carbon dioxide ( $\text{CO}_2$ ). (a) Write an equation for this reaction. (b) Identify the oxidizing and reducing agents. (c) Calculate the  $K_p$  for the reaction at 25°C. (d) Under normal atmospheric conditions, the partial pressures are  $P_{\text{N}_2} = 0.80 \text{ atm}$ ,  $P_{\text{CO}_2} = 3.0 \times 10^{-4} \text{ atm}$ ,  $P_{\text{CO}} = 5.0 \times 10^{-5} \text{ atm}$ , and  $P_{\text{NO}} = 5.0 \times 10^{-7} \text{ atm}$ . Calculate  $Q_p$  and predict the direction toward which the reaction will proceed. (e) Will raising the temperature favor the formation of  $\text{N}_2$  and  $\text{CO}_2$ ?

18.49 For reactions carried out under standard-state conditions, Equation (18.10) takes the form  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ . (a) Assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature, derive the equation

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

where  $K_1$  and  $K_2$  are the equilibrium constants at  $T_1$  and  $T_2$ , respectively. (b) Given that at 25°C  $K_c$  is  $4.63 \times 10^{-3}$  for the reaction



calculate the equilibrium constant at 65°C.

18.50 The  $K_{sp}$  of  $\text{AgCl}$  is given in Table 16.2. What is its value at 60°C? [Hint: You need the result of Problem 18.49(a) and the data in Appendix 3 to calculate  $\Delta H^\circ$ .]

18.51 Under what conditions does a substance have a standard entropy of zero? Can a substance ever have a negative standard entropy?

18.52 Water gas, a mixture of  $\text{H}_2$  and  $\text{CO}$ , is a fuel made by reacting steam with red-hot coke (a by-product of coal distillation):



From the data in Appendix 3, estimate the temperature at which the reaction begins to favor the formation of products.

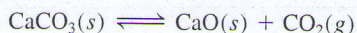
18.53 Consider the following Brønsted acid-base reaction at 25°C:



(a) Predict whether  $K$  will be greater or smaller than unity. (b) Does  $\Delta S^\circ$  or  $\Delta H^\circ$  make a greater contribution to  $\Delta G^\circ$ ? (c) Is  $\Delta H^\circ$  likely to be positive or negative?

**18.54** **ARIS** Crystallization of sodium acetate from a supersaturated solution occurs spontaneously (see p. 514). What can you deduce about the signs of  $\Delta S$  and  $\Delta H$ ?

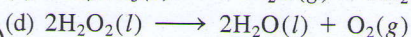
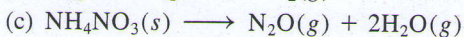
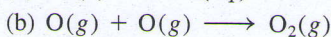
**18.55** Consider the thermal decomposition of  $\text{CaCO}_3$ :



The equilibrium vapor pressures of  $\text{CO}_2$  are 22.6 mmHg at  $700^\circ\text{C}$  and 1829 mmHg at  $950^\circ\text{C}$ . Calculate the standard enthalpy of the reaction. [Hint: See Problem 18.49(a).]

**18.56** **ARIS** A certain reaction is spontaneous at  $72^\circ\text{C}$ . If the enthalpy change for the reaction is 19 kJ/mol, what is the *minimum* value of  $\Delta S$  (in  $\text{J/K} \cdot \text{mol}$ ) for the reaction?

**18.57** Predict whether the entropy change is positive or negative for each of these reactions:



**18.58** The reaction  $\text{NH}_3(g) + \text{HCl}(g) \longrightarrow \text{NH}_4\text{Cl}(s)$  proceeds spontaneously at  $25^\circ\text{C}$  even though there is a decrease in the number of microstates of the system (gases are converted to a solid). Explain.

**18.59** **ARIS** Use the following data to determine the normal boiling point, in kelvins, of mercury. What assumptions must you make in order to do the calculation?

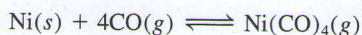
$$\begin{array}{ll} \text{Hg}(l): & \Delta H_f^\circ = 0 \text{ (by definition)} \\ & S^\circ = 77.4 \text{ J/K} \cdot \text{mol} \end{array}$$

$$\begin{array}{ll} \text{Hg}(g): & \Delta H_f^\circ = 60.78 \text{ kJ/mol} \\ & S^\circ = 174.7 \text{ J/K} \cdot \text{mol} \end{array}$$

**18.60** **ARIS** The molar heat of vaporization of ethanol is 39.3 kJ/mol and the boiling point of ethanol is  $78.3^\circ\text{C}$ . Calculate  $\Delta S$  for the vaporization of 0.50 mol ethanol.

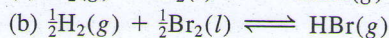
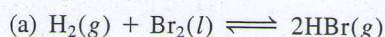
**18.61** A certain reaction is known to have a  $\Delta G^\circ$  value of  $-122 \text{ kJ/mol}$ . Will the reaction necessarily occur if the reactants are mixed together?

**18.62** **ARIS** In the Mond process for the purification of nickel, carbon monoxide is reacted with heated nickel to produce  $\text{Ni}(\text{CO})_4$ , which is a gas and can therefore be separated from solid impurities:



Given that the standard free energies of formation of  $\text{CO}(g)$  and  $\text{Ni}(\text{CO})_4(g)$  are  $-137.3 \text{ kJ/mol}$  and  $-587.4 \text{ kJ/mol}$ , respectively, calculate the equilibrium constant of the reaction at  $80^\circ\text{C}$ . Assume that  $\Delta G_f^\circ$  is temperature independent.

**18.63** Calculate  $\Delta G^\circ$  and  $K_p$  for the following processes at  $25^\circ\text{C}$ :



Account for the differences in  $\Delta G^\circ$  and  $K_p$  obtained for (a) and (b).

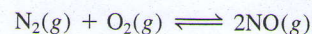
**18.64** **ARIS** Calculate the pressure of  $\text{O}_2$  (in atm) over a sample of  $\text{NiO}$  at  $25^\circ\text{C}$  if  $\Delta G^\circ = 212 \text{ kJ/mol}$  for the reaction



**18.65** Comment on the statement: "Just talking about entropy increases its value in the universe."

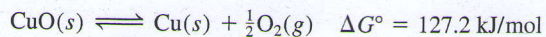
**18.66** For a reaction with a negative  $\Delta G^\circ$  value, which of the following statements is false? (a) The equilibrium constant  $K$  is greater than one, (b) the reaction is spontaneous when all the reactants and products are in their standard states, and (c) the reaction is always exothermic.

**18.67** Consider the reaction



Given that  $\Delta G^\circ$  for the reaction at  $25^\circ\text{C}$  is  $173.4 \text{ kJ/mol}$ , (a) calculate the standard free energy of formation of  $\text{NO}$ , and (b) calculate  $K_p$  of the reaction. (c) One of the starting substances in smog formation is  $\text{NO}$ . Assuming that the temperature in a running automobile engine is  $1100^\circ\text{C}$ , estimate  $K_p$  for the above reaction. (d) As farmers know, lightning helps to produce a better crop. Why?

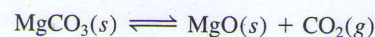
**18.68** Heating copper(II) oxide at  $400^\circ\text{C}$  does not produce any appreciable amount of  $\text{Cu}$ :



However, if this reaction is coupled to the conversion of graphite to carbon monoxide, it becomes spontaneous. Write an equation for the coupled process and calculate the equilibrium constant for the coupled reaction.

**18.69** The internal engine of a 1200-kg car is designed to run on octane ( $\text{C}_8\text{H}_{18}$ ), whose enthalpy of combustion is  $5510 \text{ kJ/mol}$ . If the car is moving up a slope, calculate the maximum height (in meters) to which the car can be driven on 1.0 gallon of the fuel. Assume that the engine cylinder temperature is  $2200^\circ\text{C}$  and the exit temperature is  $760^\circ\text{C}$ , and neglect all forms of friction. The mass of 1 gallon of fuel is 3.1 kg. [Hint: See the Chemistry in Action essay on p. 814. The work done in moving the car over a vertical distance is  $mgh$ , where  $m$  is the mass of the car in kg,  $g$  the acceleration due to gravity ( $9.81 \text{ m/s}^2$ ), and  $h$  the height in meters.]

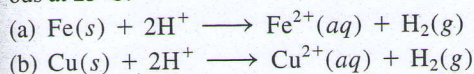
**18.70** Consider the decomposition of magnesium carbonate:



Calculate the temperature at which the decomposition begins to favor products. Assume that both  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature.

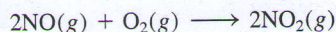
18.71 (a) Over the years there have been numerous claims about "perpetual motion machines," machines that will produce useful work with no input of energy. Explain why the first law of thermodynamics prohibits the possibility of such a machine existing. (b) Another kind of machine, sometimes called a "perpetual motion of the second kind," operates as follows. Suppose an ocean liner sails by scooping up water from the ocean and then extracting heat from the water, converting the heat to electric power to run the ship, and dumping the water back into the ocean. This process does not violate the first law of thermodynamics, for no energy is created—energy from the ocean is just converted to electrical energy. Show that the second law of thermodynamics prohibits the existence of such a machine.

18.72 The activity series in Section 4.4 shows that reaction (a) is spontaneous while reaction (b) is nonspontaneous at 25°C:



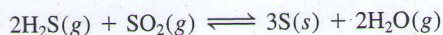
Use the data in Appendix 3 to calculate the equilibrium constant for these reactions and hence confirm that the activity series is correct.

18.73 The rate constant for the elementary reaction



is  $7.1 \times 10^9 / \text{M}^2 \cdot \text{s}$  at 25°C. What is the rate constant for the reverse reaction at the same temperature?

18.74 The following reaction was described as the cause of sulfur deposits formed at volcanic sites (see p. 780):



It may also be used to remove  $\text{SO}_2$  from power-plant stack gases. (a) Identify the type of redox reaction it is. (b) Calculate the equilibrium constant ( $K_p$ ) at 25°C and comment on whether this method is feasible for removing  $\text{SO}_2$ . (c) Would this procedure become more or less effective at a higher temperature?

18.75 Describe two ways that you could measure  $\Delta G^\circ$  of a reaction.

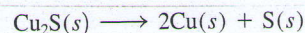
18.76 The following reaction represents the removal of ozone in the stratosphere:



Calculate the equilibrium constant ( $K_p$ ) for the reaction. In view of the magnitude of the equilibrium constant, explain why this reaction is not considered a major cause of ozone depletion in the absence of man-made pollutants such as the nitrogen oxides and CFCs? Assume the temperature of the stratosphere to be  $-30^\circ\text{C}$  and  $\Delta G_f^\circ$  to be temperature independent.

18.77 A 74.6-g ice cube floats in the Arctic Sea. The temperature and pressure of the system and surroundings are at 1 atm and  $0^\circ\text{C}$ . Calculate  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{surr}}$ , and  $\Delta S_{\text{univ}}$  for the melting of the ice cube. What can you conclude about the nature of the process from the value of  $\Delta S_{\text{univ}}$ ? (The molar heat of fusion of water is 6.01 kJ/mol.)

18.78 Comment on the feasibility of extracting copper from its ore chalcocite ( $\text{Cu}_2\text{S}$ ) by heating:



Calculate the  $\Delta G^\circ$  for the overall reaction if the above process is coupled to the conversion of sulfur to sulfur dioxide. Given that  $\Delta G_f^\circ(\text{Cu}_2\text{S}) = -86.1 \text{ kJ/mol}$ .

18.79 Active transport is the process in which a substance is transferred from a region of lower concentration to one of higher concentration. This is a nonspontaneous process and must be coupled to a spontaneous process, such as the hydrolysis of ATP. The concentrations of  $\text{K}^+$  ions in the blood plasma and in nerve cells are 15 mM and 400 mM, respectively ( $1 \text{ mM} = 1 \times 10^{-3} \text{ M}$ ). Use Equation (18.13) to calculate  $\Delta G$  for the process at the physiological temperature of  $37^\circ\text{C}$ :



In this calculation, the  $\Delta G^\circ$  term can be set to zero. What is the justification for this step?

18.80 Large quantities of hydrogen are needed for the synthesis of ammonia. One preparation of hydrogen involves the reaction between carbon monoxide and steam at  $300^\circ\text{C}$  in the presence of a copper-zinc catalyst:



Calculate the equilibrium constant ( $K_p$ ) for the reaction and the temperature at which the reaction favors the formation of  $\text{CO}$  and  $\text{H}_2\text{O}$ . Will a larger  $K_p$  be attained at the same temperature if a more efficient catalyst is used?

18.81 Consider two carboxylic acids (acids that contain the  $-\text{COOH}$  group):  $\text{CH}_3\text{COOH}$  (acetic acid,  $K_a = 1.8 \times 10^{-5}$ ) and  $\text{CH}_2\text{ClCOOH}$  (chloroacetic acid,  $K_a = 1.4 \times 10^{-3}$ ). (a) Calculate  $\Delta G^\circ$  for the ionization of these acids at  $25^\circ\text{C}$ . (b) From the equation  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ , we see that the contributions to the  $\Delta G^\circ$  term are an enthalpy term ( $\Delta H^\circ$ ) and a temperature times entropy term ( $T\Delta S^\circ$ ). These contributions are listed below for the two acids:

	$\Delta H^\circ(\text{kJ/mol})$	$T\Delta S^\circ(\text{kJ/mol})$
$\text{CH}_3\text{COOH}$	-0.57	-27.6
$\text{CH}_2\text{ClCOOH}$	-4.7	-21.1

Which is the dominant term in determining the value of  $\Delta G^\circ$  (and hence  $K_a$  of the acid)? (c) What processes contribute to  $\Delta H^\circ$ ? (Consider the ionization of the acids as a Brønsted acid-base reaction.) (d) Explain why the  $T\Delta S^\circ$  term is more negative for  $\text{CH}_3\text{COOH}$ .

- 18.82** Many hydrocarbons exist as structural isomers, which are compounds that have the same molecular formula but different structures. For example, both butane and isobutane have the same molecular formula of  $\text{C}_4\text{H}_{10}$  (see Problem 11.19 on p. 505). Calculate the mole percent of these molecules in an equilibrium mixture at  $25^\circ\text{C}$ , given that the standard free energy of formation of butane is  $-15.9$  kJ/mol and that of isobutane is  $-18.0$  kJ/mol. Does your result support the notion that straight-chain hydrocarbons (that is, hydrocarbons in which the C atoms are joined along a line) are less stable than branch-chain hydrocarbons?

**18.83** A rubber band is stretched vertically by attaching a weight to one end and holding the other end by hand. On heating the rubber band with a hot-air blower, it is observed to shrink slightly in length. Give a thermodynamic analysis for this behavior. (*Hint:* See the Chemistry in Action essay on p. 826.)

- 18.84** One of the steps in the extraction of iron from its ore (FeO) is the reduction of iron(II) oxide by carbon monoxide at  $900^\circ\text{C}$ :



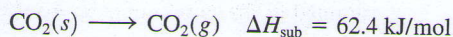
If CO is allowed to react with an excess of FeO, calculate the mole fractions of CO and  $\text{CO}_2$  at equilibrium. State any assumptions.

- 18.85** Derive the following equation

$$\Delta G = RT \ln (Q/K)$$

where  $Q$  is the reaction quotient and describe how you would use it to predict the spontaneity of a reaction.

- 18.86** The sublimation of carbon dioxide at  $-78^\circ\text{C}$  is



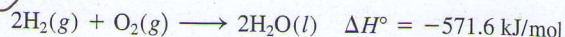
Calculate  $\Delta S_{\text{sub}}$  when 84.8 g of  $\text{CO}_2$  sublimates at this temperature.

- 18.87** Entropy has sometimes been described as “time’s arrow” because it is the property that determines the forward direction of time. Explain.

**18.88** Referring to Figure 18.1, we see that the probability of finding all 100 molecules in the same bulb is  $8 \times 10^{-31}$ . Assuming that the age of the universe is 13 billion years, calculate the time in seconds during which this event can be observed.

**18.89** A student looked up the  $\Delta G_f^\circ$ ,  $\Delta H_f^\circ$ , and  $S^\circ$  values for  $\text{CO}_2$  in Appendix 3. Plugging these values into Equation (18.10), he found that  $\Delta G_f^\circ \neq \Delta H_f^\circ - TS^\circ$  at  $298 \text{ K}$ . What is wrong with his approach?

- 18.90** Consider the following reaction at  $298 \text{ K}$ :



Calculate  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{surr}}$ , and  $\Delta S_{\text{univ}}$  for the reaction.

- 18.91** As an approximation, we can assume that proteins exist either in the native (or physiologically functioning) state and the denatured state



The standard molar enthalpy and entropy of the denaturation of a certain protein are  $512$  kJ/mol and  $1.60$  kJ/K · mol, respectively. Comment on the signs and magnitudes of these quantities, and calculate the temperature at which the process favors the denatured state.

- 18.92** Which of the following are not state functions:  $S$ ,  $H$ ,  $q$ ,  $w$ ,  $T$ ?

**18.93** Which of the following is not accompanied by an increase in the entropy of the system? (a) mixing of two gases at the same temperature and pressure, (b) mixing of ethanol and water, (c) discharging a battery, (d) expansion of a gas followed by compression to its original temperature, pressure, and volume.

**18.94** Hydrogenation reactions (for example, the process of converting  $\text{C}=\text{C}$  bonds to  $\text{C}-\text{C}$  bonds in food industry) are facilitated by the use of a transition metal catalyst, such as Ni or Pt. The initial step is the adsorption, or binding, of hydrogen gas onto the metal surface. Predict the signs of  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  when hydrogen gas is adsorbed onto the surface of Ni metal.

## Special Problems

- 18.95** Give a detailed example of each of the following, with an explanation: (a) a thermodynamically spontaneous process; (b) a process that would violate the first law of thermodynamics; (c) a process that would violate the second law of thermodynamics; (d) an irreversible process; (e) an equilibrium process.
- 18.96** At  $0 \text{ K}$ , the entropy of carbon monoxide crystal is not zero but has a value of  $4.2 \text{ J/K} \cdot \text{mol}$ , called the residual

entropy. According to the third law of thermodynamics, this means that the crystal does not have a perfect arrangement of the CO molecules. (a) What would be the residual entropy if the arrangement were totally random? (b) Comment on the difference between the result in (a) and  $4.2 \text{ J/K} \cdot \text{mol}$ . [*Hint:* Assume that each CO molecule has two choices for orientation and use Equation (18.1) to calculate the residual entropy.]

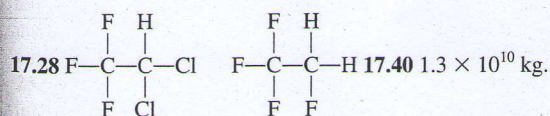
15.126 -0.20. 15.128 (a) Equilibrium will shift to the right. (b) To the left. (c) No effect. (d) To the right. 15.130 The amines are converted to their salts  $\text{RNH}_3^+$ . 15.132  $1.4 \times 10^{-4}$ . 15.134 4.40. 15.136 In a basic medium, the ammonium salt is converted to the pungent-smelling ammonia. 15.138 (c). 15.140 21 mL. 15.142 HX is the stronger acid. 15.144 Mg. 15.146 1.57.  $[\text{CN}^-] = 1.8 \times 10^{-8} \text{ M}$  in 1.00 M HF and  $2.2 \times 10^{-5} \text{ M}$  in 1.00 M HCN. HF is a stronger acid than HCN. 15.148 6.02. 15.150 1.18.

## CHAPTER 16

16.6 (a) 11.28. (b) 9.08. 16.10 (a), (b), and (c). 16.12 4.74 for both. (a) is more effective because it has a higher concentration. 16.14 7.03. 16.16 10. More effective against the acid. 16.18 (a) 4.82. (b) 4.64. 16.20 HC. 16.22 (l) (a): 5.10. (b): 4.82. (c): 5.22. (d): 5.00. (2) 4.90. (3) 5.22. 16.26 90.1 g/mol. 16.28 0.467 M. 16.30  $[\text{H}^+] = 3.0 \times 10^{-13} \text{ M}$ ,  $[\text{OH}^-] = 0.0335 \text{ M}$ ,  $[\text{Na}^+] = 0.0835 \text{ M}$ ,  $[\text{CH}_3\text{COO}^-] = 0.0500 \text{ M}$ ,  $[\text{CH}_3\text{COOH}] = 8.4 \times 10^{-10} \text{ M}$ . 16.32 8.23. 16.34 (a) 11.36. (b) 9.55. (c) 8.95. (d) 5.19. (e) 1.70. 16.36 (1) (c). (2) (a). (3) (d). (4) (b).  $\text{pH} < 7$  at the equivalence point. 16.40  $\text{CO}_2$  dissolves in water to form  $\text{H}_2\text{CO}_3$ , which neutralizes NaOH. 16.42 5.70. 16.50 (a)  $7.8 \times 10^{-10}$ . (b)  $1.8 \times 10^{-18}$ . 16.52  $1.80 \times 10^{-10}$ . 16.54  $2.2 \times 10^{-4} \text{ M}$ . 16.56  $2.3 \times 10^{-9}$ . 16.58  $[\text{Na}^+] = 0.045 \text{ M}$ ,  $[\text{NO}_3^-] = 0.076 \text{ M}$ ,  $[\text{Sr}^{2+}] = 0.016 \text{ M}$ ,  $[\text{F}^-] = 1.1 \times 10^{-4} \text{ M}$ . 16.60  $\text{pH}$  greater than 2.68 and less than 8.11. 16.64 (a) 0.013 M. (b)  $2.2 \times 10^{-4} \text{ M}$ . (c)  $3.3 \times 10^{-3} \text{ M}$ . 16.66 (a)  $1.0 \times 10^{-5} \text{ M}$ . (b)  $1.1 \times 10^{-10} \text{ M}$ . 16.68 (b), (c), (d), and (e). 16.70 (a) 0.016 M. (b)  $1.6 \times 10^{-6} \text{ M}$ . 16.72 Yes. 16.76  $[\text{Cd}^{2+}] = 1.1 \times 10^{-18} \text{ M}$ ,  $[\text{Cd}(\text{CN})_2] = 4.2 \times 10^{-3} \text{ M}$ ,  $[\text{CN}^-] = 0.48 \text{ M}$ . 16.78  $3.5 \times 10^{-5} \text{ M}$ . 16.80 (a)  $\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}$ . (b)  $\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons \text{Ag}(\text{CN})_2^-$ . (c)  $\text{Hg}^{2+} + 4\text{Cl}^- \rightleftharpoons \text{HgCl}_4^{2-}$ . 16.84 0.011 M. 16.86 Use  $\text{Cl}^-$  ions or flame test. 16.88 From 2.51 to 4.41. 16.90 1.28 M. 16.92  $[\text{H}^+] = 3.0 \times 10^{-13} \text{ M}$ ,  $[\text{OH}^-] = 0.0335 \text{ M}$ ,  $[\text{HCOO}^-] = 0.0500 \text{ M}$ ,  $[\text{HCOOH}] = 8.8 \times 10^{-11} \text{ M}$ ,  $[\text{Na}^+] = 0.0835 \text{ M}$ . 16.94 9.97 g.  $\text{pH} = 13.04$ . 16.96  $6.0 \times 10^3$ . 16.98 0.036 g/L. 16.100 (a) 1.37. (b) 5.97. (c) 10.24. 16.102 Original precipitate was  $\text{HgI}_2$ . In the presence of excess KI, it redissolves as  $\text{HgI}_4^{2-}$ . 16.104 7.82 - 10.38. 16.106 (a) 3.60. (b) 9.69. (c) 6.07. 16.108 (a)  $\text{MCO}_3 + 2\text{HCl} \rightarrow \text{MCl}_2 + \text{H}_2\text{O} + \text{CO}_2$ .  $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ . (b) 197 g/mol. Ba. 16.110 2. 16.112 (a) 12.6. (b)  $8.8 \times 10^{-6} \text{ M}$ . 16.114 (a) Sulfate. (b) Sulfide. (c) Iodide. 16.116 They are insoluble. 16.118 The ionized polyphenols have a dark color. The  $\text{H}^+$  ions from lemon juice shift the equilibrium to the light color acid. 16.120 Yes. 16.122 (c). 16.124 (a)  $1.7 \times 10^{-7} \text{ M}$ . (b)  $\text{MgCO}_3$  is more soluble than  $\text{CaCO}_3$ . (c) 12.40. (d)  $1.9 \times 10^{-8} \text{ M}$ . (e)  $\text{Ca}^{2+}$  because it is present in larger amount. 16.126  $\text{pH} = 1.0$ , fully protonated;  $\text{pH} = 7.0$ , dipolar ion;  $\text{pH} = 12.0$ , fully ionized. 16.128 (a) 8.4 mL. (b) 12.5 mL. (c) 27.0 mL. 16.130 (a) 4.74 before and after dilution. (b) 2.52 before and 3.02 after dilution. 16.132 4.75. 16.134 (a) Moving upward from left to right:  $\text{H}_2\text{A}/\text{HA}^-$ ;  $\text{HA}^-$ ;  $\text{HA}^-/\text{A}^{2-}$ ;  $\text{A}^{2-}$ ;  $\text{A}^{2-}/\text{OH}^-$ . (b)  $\text{p}K_{a1} \approx 4.8$ .  $\text{p}K_{a2} \approx 9.0$ .

## CHAPTER 17

17.6  $3.3 \times 10^{-4} \text{ atm}$ . 17.8  $\text{N}_2$ :  $3.96 \times 10^{18} \text{ kg}$ ;  $\text{O}_2$ :  $1.22 \times 10^{18} \text{ kg}$ ;  $\text{CO}_2$ :  $2.63 \times 10^{15} \text{ kg}$ . 17.12  $3.57 \times 10^{-19} \text{ J}$ . 17.22  $5.2 \times 10^6 \text{ kg}$ .  $5.6 \times 10^{14} \text{ kJ}$ . 17.24 The wavelength is not short enough. 17.26 434 nm. Both.



17.42 Ethane and propane are greenhouse gases. 17.50 4.34. 17.58  $1.2 \times 10^{-11} \text{ M/s}$ . 17.60 (b). 17.66 0.12%. 17.68 Endothermic. 17.70  $\text{O}_2$ . 17.72 5.72. 17.74 394 nm. 17.76 It has a high activation energy. 17.78 Size of tree rings are related to  $\text{CO}_2$  content. Age of  $\text{CO}_2$  in ice can be determined by radiocarbon dating. 17.80 165 kJ/mol. 17.82  $5.1 \times 10^{20}$  photons. 17.84 (a) 62.6 kJ/mol. (b) 38 min. 17.86  $5.6 \times 10^{23}$ .

## CHAPTER 18

18.6 (a) 0.25. (b)  $8 \times 10^{-31}$ . (c)  $\approx 0$ . For a macroscopic system, the probability is practically zero that all the molecules will be found only in one bulb. 18.10 (c)  $<$  (d)  $<$  (e)  $<$  (a)  $<$  (b). Solids have smaller entropies than gases. More complex structures have higher entropies. 18.12 (a) 47.5 J/K · mol. (b) -12.5 J/K · mol. (c) -242.8 J/K · mol. 18.14 (a)  $\Delta S < 0$ . (b)  $\Delta S > 0$ . (c)  $\Delta S > 0$ . (d)  $\Delta S < 0$ . 18.18 (a) -1139 kJ/mol. (b) -140.0 kJ/mol. (c) -2935.0 kJ/mol. 18.20 (a) At all temperatures. (b) Below 111 K. 18.24  $8.0 \times 10^1 \text{ kJ/mol}$ . 18.26  $4.572 \times 10^2 \text{ kJ/mol}$ .  $7.2 \times 10^{-81}$ . 18.28 (a) -24.6 kJ/mol. (b) -1.33 kJ/mol. 18.30 -341 kJ/mol. 18.32 -2.87 kJ/mol. The process has a high activation energy. 18.36  $1 \times 10^3$ . glucose + ATP  $\rightarrow$  glucose 6-phosphate + ADP. 18.38 (a) 0. (b)  $4.0 \times 10^4 \text{ J/mol}$ . (c)  $-3.2 \times 10^4 \text{ J/mol}$ . (d)  $6.4 \times 10^4 \text{ J/mol}$ . 18.40 (a) No reaction is possible because  $\Delta G > 0$ . (b) The reaction has a very large activation energy. (c) Reactants and products already at their equilibrium concentrations. 18.42 In all cases  $\Delta H > 0$  and  $\Delta S > 0$ .  $\Delta G < 0$  for (a), = 0 for (b), and  $> 0$  for (c). 18.44  $\Delta S > 0$ . 18.46 (a) Most liquids have similar structure so the changes in entropy from liquid to vapor are similar. (b)  $\Delta S_{\text{vap}}$  are larger for ethanol and water because of hydrogen bonding (there are fewer microstates in these liquids). 18.48 (a)  $2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2$ . (b) Oxidizing agent: NO; reducing agent: CO. (c)  $3 \times 10^{120}$ . (d)  $1.2 \times 10^{18}$ . From left to right. (e) No. 18.50  $2.6 \times 10^{-9}$ . 18.52 976 K. 18.54  $\Delta S < 0$ ;  $\Delta H < 0$ . 18.56 55 J/K · mol. 18.58 Increase in entropy of the surroundings offsets the decrease in entropy of the system. 18.60 56 J/K. 18.62  $4.5 \times 10^3$ . 18.64  $4.8 \times 10^{-75} \text{ atm}$ . 18.66 (a) True. (b) True. (c) False. 18.68 C + CuO  $\rightleftharpoons$  CO + Cu. 6.1. 18.70 673.2 K. 18.72 (a)  $7.6 \times 10^{14}$ . (b)  $4.1 \times 10^{-12}$ . 18.74 (a) A reverse disproportionation reaction. (b)  $8.2 \times 10^{15}$ . Yes, a large K makes this an efficient process. (c) Less effective. 18.76  $1.8 \times 10^{70}$ . Reaction has a large activation energy. 18.78 Heating the ore alone is not a feasible process. -214.3 kJ/mol. 18.80  $K_p = 36$ . 981 K. No. 18.82 Mole percents: butane = 30%; isobutane = 70%. Yes. 18.84  $X_{\text{CO}} = 0.45$ ;  $X_{\text{CO}_2} = 0.55$ . Use  $\Delta G_f^\circ$  values at 25°C for 900°C. 18.86 617 J/K. 18.88  $3 \times 10^{-13} \text{ s}$ . 18.90  $\Delta S_{\text{sys}} = -327 \text{ J/K} \cdot \text{mol}$ ,  $\Delta S_{\text{surr}} = 1918 \text{ J/K} \cdot \text{mol}$ ,  $\Delta S_{\text{univ}} = 1591 \text{ J/K} \cdot \text{mol}$ . 18.92 q, w. 18.94  $\Delta H < 0$ ,  $\Delta S < 0$ ,  $\Delta G < 0$ . 18.96 (a) 5.76 J/K · mol. (b) The orientation is not totally random. 18.98  $\Delta H^\circ = 33.89 \text{ kJ/mol}$ ;  $\Delta S^\circ = 96.4 \text{ J/K} \cdot \text{mol}$ ;  $\Delta G^\circ = 5.2 \text{ kJ/mol}$ . This is an endothermic liquid to vapor process so both  $\Delta H^\circ$  and  $\Delta S^\circ$  are positive.  $\Delta G^\circ$  is positive because the temperature is below the boiling point of benzene (80.1°C). 18.100  $\Delta G^\circ = 62.5 \text{ kJ/mol}$ ;  $\Delta H^\circ = 157.8 \text{ kJ/mol}$ ;  $\Delta S^\circ = 109 \text{ J/K} \cdot \text{mol}$ . 18.102 (1) (c). (2) (a). (3) (b).

## CHAPTER 19

19.2 (a)  $\text{Mn}^{2+} + \text{H}_2\text{O}_2 + 2\text{OH}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$ . (b)  $2\text{Bi}(\text{OH})_3 + 3\text{SnO}_2^{2-} \rightarrow 2\text{Bi} + 3\text{H}_2\text{O} + 3\text{SnO}_3^{2-}$ . (c)  $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 3\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Cr}^{3+} + 6\text{CO}_2 + 7\text{H}_2\text{O}$ . (d)  $2\text{Cl}^- + 2\text{ClO}_3^- + 4\text{H}^+ \rightarrow \text{Cl}_2 + 2\text{ClO}_2 + 2\text{H}_2\text{O}$ . 19.12 2.46 V. Al + 3Ag<sup>+</sup>  $\rightarrow$  3Ag + Al<sup>3+</sup>. 19.14  $\text{Cl}_2(\text{g})$  and  $\text{MnO}_4^-(\text{aq})$ . 19.16 Only (a) and (d) are spontaneous. 19.18 (a) Li. (b)  $\text{H}_2$ . (c)  $\text{Fe}^{2+}$ . (d)  $\text{Br}^-$ . 19.22 0.368 V.