Q14. Which process results in the increase in entropy of the universe?
MISSED THIS? *Read Section 19.3; Watch KCV 19.3*

a) the cooling of a hot cup of coffee in room temperature air
b) the evaporation of water from a desk at room temperature
c) the melting of snow above 0 °C
d) all of the above

Q15. Under which set of conditions is ΔG_{rxn} for the reaction $A(g) \longrightarrow B(g)$ most likely to be negative?
MISSED THIS? *Read Section 19.9*

a) $P_A = 10.0$ atm; $P_B = 10.0$ atm
b) $P_A = 10.0$ atm; $P_B = 0.010$ atm
c) $P_A = 0.010$ atm; $P_B = 10.0$ atm
d) $P_A = 0.010$ atm; $P_B = 0.010$ atm

Q16. Which statement is true for the freezing of liquid water below 0 °C?
MISSED THIS? *Read Section 19.6; Watch KCV 19.6*

a) ΔH is positive; ΔS is negative; ΔG is negative
b) ΔH is negative; ΔS is negative; ΔG is negative
c) ΔH is positive; ΔS is positive; ΔG is positive
d) ΔH is positive; ΔS is negative; ΔG is positive

Answers: **1.** (a) **2.** (c) **3.** (d) **4.** (a) **5.** (c) **6.** (d) **7.** (a) **8.** (b) **9.** (d) **10.** (c) **11.** (c) **12.** (d) **13.** (b) **14.** (d) **15.** (b) **16.** (b)

CHAPTER 19 IN REVIEW

TERMS

Section 19.2

spontaneous process (848)

Section 19.3

entropy (S) (852)
second law of thermodynamics (854)

Section 19.4

reversible process (859)

Section 19.6

Gibbs free energy (G) (863)

Section 19.7

standard entropy change for a reaction (ΔS°_{rxn}) (867)
standard molar entropies (S°) (867)
third law of thermodynamics (868)

Section 19.8

standard change in free energy (ΔG°_{rxn}) (872)
free energy of formation (ΔG°_f) (873)

Section 19.9

free energy change of a reaction under nonstandard conditions (ΔG_{rxn}) (878)

CONCEPTS

Spontaneous and Nonspontaneous Processes (19.2)

- Both spontaneous and nonspontaneous processes can occur, but only spontaneous processes can take place without outside intervention.
- Thermodynamics is the study of the *spontaneity* of reactions, *not* to be confused with kinetics, the study of the *rate* of reactions.

Entropy and the Second Law of Thermodynamics (19.3)

- The second law of thermodynamics states that for *any* spontaneous process, the entropy of the universe increases.
- Entropy (S) is proportional to the number of energetically equivalent ways in which the components of a system can be arranged and is a measure of energy dispersal per unit temperature.

The Entropy Changes Associated with Changes of State (19.4)

- The entropy of a substance increases as it changes state from a solid to a liquid and when it changes from a liquid to a gas.
- The change in entropy for a system undergoing a reversible change in state is $\Delta S = q_{rev}/T$.

Heat Transfer and Changes in the Entropy of the Surroundings (19.5)

- For a process to be spontaneous, the total entropy of the universe (system plus surroundings) must increase.
- The entropy of the surroundings increases when the change in *enthalpy* of the system (ΔH_{sys}) is negative (i.e., for exothermic reactions).
- The change in entropy of the surroundings for a given ΔH_{sys} depends inversely on temperature—the greater the temperature, the smaller the magnitude of ΔS_{surr}.

Gibbs Free Energy (19.6)

- Gibbs free energy, G, is a thermodynamic function that is proportional to the negative of the change in the entropy of the universe. A negative ΔG represents a spontaneous reaction, and a positive ΔG represents a nonspontaneous reaction.
- We can calculate the value of ΔG for a reaction from the values of ΔH and ΔS for the *system* using the equation $\Delta G = \Delta H - T\Delta S$.

Entropy Changes in Chemical Reactions: Calculating ΔS°_{rxn} (19.7)

- We calculate the standard change in entropy for a reaction similarly to the way we calculate the standard change in enthalpy for a reaction: by subtracting the sum of the standard entropies of the reactants multiplied by their stoichiometric coefficients from the sum of the standard entropies of the products multiplied by their stoichiometric coefficients.

- Standard entropies are *absolute*; an entropy of zero is established by the third law of thermodynamics as the entropy of a perfect crystal at absolute zero.
- The entropy of a substance at a given temperature depends on factors that affect the number of energetically equivalent arrangements of the substance; these include the state, size, and molecular complexity of the substance.

Free Energy Changes in Chemical Reactions: Calculating ΔG°_{rxn} (19.8)

- There are three ways to calculate ΔG°_{rxn}: (1) from ΔH° and ΔS°, (2) from free energies of formation (only at 25 °C), and (3) from the ΔG°'s of reactions that sum to the reaction of interest.
- The magnitude of a negative ΔG°_{rxn} represents the theoretical amount of energy available to do work, while a positive ΔG°_{rxn} represents the minimum amount of energy required to make a nonspontaneous process occur.

Free Energy Changes for Nonstandard States: The Relationship between ΔG°_{rxn} and ΔG_{rxn} (19.9)

- The value of ΔG°_{rxn} applies only to standard conditions, and most real conditions are not standard.
- Under nonstandard conditions, we can calculate ΔG_{rxn} from the equation $\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT \ln Q$.

Free Energy and Equilibrium: Relating ΔG°_{rxn} to the Equilibrium Constant (K) (19.10)

- Under standard conditions, the free energy change for a reaction is directly proportional to the negative of the natural log of the equilibrium constant, K; the more negative the free energy change (i.e., the more spontaneous the reaction), the larger the equilibrium constant.
- We can use the temperature dependence of ΔG°_{rxn}, as given by $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, to derive an equation for the temperature dependence of the equilibrium constant.

EQUATIONS AND RELATIONSHIPS

The Definition of Entropy (19.3)

$$S = k \ln W \quad k = 1.38 \times 10^{-23}\ \text{J/K}$$

Change in Entropy (19.3, 19.4)

$$\Delta S = S_{\text{final}} - S_{\text{intial}}$$

$$\Delta S = q_{\text{rev}}/T \quad \text{(Isothermal, reversible process)}$$

Change in the Entropy of the Universe (19.5)

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

Change in the Entropy of the Surroundings (19.5)

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \ (\text{constant}\ T, P)$$

Change in Gibbs Free Energy (19.6)

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

The Relationship between Spontaneity and ΔH, ΔS, and T (19.6)

ΔH	ΔS	Low Temperature	High Temperature
−	+	Spontaneous	Spontaneous
+	−	Nonspontaneous	Nonspontaneous
−	−	Spontaneous	Nonspontaneous
+	+	Nonspontaneous	Spontaneous

Standard Change in Entropy (19.7)

$$\Delta S^\circ_{rxn} = \sum n_p S^\circ(\text{products}) - \sum n_r S^\circ(\text{reactants})$$

Methods for Calculating the Free Energy of Formation (ΔG°_{rxn}) (19.8)

1. $\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$
2. $\Delta G^\circ_{rxn} = \sum n_p \Delta G^\circ_f(\text{products}) - \sum n_r \Delta G^\circ_f(\text{reactants})$
3. $\Delta G^\circ_{rxn(\text{overall})} = \Delta G^\circ_{rxn(\text{step 1})} + \Delta G^\circ_{rxn(\text{step 2})} + \Delta G^\circ_{rxn(\text{step 3})} + \ldots$

The Relationship between ΔG°_{rxn} and ΔG_{rxn} (19.9)

$$\Delta G_{rxn} = \Delta G^\circ_{rxn} + RT \ln Q \qquad R = 8.314\ \text{J/mol} \cdot \text{K}$$

The Relationship between ΔG°_{rxn} and K (19.10)

$$\Delta G^\circ_{rxn} = -RT \ln K$$

The Temperature Dependence of the Equilibrium Constant (19.10)

$$\ln K = -\frac{\Delta H^\circ_{rxn}}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ_{rxn}}{R}$$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ_{rxn}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

LEARNING OUTCOMES

Chapter Objectives	Assessment
Identify spontaneous and nonspontaneous processes (19.2)	Exercises 27–28
Analyze systems of particles and reactions in terms of entropy change (19.3)	Example 19.1 **For Practice** 19.1 **Exercises** 29–30
Calculate the entropy change for a change in state (19.4)	Example 19.2 **For Practice** 19.2 **Exercises** 31–34

Calculate entropy changes in the system (ΔS_{sys}), the surroundings (ΔS_{surr}), and the universe (ΔS_{univ}) (**19.5**)	Example 19.3 **For Practice** 19.3 **For More Practice** 19.3 **Exercises** 35–42
Analyze reaction spontaneity using Gibbs free energy change (ΔG), ΔH, and ΔS (**19.6**)	Example 19.4 **For Practice** 19.4 **Exercises** 43–47
Calculate the standard entropy change for a reaction (ΔS°_{rxn}) (**19.7**)	Example 19.5 **For Practice** 19.5 **Exercises** 48–58
Analyze reaction spontaneity using standard Gibbs free energy change (ΔG°_{rxn}), ΔH°_{rxn}, and ΔS°_{rxn} (**19.8**)	Examples 19.6, 19.7 **For Practice** 19.6, 19.7 **Exercises** 59–62
Calculate ΔG°_{rxn} using free energies of formation (ΔG°_f) (**19.8**)	Example 19.8 **For Practice** 19.8 **For More Practice** 19.8 **Exercises** 63–66
Calculate ΔG°_{rxn} for a stepwise reaction (**19.8**)	Example 19.9 **For Practice** 19.9 **Exercises** 67–68
Calculate ΔG_{rxn} for nonstandard conditions (**19.9**)	Example 19.10 **For Practice** 19.10 **Exercises** 69–72
Perform ΔG°_{rxn} calculations using equilibrium constants (K) (**19.10**)	Example 19.11 **For Practice** 19.11 **Exercises** 73–82

EXERCISES

Mastering Chemistry provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.

REVIEW QUESTIONS

1. What is the first law of thermodynamics, and how does it relate to energy use?
2. What is nature's heat tax, and how does it relate to energy use?
3. What is a perpetual motion machine? Can such a machine exist given the laws of thermodynamics?
4. Is it more efficient to heat your home with a natural gas furnace or an electric furnace? Explain.
5. What is a spontaneous process? Provide an example.
6. Explain the difference between the spontaneity of a reaction (which depends on thermodynamics) and the speed at which the reaction occurs (which depends on kinetics). Can a catalyst make a nonspontaneous reaction spontaneous?
7. What is the precise definition of entropy? What is the significance of entropy being a state function?
8. Why does the entropy of a gas increase when it expands into a vacuum?
9. Explain the difference between macrostates (external arrangements of particles) and microstates (internal arrangements of particles).
10. Based on its fundamental definition, explain why entropy is a measure of energy dispersion.
11. State the second law of thermodynamics. How does the second law explain why heat travels from a substance at higher temperature to one at lower temperature?
12. What happens to the entropy of a sample of matter when it changes state from a solid to a liquid? From a liquid to a gas?
13. Explain why water spontaneously freezes to form ice below 0 °C even though the entropy of the water decreases during the state transition. Why is the freezing of water not spontaneous above 0 °C?
14. Why do exothermic processes tend to be spontaneous at low temperatures? Why does their tendency toward spontaneity decrease with increasing temperature?
15. What is the significance of the change in Gibbs free energy (ΔG) for a reaction?
16. Predict the spontaneity of a reaction (and the temperature dependence of the spontaneity) for each possible combination of signs for ΔH and ΔS (for the system).
    - **a.** ΔH negative, ΔS positive
    - **b.** ΔH positive, ΔS negative
    - **c.** ΔH negative, ΔS negative
    - **d.** ΔH positive, ΔS positive
17. State the third law of thermodynamics and explain its significance.
18. Why is the standard entropy of a substance in the gas state greater than its standard entropy in the liquid state?
19. How does the standard entropy of a substance depend on its molar mass? On its molecular complexity?
20. How can you calculate the standard entropy change for a reaction from tables of standard entropies?
21. What are three different methods to calculate ΔG° for a reaction? Which method would you choose to calculate ΔG° for a reaction at a temperature other than 25 °C?
22. Why is free energy "free"?
23. Explain the difference between ΔG° and ΔG.
24. Why does water spilled on the floor evaporate even though ΔG° for the evaporation process is positive at room temperature?
25. How do you calculate the change in free energy for a reaction under nonstandard conditions?
26. How does the value of ΔG° for a reaction relate to the equilibrium constant for the reaction? What does a negative ΔG° for a reaction imply about K for the reaction? A positive ΔG°?

PROBLEMS BY TOPIC

Entropy, the Second Law of Thermodynamics, and the Direction of Spontaneous Change

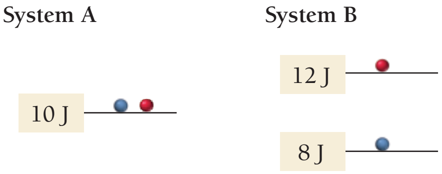
27. Which of these processes is spontaneous?
MISSED THIS? *Read Section 19.2*

a. the combustion of natural gas
b. the extraction of iron metal from iron ore
c. a hot drink cooling to room temperature
d. drawing heat energy from the ocean's surface to power a ship

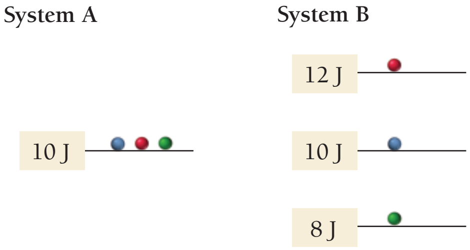
28. Which of these processes are nonspontaneous? Are the nonspontaneous processes impossible?

a. a bike going up a hill
b. a meteor falling to Earth
c. obtaining hydrogen gas from liquid water
d. a ball rolling down a hill

29. Two systems, each composed of two particles represented by circles, have 20 J of total energy. Which system, A or B, has the greater entropy? Why? **MISSED THIS?** *Read Section 19.3*



30. Two systems, each composed of three particles represented by circles, have 30 J of total energy. In how many energetically equivalent ways can you distribute the particles in each system? Which system has greater entropy?



31. Calculate the change in entropy that occurs in the system when 1.00 mole of isopropyl alcohol (C_3H_8O) melts at its melting point (–89.5 °C). See Table 12.9 for heats of fusion.
MISSED THIS? *Read Section 19.4; Watch IWE 19.2*

32. Calculate the change in entropy that occurs in the system when 1.00 mole of diethyl ether ($C_4H_{10}O$) condenses from a gas to a liquid at its normal boiling point (34.6 °C). See Table 12.7 for heats of vaporization.

33. Calculate the change in entropy that occurs in the system when 45.0 g of acetone (C_3H_6O) freezes at its melting point (–94.8 °C). See Table 12.9 for heats of fusion.
MISSED THIS? *Read Section 19.4; Watch IWE 19.2*

34. Calculate the change in entropy that occurs in the system when 55.0 g of water vaporizes from a liquid to a gas at its boiling point (100.0 °C). See Table 12.7 for heats of vaporization.

35. Without doing any calculations, determine the sign of ΔS_{sys} for each chemical reaction. **MISSED THIS?** *Read Section 19.4*

a. $2\,KClO_3(s) \longrightarrow 2\,KCl(s) + 3\,O_2(g)$
b. $CH_2{=}CH_2(g) + H_2(g) \longrightarrow CH_3CH_3(g)$
c. $Na(s) + 1/2\,Cl_2(g) \longrightarrow NaCl(s)$
d. $N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$

36. Without doing any calculations, determine the sign of ΔS_{sys} for each chemical reaction.

a. $Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$
b. $2\,H_2S(g) + 3\,O_2(g) \longrightarrow 2\,H_2O(g) + 2\,SO_2(g)$
c. $2\,O_3(g) \longrightarrow 3\,O_2(g)$
d. $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$

37. Without doing any calculations, determine the signs of ΔS_{sys} and ΔS_{surr} for each chemical reaction. In addition, predict under what temperatures (all temperatures, low temperatures, or high temperatures), if any, the reaction is spontaneous.
MISSED THIS? *Read Sections 19.4, 19.5; Watch IWE 19.3*

a. $C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(g)$ $\quad \Delta H^\circ_{\text{rxn}} = -2044\text{ kJ}$
b. $N_2(g) + O_2(g) \longrightarrow 2\,NO(g) \quad \Delta H^\circ_{\text{rxn}} = +182.6\text{ kJ}$
c. $2\,N_2(g) + O_2(g) \longrightarrow 2\,N_2O(g) \quad \Delta H^\circ_{\text{rxn}} = +163.2\text{ kJ}$
d. $4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$ $\quad \Delta H^\circ_{\text{rxn}} = -906\text{ kJ}$

38. Without doing any calculations, determine the signs of ΔS_{sys} and ΔS_{surr} for each chemical reaction. In addition, predict under what temperatures (all temperatures, low temperatures, or high temperatures), if any, the reaction is spontaneous.

a. $2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g) \quad \Delta H^\circ_{\text{rxn}} = -566.0\text{ kJ}$
b. $2\,NO_2(g) \longrightarrow 2\,NO(g) + O_2(g) \quad \Delta H^\circ_{\text{rxn}} = +113.1\text{ kJ}$
c. $2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) \quad \Delta H^\circ_{\text{rxn}} = -483.6\text{ kJ}$
d. $CO_2(g) \longrightarrow C(s) + O_2(g) \quad \Delta H^\circ_{\text{rxn}} = +393.5\text{ kJ}$

39. Calculate ΔS_{surr} at the indicated temperature for each reaction.
MISSED THIS? *Read Section 19.5; Watch IWE 19.3*

a. $\Delta H^\circ_{\text{rxn}} = -385\text{ kJ}; 298\text{ K}$ **b.** $\Delta H^\circ_{\text{rxn}} = -385\text{ kJ}; 77\text{ K}$
c. $\Delta H^\circ_{\text{rxn}} = +114\text{ kJ}; 298\text{ K}$ **d.** $\Delta H^\circ_{\text{rxn}} = +114\text{ kJ}; 77\text{ K}$

40. A reaction has $\Delta H^\circ_{\text{rxn}} = -112\text{ kJ}$ and $\Delta S^\circ_{\text{rxn}} = 354\text{ J/K}$. At what temperature is the change in entropy for the reaction equal to the change in entropy for the surroundings?

41. Given the values of $\Delta H^\circ_{\text{rxn}}$, $\Delta S^\circ_{\text{rxn}}$, and T, determine ΔS_{univ} and predict whether or not each reaction is spontaneous. (Assume that all reactants and products are in their standard states.) **MISSED THIS?** *Read Section 19.5; Watch IWE 19.3*

a. $\Delta H^\circ_{\text{rxn}} = +115\text{ kJ}; \Delta S^\circ_{\text{rxn}} = -263\text{ J/K}; T = 298\text{ K}$
b. $\Delta H^\circ_{\text{rxn}} = -115\text{ kJ}; \Delta S^\circ_{\text{rxn}} = +263\text{ J/K}; T = 298\text{ K}$
c. $\Delta H^\circ_{\text{rxn}} = -115\text{ kJ}; \Delta S^\circ_{\text{rxn}} = -263\text{ J/K}; T = 298\text{ K}$
d. $\Delta H^\circ_{\text{rxn}} = -115\text{ kJ}; \Delta S^\circ_{\text{rxn}} = -263\text{ J/K}; T = 615\text{ K}$

42. Given the values of ΔH_{rxn}, and T, determine ΔS_{rxn}, and predict whether or not each reaction is spontaneous. (Assume that all reactants and products are in their standard states.)

a. $\Delta H^\circ_{\text{rxn}} = -95\text{ kJ}; \Delta S^\circ_{\text{rxn}} = -157\text{ J/K}; T = 298\text{ K}$
b. $\Delta H^\circ_{\text{rxn}} = -95\text{ kJ}; \Delta S^\circ_{\text{rxn}} = -157\text{ J/K}; T = 855\text{ K}$
c. $\Delta H^\circ_{\text{rxn}} = +95\text{ kJ}; \Delta S^\circ_{\text{rxn}} = -157\text{ J/K}; T = 298\text{ K}$
d. $\Delta H^\circ_{\text{rxn}} = -95\text{ kJ}; \Delta S^\circ_{\text{rxn}} = +157\text{ J/K}; T = 398\text{ K}$

Standard Entropy Changes and Gibbs Free Energy

43. Calculate the change in Gibbs free energy for each of the sets of ΔH_{rxn}, ΔS_{rxn}, and T given in Problem 41. Predict whether or not each reaction is spontaneous at the temperature indicated. (Assume that all reactants and products are in their standard states.)
MISSED THIS? *Read Section 19.6; Watch KCV 19.6, IWE 19.4*

44. Calculate the change in Gibbs free energy for each of the sets of ΔH_{rxn}, ΔS_{rxn}, and T given in Problem 42. Predict whether or not each reaction is spontaneous at the temperature indicated. (Assume that all reactants and products are in their standard states.)

45. Calculate the free energy change for this reaction at 25 °C. Is the reaction spontaneous? (Assume that all reactants and products are in their standard states.)
MISSED THIS? *Read Section 19.6; Watch KCV 19.6, IWE 19.4*

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(g)$$
$$\Delta H^\circ_{\text{rxn}} = -2217\text{ kJ};\ \Delta S^\circ_{\text{rxn}} = 101.1\text{ J/K}$$

46. Calculate the free energy change for this reaction at 25 °C. Is the reaction spontaneous? (Assume that all reactants and products are in their standard states.)

$$2\,Ca(s) + O_2(g) \longrightarrow 2\,CaO(s)$$
$$\Delta H^\circ_{\text{rxn}} = -1269.8\text{ kJ};\ \Delta S^\circ_{\text{rxn}} = -364.6\text{ J/K}$$

47. Fill in the blanks in the table. Both ΔH and ΔS refer to the system.
MISSED THIS? *Read Section 19.6; Watch KCV 19.6*

ΔH	ΔS	ΔG	Low Temperature	High Temperature
−	+	−	Spontaneous	________
−	−	Temperature dependent	________	________
+	+	________	________	Spontaneous
________	−	________	Nonspontaneous	Nonspontaneous

48. Predict the conditions (high temperature, low temperature, all temperatures, or no temperatures) under which each reaction is spontaneous.
a. $H_2O(g) \longrightarrow H_2O(l)$
b. $CO_2(s) \longrightarrow CO_2(g)$
c. $H_2(g) \longrightarrow 2\,H(g)$
d. $2\,NO_2(g) \longrightarrow 2\,NO(g) + O_2(g)$ (endothermic)

49. How does the molar entropy of a substance change with increasing temperature?
MISSED THIS? *Read Section 19.7; Watch KCV 19.7*

50. What is the molar entropy of a pure crystal at 0 K? What is the significance of the answer to this question?

51. For each pair of substances, choose the one that you expect to have the higher standard molar entropy (S°) at 25 °C. Explain your choices. **MISSED THIS?** *Read Section 19.7; Watch KCV 19.7*
a. $CO(g)$; $CO_2(g)$
b. $CH_3OH(l)$; $CH_3OH(g)$
c. $Ar(g)$; $CO_2(g)$
d. $CH_4(g)$; $SiH_4(g)$
e. $NO_2(g)$; $CH_3CH_2CH_3(g)$
f. $NaBr(s)$; $NaBr(aq)$

52. For each pair of substances, choose the one that you expect to have the higher standard molar entropy (S°) at 25 °C. Explain your choices.
a. $NaNO_3(s)$; $NaNO_3(aq)$
b. $CH_4(g)$; $CH_3CH_3(g)$
c. $Br_2(l)$; $Br_2(g)$
d. $Br_2(g)$; $F_2(g)$
e. $PCl_3(g)$; $PCl_5(g)$
f. $CH_3CH_2CH_2CH_3(g)$; $SO_2(g)$

53. Rank each set of substances in order of increasing standard molar entropy (S°). Explain your reasoning.
MISSED THIS? *Read Section 19.7; Watch KCV 19.7*
a. $NH_3(g)$; $Ne(g)$; $SO_2(g)$; $CH_3CH_2OH(g)$; $He(g)$
b. $H_2O(s)$; $H_2O(l)$; $H_2O(g)$
c. $CH_4(g)$; $CF_4(g)$; $CCl_4(g)$

54. Rank each set of substances in order of increasing standard molar entropy (S°). Explain your reasoning.
a. $I_2(g)$; $F_2(g)$; $Br_2(g)$; $Cl_2(g)$
b. $H_2O(g)$; $H_2O_2(g)$; $H_2S(g)$
c. C(*s*, graphite); C(*s*, diamond); C(*s*, amorphous)

55. Use data from Appendix IIB to calculate $\Delta S^\circ_{\text{rxn}}$ for each of the reactions. In each case, try to rationalize the sign of $\Delta S^\circ_{\text{rxn}}$.
MISSED THIS? *Read Section 19.7; Watch IWE 19.5*
a. $C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$
b. $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$
c. $CO(g) + H_2O(g) \longrightarrow H_2(g) + CO_2(g)$
d. $2\,H_2S(g) + 3\,O_2(g) \longrightarrow 2\,H_2O(l) + 2\,SO_2(g)$

56. Use data from Appendix IIB to calculate $\Delta S^\circ_{\text{rxn}}$ for each of the reactions. In each case, try to rationalize the sign of $\Delta S^\circ_{\text{rxn}}$.
a. $3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g)$
b. $Cr_2O_3(s) + 3\,CO(g) \longrightarrow 2\,Cr(s) + 3\,CO_2(g)$
c. $SO_2(g) + \frac{1}{2}\,O_2(g) \longrightarrow SO_3(g)$
d. $N_2O_4(g) + 4\,H_2(g) \longrightarrow N_2(g) + 4\,H_2O(g)$

57. Find ΔS° for the formation of $CH_2Cl_2(g)$ from its gaseous elements in their standard states. Rationalize the sign of ΔS°.
MISSED THIS? *Read Section 19.7; Watch IWE 19.5*

58. Find ΔS° for the reaction between nitrogen gas and fluorine gas to form nitrogen trifluoride gas. Rationalize the sign of ΔS°.

59. Methanol (CH_3OH) burns in oxygen to form carbon dioxide and water. Write a balanced equation for the combustion of liquid methanol and calculate $\Delta H^\circ_{\text{rxn}}$, $\Delta S^\circ_{\text{rxn}}$, and $\Delta G^\circ_{\text{rxn}}$ at 25 °C. Is the combustion of methanol spontaneous?
MISSED THIS? *Read Section 19.8; Watch IWE 19.6*

60. In photosynthesis, plants form glucose ($C_6H_{12}O_6$) and oxygen from carbon dioxide and water. Write a balanced equation for photosynthesis and calculate $\Delta H^\circ_{\text{rxn}}$, $\Delta S^\circ_{\text{rxn}}$, and $\Delta G^\circ_{\text{rxn}}$ at 25 °C. Is photosynthesis spontaneous?

61. For each reaction, calculate $\Delta H^\circ_{\text{rxn}}$, $\Delta S^\circ_{\text{rxn}}$, and $\Delta G^\circ_{\text{rxn}}$ at 25 °C and state whether or not the reaction is spontaneous. If the reaction is not spontaneous, would a change in temperature make it spontaneous? If so, should the temperature be raised or lowered from 25 °C? **MISSED THIS?** *Read Section 19.8; Watch IWE 19.6*
a. $N_2O_4(g) \longrightarrow 2\,NO_2(g)$
b. $NH_4Cl(s) \longrightarrow HCl(g) + NH_3(g)$
c. $3\,H_2(g) + Fe_2O_3(s) \longrightarrow 2\,Fe(s) + 3\,H_2O(g)$
d. $N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$

62. For each reaction, calculate $\Delta H^\circ_{\text{rxn}}$, $\Delta S^\circ_{\text{rxn}}$, and $\Delta G^\circ_{\text{rxn}}$ at 25 °C and state whether or not the reaction is spontaneous. If the reaction is not spontaneous, would a change in temperature make it spontaneous? If so, should the temperature be raised or lowered from 25 °C?
a. $2\,CH_4(g) \longrightarrow C_2H_6(g) + H_2(g)$
b. $2\,NH_3(g) \longrightarrow N_2H_4(g) + H_2(g)$
c. $N_2(g) + O_2(g) \longrightarrow 2\,NO(g)$
d. $2\,KClO_3(s) \longrightarrow 2\,KCl(s) + 3\,O_2(g)$

63. Use standard free energies of formation to calculate ΔG° at 25 °C for each reaction in Problem 61. How do the values of ΔG° calculated this way compare to those calculated from ΔH° and ΔS°? Which of the two methods could be used to determine how ΔG° changes with temperature?
MISSED THIS? *Read Section 19.8*

64. Use standard free energies of formation to calculate ΔG° at 25 °C for each reaction in Problem 62. How well do the values of ΔG° calculated this way compare to those calculated from ΔH° and ΔS°? Which of the two methods could be used to determine how ΔG° changes with temperature?

65. Consider the reaction:
MISSED THIS? *Read Section 19.8; Watch IWE 19.6*

$$2\,\mathrm{NO}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO_2}(g)$$

Estimate $\Delta G°$ for this reaction at each temperature and predict whether or not the reaction is spontaneous. (Assume that $\Delta H°$ and $\Delta S°$ do not change too much within the given temperature range.)

a. 298 K **b.** 715 K **c.** 855 K

66. Consider the reaction:

$$\mathrm{CaCO_3}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

Estimate $\Delta G°$ for this reaction at each temperature and predict whether or not the reaction is spontaneous. (Assume that $\Delta H°$ and $\Delta S°$ do not change too much within the given temperature range.)

a. 298 K **b.** 1055 K **c.** 1455 K

67. Determine $\Delta G°$ for the reaction:
MISSED THIS? *Read Section 19.8*

$$\mathrm{Fe_2O_3}(s) + 3\,\mathrm{CO}(g) \longrightarrow 2\,\mathrm{Fe}(s) + 3\,\mathrm{CO_2}(g)$$

Use the following reactions with known $\Delta G°_{\mathrm{rxn}}$ values:

$$2\,\mathrm{Fe}(s) + \tfrac{3}{2}\,\mathrm{O_2}(g) \longrightarrow \mathrm{Fe_2O_3}(s) \qquad \Delta G°_{\mathrm{rxn}} = -742.2\ \mathrm{kJ}$$
$$\mathrm{CO}(g) + \tfrac{1}{2}\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) \qquad \Delta G°_{\mathrm{rxn}} = -257.2\ \mathrm{kJ}$$

68. Calculate $\Delta G°_{\mathrm{rxn}}$ for the reaction:

$$\mathrm{CaCO_3}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

Use the following reactions and given $\Delta G°_{\mathrm{rxn}}$ values:

$$\mathrm{Ca}(s) + \mathrm{CO_2}(g) + \tfrac{1}{2}\,\mathrm{O_2}(g) \longrightarrow \mathrm{CaCO_3}(s) \quad \Delta G°_{\mathrm{rxn}} = -734.4\ \mathrm{kJ}$$
$$2\,\mathrm{Ca}(s) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CaO}(s) \qquad \Delta G°_{\mathrm{rxn}} = -1206.6\ \mathrm{kJ}$$

Free Energy Changes, Nonstandard Conditions, and the Equilibrium Constant

69. Consider the sublimation of iodine at 25.0 °C:
MISSED THIS? *Read Section 19.9; Watch IWE 19.10*

$$\mathrm{I_2}(s) \longrightarrow \mathrm{I_2}(g)$$

a. Find $\Delta G°_{\mathrm{rxn}}$ at 25.0 °C.
b. Find $\Delta G°_{\mathrm{rxn}}$ at 25.0 °C under the following nonstandard conditions:
  i. $P_{\mathrm{I_2}} = 1.00$ mmHg
  ii. $P_{\mathrm{I_2}} = 0.100$ mmHg
c. Explain why iodine spontaneously sublimes in open air at 25.0 °C.

70. Consider the evaporation of methanol at 25.0 °C:

$$\mathrm{CH_3OH}(l) \longrightarrow \mathrm{CH_3OH}(g)$$

a. Find $\Delta G°_{\mathrm{r}}$ at 25.0 °C.
b. Find ΔG_{r} at 25.0 °C under the following nonstandard conditions:
  i. $P_{\mathrm{CH_3OH}} = 150.0$ mmHg
  ii. $P_{\mathrm{CH_3OH}} = 100.0$ mmHg
  iii. $P_{\mathrm{CH_3OH}} = 10.0$ mmHg
c. Explain why methanol spontaneously evaporates in open air at 25.0 °C.

71. Consider the reaction:
MISSED THIS? *Read Section 19.9; Watch IWE 19.10*

$$\mathrm{CH_3OH}(g) \rightleftharpoons \mathrm{CO}(g) + 2\,\mathrm{H_2}(g)$$

Calculate ΔG for this reaction at 25 °C under the following conditions:

i. $P_{\mathrm{CH_3OH}} = 0.855$ atm
ii. $P_{\mathrm{CO}} = 0.125$ atm
iii. $P_{\mathrm{H_2}} = 0.183$ atm

72. Consider the reaction:

$$\mathrm{CO_2}(g) + \mathrm{CCl_4}(g) \rightleftharpoons 2\,\mathrm{COCl_2}(g)$$

Calculate ΔG for this reaction at 25 °C under the following conditions:

i. $P_{\mathrm{CO_2}} = 0.112$ atm
ii. $P_{\mathrm{CCl_4}} = 0.174$ atm
iii. $P_{\mathrm{COCl_2}} = 0.744$ atm

73. Use data from Appendix IIB to calculate the equilibrium constants at 25 °C for each reaction.
MISSED THIS? *Read Section 19.10; Watch IWE 19.11*

a. $2\,\mathrm{CO}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{CO_2}(g)$
b. $2\,\mathrm{H_2S}(g) \rightleftharpoons 2\,\mathrm{H_2}(g) + \mathrm{S_2}(g)$

74. Use data from Appendix IIB to calculate the equilibrium constants at 25 °C for each reaction. $\Delta G°_{\mathrm{f}}$ for $\mathrm{BrCl}(g)$ is -1.0 kJ/mol.

a. $2\,\mathrm{NO_2}(g) \rightleftharpoons \mathrm{N_2O_4}(g)$
b. $\mathrm{Br_2}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\,\mathrm{BrCl}(g)$

75. Consider the reaction:
MISSED THIS? *Read Sections 19.9, 19.10; Watch IWE 19.10, 19.11*

$$\mathrm{CO}(g) + 2\,\mathrm{H_2}(g) \rightleftharpoons \mathrm{CH_3OH}(g)$$
$$K_{\mathrm{p}} = 2.26 \times 10^4 \text{ at } 25\ °\mathrm{C}$$

Calculate ΔG_{rxn} for the reaction at 25 °C under each of the following conditions:

a. standard conditions
b. at equilibrium
c. $P_{\mathrm{CH_3OH}} = 1.0$ atm; $P_{\mathrm{CO}} = P_{\mathrm{H_2}} = 0.010$ atm

76. Consider the reaction:

$$\mathrm{I_2}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\,\mathrm{ICl}(g)$$
$$K_{\mathrm{p}} = 81.9 \text{ at } 25\ °\mathrm{C}$$

Calculate ΔG_{rxn} for the reaction at 25 °C under each of the following conditions:

a. standard conditions
b. at equilibrium
c. $P_{\mathrm{ICl}} = 2.55$ atm; $P_{\mathrm{I_2}} = 0.325$ atm; $P_{\mathrm{Cl_2}} = 0.221$ atm

77. Estimate the value of the equilibrium constant at 525 K for each reaction in Problem 73.
MISSED THIS? *Read Sections 19.8, 19.10; Watch IWE 19.11*

78. Estimate the value of the equilibrium constant at 655 K for each reaction in Problem 74. ($\Delta H°_{\mathrm{f}}$ for BrCl is 14.6 kJ/mol.)

79. Consider the reaction: **MISSED THIS?** *Read Section 19.10*

$$\mathrm{H_2}(g) + \mathrm{I_2}(g) \rightleftharpoons 2\,\mathrm{HI}(g)$$

The following data show the equilibrium constant for this reaction measured at several different temperatures. Use the data to find $\Delta H°_{\mathrm{rxn}}$ and $\Delta S°_{\mathrm{rxn}}$ for the reaction.

Temperature	K_{p}
150 K	1.4×10^{-6}
175 K	4.6×10^{-4}
200 K	3.6×10^{-2}
225 K	1.1
250 K	15.5

80. Consider the reaction:

$$2\,\mathrm{NO}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{NO_2}(g)$$

The following data show the equilibrium constant for this reaction measured at several different temperatures. Use the data to find $\Delta H°_{\mathrm{rxn}}$ and $\Delta S°_{\mathrm{rxn}}$ for the reaction.

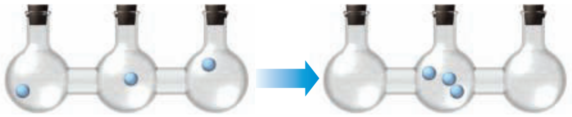
Temperature	K_p
170 K	3.8×10^{-3}
180 K	0.34
190 K	18.4
200 K	681

81. The change in enthalpy (ΔH°_{rxn}) for a reaction is -25.8 kJ/mol. The equilibrium constant for the reaction is 1.4×10^3 at 298 K. What is the equilibrium constant for the reaction at 655 K?
MISSED THIS? *Read Section 19.10*

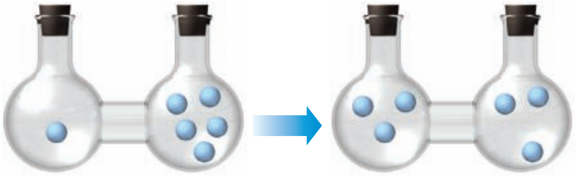
82. A reaction has an equilibrium constant of 8.5×10^3 at 298 K. At 755 K, the equilibrium constant is 0.65. Find ΔH°_{rxn} for the reaction.

CUMULATIVE PROBLEMS

83. Determine the sign of ΔS_{sys} for each process.
- **a.** water boiling
- **b.** water freezing
- **c.**



84. Determine the sign of ΔS_{sys} for each process.
- **a.** dry ice subliming
- **b.** dew forming
- **c.**



85. Our atmosphere is composed primarily of nitrogen and oxygen, which coexist at 25 °C without reacting to any significant extent. However, the two gases can react to form nitrogen monoxide according to the reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$

- **a.** Calculate ΔG° and K_p for this reaction at 298 K. Is the reaction spontaneous?
- **b.** Estimate ΔG° at 2000 K. Does the reaction become more spontaneous as temperature increases?

86. Nitrogen dioxide, a pollutant in the atmosphere, can combine with water to form nitric acid. One of the possible reactions is shown here. Calculate ΔG° and K_p for this reaction at 25 °C and comment on the spontaneity of the reaction.

$$3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g)$$

87. Ethene (C_2H_4) can be halogenated by the reaction:

$$C_2H_4(g) + X_2(g) \rightleftharpoons C_2H_4X_2(g)$$

where X_2 can be Cl_2, Br_2, or I_2. Use the thermodynamic data given to calculate ΔH°, ΔS°, ΔG°, and K_p for the halogenation reaction by each of the three halogens at 25 °C. Which reaction is most spontaneous? Least spontaneous? What is the main factor responsible for the difference in the spontaneity of the three reactions? Does higher temperature make the reactions more spontaneous or less spontaneous?

Compound	ΔH°_f (kJ/mol)	S° (J/mol · K)
$C_2H_4Cl_2(g)$	-129.7	308.0
$C_2H_4Br_2(g)$	$+38.3$	330.6
$C_2H_4I_2(g)$	$+66.5$	347.8

88. H_2 reacts with the halogens (X_2) according to the reaction:

$$H_2(g) + X_2(g) \rightleftharpoons 2\,HX(g)$$

where X_2 can be Cl_2, Br_2, or I_2. Use the thermodynamic data in Appendix IIB to calculate ΔH°, ΔS°, ΔG°, and K_p for the reaction between hydrogen and each of the three halogens. Which reaction is most spontaneous? Least spontaneous? What is the main factor responsible for the difference in the spontaneity of the three reactions? Does higher temperature make the reactions more spontaneous or less spontaneous?

89. Consider this reaction occurring at 298 K:

$$N_2O(g) + NO_2(g) \rightleftharpoons 3\,NO(g)$$

- **a.** Show that the reaction is not spontaneous under standard conditions by calculating ΔG°_{rxn}.
- **b.** If a reaction mixture contains only N_2O and NO_2 at partial pressures of 1.0 atm each, the reaction will be spontaneous until some NO forms in the mixture. What maximum partial pressure of NO builds up before the reaction ceases to be spontaneous?
- **c.** Can the reaction be made more spontaneous by an increase or decrease in temperature? If so, what temperature is required to make the reaction spontaneous under standard conditions?

90. Consider this reaction occurring at 298 K:

$$BaCO_3(s) \rightleftharpoons BaO(s) + CO_2(g)$$

- **a.** Show that the reaction is not spontaneous under standard conditions by calculating ΔG°_{rxn}.
- **b.** If $BaCO_3$ is placed in an evacuated flask, what is the partial pressure of CO_2 when the reaction reaches equilibrium?
- **c.** Can the reaction be made more spontaneous by an increase or decrease in temperature? If so, at what temperature is the partial pressure of carbon dioxide 1.0 atm?

91. Living organisms use energy from the metabolism of food to create an energy-rich molecule called adenosine triphosphate (ATP). The ATP acts as an energy source for a variety of reactions that the living organism must carry out to survive. ATP provides energy through its hydrolysis, which can be symbolized as follows:

$$ATP(aq) + H_2O(l) \longrightarrow ADP(aq) + P_i(aq) \quad \Delta G^\circ_{rxn} = -30.5\text{ kJ}$$

where ADP represents adenosine diphosphate and P_i represents an inorganic phosphate group (such as HPO_4^{2-}).
- **a.** Calculate the equilibrium constant, K, for the given reaction at 298 K.
- **b.** The free energy obtained from the oxidation (reaction with oxygen) of glucose ($C_6H_{12}O_6$) to form carbon dioxide and water can be used to re-form ATP by driving the given reaction in reverse. Calculate the standard free energy change for the oxidation of glucose and estimate the maximum number of moles of ATP that can be formed by the oxidation of one mole of glucose.

92. The standard free energy change for the hydrolysis of ATP was given in Problem 91. In a particular cell, the concentrations of ATP, ADP, and P_i are 0.0031 M, 0.0014 M, and 0.0048 M, respectively. Calculate the free energy change for the hydrolysis of ATP under these conditions. (Assume a temperature of 298 K.)

93. These reactions are important in catalytic converters in automobiles. Calculate $\Delta G°$ for each at 298 K. Predict the effect of increasing temperature on the magnitude of $\Delta G°$.

a. $2\,\mathrm{CO}(g) + 2\,\mathrm{NO}(g) \longrightarrow \mathrm{N_2}(g) + 2\,\mathrm{CO_2}(g)$
b. $5\,\mathrm{H_2}(g) + 2\,\mathrm{NO}(g) \longrightarrow 2\,\mathrm{NH_3}(g) + 2\,\mathrm{H_2O}(g)$
c. $2\,\mathrm{H_2}(g) + 2\,\mathrm{NO}(g) \longrightarrow \mathrm{N_2}(g) + 2\,\mathrm{H_2O}(g)$
d. $2\,\mathrm{NH_3}(g) + 2\,\mathrm{O_2}(g) \longrightarrow \mathrm{N_2O}(g) + 3\,\mathrm{H_2O}(g)$

94. Calculate $\Delta G°$ at 298 K for these reactions and predict the effect on $\Delta G°$ of lowering the temperature.

a. $\mathrm{NH_3}(g) + \mathrm{HBr}(g) \longrightarrow \mathrm{NH_4Br}(s)$
b. $\mathrm{CaCO_3}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$
c. $\mathrm{CH_4}(g) + 3\,\mathrm{Cl_2}(g) \longrightarrow \mathrm{CHCl_3}(g) + 3\,\mathrm{HCl}(g)$
($\Delta G_f°$ for $\mathrm{CHCl_3}(g)$ is -70.4 kJ/mol.)

95. All the oxides of nitrogen have positive values of $\Delta G_f°$ at 298 K, but only one common oxide of nitrogen has a positive $\Delta S_f°$. Identify that oxide of nitrogen without reference to thermodynamic data and explain.

96. The values of $\Delta G_f°$ for the hydrogen halides become less negative with increasing atomic number. The $\Delta G_f°$ of HI is slightly positive. However, the trend in $\Delta S_f°$ is to become more positive with increasing atomic number. Explain.

97. Consider the reaction $\mathrm{X_2}(g) \longrightarrow 2\,\mathrm{X}(g)$. When a vessel initially containing 755 torr of $\mathrm{X_2}$ comes to equilibrium at 298 K, the equilibrium partial pressure of X is 103 torr. The same reaction is repeated with an initial partial pressure of 748 torr of $\mathrm{X_2}$ at 755 K; the equilibrium partial pressure of X is 532 torr. Find $\Delta H°$ for the reaction.

98. Dinitrogen tetroxide decomposes to nitrogen dioxide:

$$\mathrm{N_2O_4}(g) \longrightarrow 2\,\mathrm{NO_2}(g) \quad \Delta H°_{\mathrm{rxn}} = 55.3\ \mathrm{kJ}$$

At 298 K, a reaction vessel initially contains 0.100 atm of $\mathrm{N_2O_4}$. When equilibrium is reached, 58% of the $\mathrm{N_2O_4}$ has decomposed to $\mathrm{NO_2}$. What percentage of $\mathrm{N_2O_4}$ decomposes at 388 K? Assume that the initial pressure of $\mathrm{N_2O_4}$ is the same (0.100 atm).

99. Indicate and explain the sign of ΔS_{univ} for each process.

a. $2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{H_2O}(l)$ at 298 K
b. the electrolysis of $\mathrm{H_2O}(l)$ to $\mathrm{H_2}(g)$ and $\mathrm{O_2}(g)$ at 298 K
c. the growth of an oak tree from a little acorn

100. The Haber process is very important for agriculture because it converts $\mathrm{N_2}(g)$ from the atmosphere into bound nitrogen, which can be taken up and used by plants. The Haber process reaction is $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g)$. The reaction is exothermic but is carried out at relatively high temperatures. Why?

101. A metal salt with the formula $\mathrm{MCl_2}$ crystallizes from water to form a solid with the composition $\mathrm{MCl_2 \cdot 6\,H_2O}$. The equilibrium vapor pressure of water above this solid at 298 K is 18.3 mmHg. What is the value of ΔG for the reaction $\mathrm{MCl_2 \cdot 6\,H_2O}(s) \rightleftharpoons \mathrm{MCl_2}(s) + 6\,\mathrm{H_2O}(g)$ when the pressure of water vapor is 18.3 mmHg? When the pressure of water vapor is 760 mmHg?

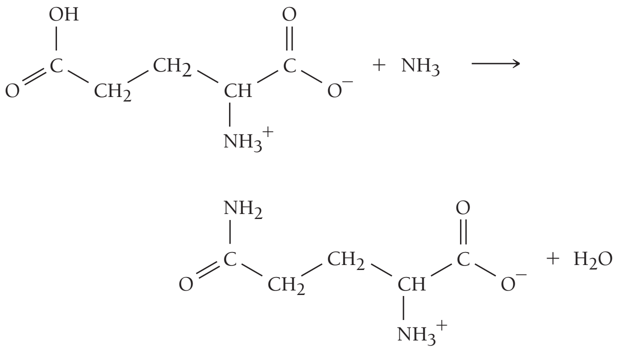
102. The solubility of AgCl(s) in water at 25 °C is 1.33×10^{-5} mol/L and its $\Delta H°$ of solution is 65.7 kJ/mol. What is its solubility at 50.0 °C?

CHALLENGE PROBLEMS

103. Review the box in this chapter entitled *Chemistry in Your Day: Making a Nonspontaneous Process Spontaneous.* The hydrolysis of ATP, shown in Problem 91, is often used to drive nonspontaneous processes—such as muscle contraction and protein synthesis—in living organisms. The nonspontaneous process to be driven must be coupled to the ATP hydrolysis reaction. For example, suppose the nonspontaneous process is $\mathrm{A + B \longrightarrow AB}$ ($\Delta G°$ positive). The coupling of a nonspontaneous reaction such as this one to the hydrolysis of ATP is often accomplished by the mechanism:

$$\begin{array}{c} \mathrm{A + ATP + H_2O \longrightarrow A{-}P_i + ADP} \\ \mathrm{A{-}P_i + B \longrightarrow AB + P_i} \\ \hline \mathrm{A + B + ATP + H_2O \longrightarrow AB + ADP + P_i} \end{array}$$

As long as $\Delta G°_{\mathrm{rxn}}$ for the nonspontaneous reaction is less than 30.5 kJ, the reaction can be made spontaneous by coupling in this way to the hydrolysis of ATP. Suppose that ATP is to drive the reaction between glutamate and ammonia to form glutamine:



a. Calculate K for the reaction between glutamate and ammonia. (The standard free energy change for the reaction is $+14.2$ kJ/mol. Assume a temperature of 298 K.)
b. Write a set of reactions such as those given showing how the glutamate and ammonia reaction can couple with the hydrolysis of ATP. What are $\Delta G°_{\mathrm{rxn}}$ and K for the coupled reaction?

104. Calculate the entropy of each state and rank the states in order of increasing entropy.


(a)


(b)


(c)

105. Suppose we redefine the standard state as $P = 2$ atm. Find the new standard ΔG_f° values of each substance.

a. $HCl(g)$ **b.** $N_2O(g)$ **c.** $H(g)$

Explain the results in terms of the relative entropies of reactants and products of each reaction.

106. The ΔG for the freezing of $H_2O(l)$ at -10 °C is -210 J/mol, and the heat of fusion of ice at this temperature is 5610 J/mol. Find the entropy change of the universe when 1 mol of water freezes at -10 °C.

107. Consider the reaction that occurs during the Haber process:

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

The equilibrium constant is 3.9×10^5 at 300 K and 1.2×10^{-1} at 500 K. Calculate ΔH_{rxn}° and ΔS_{rxn}° for this reaction.

108. The salt ammonium nitrate can follow three modes of decomposition: (a) to $HNO_3(g)$ and $NH_3(g)$, (b) to $N_2O(g)$ and $H_2O(g)$, and (c) to $N_2(g)$, $O_2(g)$, and $H_2O(g)$. Calculate ΔG_{rxn}° for each mode of decomposition at 298 K. Explain in light of these results how it is still possible to use ammonium nitrate as a fertilizer and identify the precautions that should be taken when it is used.

109. Given the data, calculate ΔS_{vap} for each of the first four liquids. ($\Delta S_{vap} = \Delta H_{vap}/T$, where T is in K)

Compound	Name	BP (°C)	ΔH_{vap} (kJ/mol) at BP
$C_4H_{10}O$	Diethyl ether	34.6	26.5
C_3H_6O	Acetone	56.1	29.1
C_6H_6O	Benzene	79.8	30.8
$CHCl_3$	Chloroform	60.8	29.4
C_2H_5OH	Ethanol	77.8	38.6
H_2O	Water	100	40.7

All four values should be close to each other. Predict whether the last two liquids in the table have ΔS_{vap} in this same range. If not, predict whether it is larger or smaller and explain. Verify your prediction.

CONCEPTUAL PROBLEMS

110. Which is more efficient, a butane lighter or an electric lighter (such as the ones traditionally found on the dashboard of automobiles)? Explain.

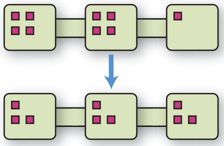
111. Which statement is true?

a. A spontaneous reaction is always a fast reaction.
b. A spontaneous reaction is always a slow reaction.
c. The spontaneity of a reaction is not necessarily related to the speed of a reaction.

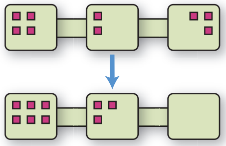
112. Which process is necessarily driven by an increase in the entropy of the surroundings?

a. the condensation of water
b. the sublimation of dry ice
c. the freezing of water

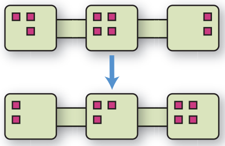
113. Consider the changes in the distribution of nine particles into three interconnected boxes shown here. Which has the most negative ΔS?



(a)



(b)



(c)

114. Which statement is true?

a. A reaction in which the entropy of the system increases can be spontaneous only if it is exothermic.
b. A reaction in which the entropy of the system increases can be spontaneous only if it is endothermic.
c. A reaction in which the entropy of the system decreases can be spontaneous only if it is exothermic.

115. Which process is spontaneous at 298 K?

a. $H_2O(l) \longrightarrow H_2O(g, 1\text{ atm})$
b. $H_2O(l) \longrightarrow H_2O(g, 0.10\text{ atm})$
c. $H_2O(l) \longrightarrow H_2O(g, 0.010\text{ atm})$

116. The free energy change of the reaction $A(g) \longrightarrow B(g)$ is zero under certain conditions. The *standard* free energy change of the reaction is -42.5 kJ. Which statement must be true about the reaction?

a. The concentration of the product is greater than the concentration of the reactant.
b. The reaction is at equilibrium.
c. The concentration of the reactant is greater than the concentration of the product.

117. The reaction $A(g) \rightleftharpoons B(g)$ has an equilibrium constant of 5.8 and under certain conditions has $Q = 336$. What can you conclude about the sign of ΔG_{rxn}° and ΔG_{rxn} for this reaction under these conditions?

QUESTIONS FOR GROUP WORK

Active Classroom Learning

Discuss these questions with the group and record your consensus answer.

118. Imagine that you roll two dice. Write down all the possible rolls that sum to 2. Write all the possible rolls that sum to 12. Write all the possible rolls that sum to 7. Which configuration has the greatest entropy: 2, 12, or 7?

119. If you roll 1 million dice, what will be the average of all the dice? If there is a room with 1 million dice and they all have a 1 on the top face, and there is an earthquake strong enough to roll dice around, what is the likelihood that after the earthquake all the top faces will sum to 1 million? To 6 million? How does this thought experiment illustrate the second law of thermodynamics?

120. Not all processes in which the system increases in entropy are spontaneous. How can this observation be consistent with the second law? Provide an example and explain your answer in complete sentences.

121. Have each group member look up $\Delta H^\circ_\mathrm{f}$ and S° for one substance in the reaction: $3\,O_2(g) + 6\,H_2(g) + 6\,C(s, \text{graphite}) \longrightarrow C_6H_{12}O_6(s, \text{glucose})$. What is ΔH° for this reaction? What is ΔS°? When is $\Delta H^\circ_\mathrm{f}$ for a substance equal to zero? When is S° for a substance equal to zero?

122. Calculate ΔG° at 25 °C for the reaction in the previous question. Is this reaction spontaneous under standard conditions? How do you know? What is the determining factor: the change in energy or the change in entropy or both? Explain.

DATA INTERPRETATION AND ANALYSIS

Thermodynamic Functions for Borax

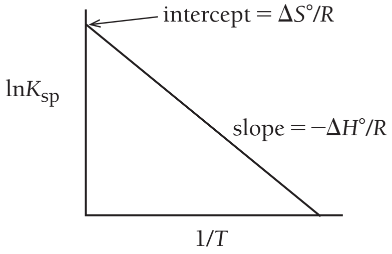
123. Borax, sodium tetraborate decahydrate, is an important mineral found in dry lakebeds in California. It is used to make soap and glass, and it is also used as a preservative. You can use the values of K_{sp} of borax at different temperatures to determine ΔH°, ΔS°, and ΔG° for the dissolution of borax:

$$\underset{\text{(Borax)}}{Na_2B_4O_5(OH)_4 \cdot 8\,H_2O(s)} \longrightarrow 2\,Na^+(aq) + \underset{\text{(Borate)}}{B_4O_5(OH)_4{}^{2-}(aq)} + 8\,H_2O(l)$$

The relationship:

$$\ln(K_{sp}) = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

has the form of a linear equation $y = mx + b$, where y is the $\ln K_{sp}$ and x is $1/T$. The slope is equal to $(-\Delta H^\circ/R)$ and the y-intercept is $\Delta S^\circ/R$, where R is the gas constant, 8.314 J/K mol. If you measure K_{sp} at several different temperatures, you can plot the $\ln K$ versus $1/T$ (T in Kelvin), as shown here.



▲ Plot of $\ln K_{sp}$ versus $1/T$ where the Units of Temperature Are in Kelvin

Knowing the values of ΔH° and ΔS° at a specific temperature allows the calculation of the change in Gibbs free energy for the reaction: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

The following table lists K_{sp} values for the dissolution of borax at several different temperatures (°C).

K_{sp} Values for the Dissolution of Borax at Several Different Temperatures (°C)

Temperature (°C)	K_{sp}
40.0	0.041
45.0	0.083
50.0	0.264
55.0	0.486
60.0	0.552

a. Plot a graph of $\ln K_{sp}$ versus $1/T$ (T in Kelvin) and find the best-fitting line.
b. Determine ΔH°. Is this process endothermic or exothermic?
c. Determine ΔS°.
d. Determine ΔG°.
e. Sketch a graph of $\ln K$ versus $1/T$ for an exothermic process.

ANSWERS TO CONCEPTUAL CONNECTIONS

The Second Law

19.1 **(c)** The second law states that energy spontaneously disperses itself. The spontaneous concentration of energy (in a closed system) is inconsistent with the second law.

Entropy

19.2 **(a)** The more spread out the particles are between the three boxes, the greater the entropy. Therefore, the entropy change is positive only in scheme **(a)**.

Entropy and State Changes

19.3 **(c)** The condensation of water is a phase transition from gas to liquid, so entropy decreases.

Entropy and Biological Systems

19.4 **(b)** Biological systems do not violate the second law of thermodynamics. The key to understanding this concept is realizing that entropy changes in the system can be negative as long as the entropy change of the universe is positive. Biological systems can decrease their own entropy, but only at the expense of creating more entropy in the surroundings (which they do primarily by emitting the heat they generate by their metabolic processes). Thus, for any biological process, ΔS_{univ} is positive.

ΔH, ΔS, and ΔG

19.5 **(a)** Sublimation is endothermic (it requires energy to overcome the intermolecular forces that hold solid carbon dioxide together), so ΔH is positive. The number of moles of gas increases when the solid turns into a gas, so the entropy of the carbon dioxide increases and ΔS is positive. Since $\Delta G = \Delta H - T\Delta S$, ΔG is positive at low temperature and negative at high temperature.

Standard Entropies

19.6 **(a)** Kr $<$ Cl_2 $<$ SO_3. Because krypton is a monoatomic gas, it has the least entropy. Because SO_3 is the most complex molecule, it has the most entropy. The molar masses of the three gases vary slightly, but not enough to overcome the differences in molecular complexity.

Free Energy Changes and Le Châtelier's Principle

19.7 **(a)** A high concentration of reactants relative to products will lead to $Q < 1$, making the term $RT \ln Q$ in Equation 19.14 negative. ΔG_{rxn} is more negative than ΔG°_{rxn}, and the reaction is more spontaneous.

K and ΔG°_{rxn}

19.8 **(c)** Since the equilibrium constant is less than 1, the reaction proceeds toward reactants under standard conditions (when $Q = 1$). Therefore, ΔG°_{rxn} is positive.

The Conditions of Spontaneity

19.9 **(b)** $\Delta G_{rxn} < 0, Q < K$ If a reaction is spontaneous, then ΔG_{rxn} is negative and Q must be less than K (because a spontaneous reaction proceeds toward products).