VISUAL PROBLEMS

(Answers to boldface end-of-chapter questions and problems are in the back of the book.)

12.1. Two tires shown in cross-section in Figure P12.1 are inflated at the same temperature to the same volume, though more air is used to inflate the tire on the right. In which tire is the gas under greater internal pressure and in which does the gas have greater entropy?

![FIGURE P12.1](image1)

12.2. Two cubic containers (Figure P12.2) contain the same quantity of gas at the same temperature.
   a. Which cube contains the gas with more entropy?
   b. If the sample in cube b is left unchanged but the sample in cube a is cooled so that it condenses, which sample has the higher entropy?

![FIGURE P12.2](image2)

12.3. Figure P12.3 shows two connected bulbs that have just been filled with a mixture of two ideal gases: A (red spheres) and B (blue spheres). If the molar mass of A is twice that of B, will the atoms of A eventually fill the bottom bulb and the atoms of B fill the top bulb? Why or why not?

![FIGURE P12.3](image3)

12.4. The box on the left in Figure P12.4 represents a mixture of two diatomic gases: A₂ (red spheres) and B₂ (blue spheres). As a result of the process depicted by the arrow, how do the entropies of A₂ and B₂ change?
12.5. Is the process in Figure P12.4 more likely to be spontaneous at high temperature or low temperature, or is it unaffected by changing temperature?

12.6. Figure P12.6 shows the plots of $\Delta H$ and $T \Delta S$ for a phase change as a function of temperature.
   a. What is the status of the process at the point where the two lines intersect?
   b. Over what temperature range is the process spontaneous?

12.7. Of the six phase changes—melting, vaporization, condensation, freezing, sublimation, and deposition—which ones have thermodynamic profiles that fit the pattern in Figure P12.6?

12.8. Figure P12.8 presents the $\Delta G^\circ_f$ values of several elements and compounds selected from Appendix 4. Which of the following conversions are spontaneous? (a) $\text{C}_6\text{H}_6(\ell)$ to $\text{CO}_2(g)$ and $\text{H}_2\text{O}(\ell)$; (b) $\text{CO}_2(g)$ to $\text{C}_2\text{H}_2(g)$; (c) $\text{H}_2(g)$ and $\text{O}_2(g)$ to $\text{H}_2\text{O}(\ell)$. Explain your reasoning.

QUESTIONS AND PROBLEMS

Spontaneous Processes; Entropy

CONCEPT REVIEW

12.9. How is the entropy change that accompanies a reaction related to the entropy change that happens when the reaction runs in reverse?

12.10. Identify the following processes as spontaneous or nonspontaneous, and explain your choice.
a. A photovoltaic cell in a solar panel produces electricity.
b. Helium gas escapes from a latex party balloon.
c. A sample of pitchblende (uranium ore) emits alpha particles.

12.11. You flip three coins, assigning the values +1 for heads and −1 for tails. Each outcome of the three flips constitutes a microstate. How many different microstates are possible from flipping the three coins? Which value or values for the sums in the microstates are most likely? *Hint: The sequence HHT (+1 +1 −1) is one possible outcome, or microstate. Note, however, that this outcome differs from THH (−1 +1 +1), even though the two sequences sum to the same value.

12.12. Imagine you have four identical chairs to arrange on four steps leading up to a stage, one chair on each step. The chairs have numbers on their backs: 1, 2, 3, and 4. How many different microstates for the chairs are possible? (Notice that when viewed from the front, all the microstates look the same. Viewed from the back, you can identify the different microstates because you can distinguish the chairs by their numbers.)

12.13. Use the appropriate standard molar entropy value in Appendix 4 to calculate how many microstates are available to a single molecule of liquid H₂O at 298 K.

12.14. Use the appropriate standard molar entropy value in Appendix 4 to calculate how many microstates are available to a single molecule of N₂ at 298 K.

12.15. The three identical glass spheres in Figure P12.15 contain the same number of particles at the same temperature. Rank the containers in order of increasing number of microstates accessible to the particles inside them.

![Figure P12.15](image)

12.16. Figure P12.16(a) shows a cylinder within a cylinder that contains a population of gaseous molecules. The volume occupied by the molecules can be increased by pulling the inside cylinder out (Figure P12.16b), much like a telescope. The number of molecules within the cylinder remains the same during this operation. Compare the number of microstates available to the molecules in Figure P12.16(a) and (b).

![Figure P12.16](image)

12.17. Which of the following ionic solutes experiences the greatest increase in entropy when 0.0100 mol of it dissolves in 1.00 liter of water? (a) CaCl₂, (b) NaBr, (c) KCl, (d) Cr(NO₃)₃, (e) LiOH

12.18. Which of the following molecular solutes experience an increase in entropy when dissolved in water? (a) CO₂(g), (b) HF(g), (c) CH₃OH(l), (d) CH₃COOH(l), (e) C₁₂H₂₂O₁₁(s)

*12.21. Diamond and the fullerenes are two allotropes of carbon. On the basis of their different structures and properties, predict which has the higher standard molar entropy.

Absolute Entropy and Molecular Structure

CONCEPT REVIEW

12.19. Which component in each of the following pairs has the greater entropy?
   a. 1 mole of S₂(g) or 1 mole of S₈(g)
   b. 1 mole of S₂(g) or 1 mole of S₈(s)
   c. 1 mole of O₂(g) or 1 mole of O₃(g)
   d. 1 gram of O₂(g) or 1 gram of O₃(g)

12.20. Digestion During digestion, complex carbohydrates decompose into simple sugars. Do the carbohydrates experience an increase or decrease in entropy?

12.21. Diamond and the fullerenes are two allotropes of carbon. On the basis of their different structures and properties, predict which has the higher standard molar entropy.
12.22. Superfluids The 1996 Nobel Prize in Physics was awarded to Douglas Osheroff, Robert Richardson, and David Lee for discovering superfluidity (apparently frictionless flow) in $^3$He. When $^3$He is cooled to 2.7 mK, the liquid settles into an ordered superfluid state. Predict the sign of the entropy change for the conversion of liquid $^3$He into its superfluid state.

PROBLEMS

12.23. Rank the compounds in each of the following groups in order of increasing standard molar entropy ($S^\circ$):
   a. CH$_3$(g), CF$_4$(g), and CCl$_4$(g)
   b. CH$_3$O(g), CH$_3$CHO(g), and CH$_2$CH$_2$CHO(g)
   c. HF(g), H$_2$O(g), and NH$_3$(g)

12.24. Rank the compounds in each of the following groups in order of increasing standard molar entropy ($S^\circ$):
   a. CH$_3$(g), CH$_3$CH$_3$(g), and CH$_2$CH$_2$(g)
   b. CCl$_4$(l), CHCl$_3$(l), and CH$_3$Cl(l)
   c. CO$_2$(l), CO$_2$(g), and CS$_2$(g)

Applications of the Second Law

CONCEPT REVIEW

12.25. Ice cubes melt in a glass of lemonade, cooling the lemonade from 10.0°C to 0.0°C. If the ice cubes are the system, what are the signs of $\Delta S_{\text{sys}}$ and $\Delta S_{\text{surr}}$?

12.26. Adding sidewalk deicer (calcium chloride) to water causes the temperature of the water to increase. If solid CaCl$_2$ is the system, what are the signs of $\Delta S_{\text{sys}}$ and $\Delta S_{\text{surr}}$?

PROBLEMS

12.27. Which of the following combinations of entropy changes for a process are mathematically possible?
   a. $\Delta S_{\text{sys}} > 0$, $\Delta S_{\text{surr}} > 0$, $\Delta S_{\text{univ}} > 0$
   b. $\Delta S_{\text{sys}} > 0$, $\Delta S_{\text{surr}} < 0$, $\Delta S_{\text{univ}} > 0$
   c. $\Delta S_{\text{sys}} > 0$, $\Delta S_{\text{surr}} < 0$, $\Delta S_{\text{univ}} < 0$

12.28. Which of the following combinations of entropy changes for a process are mathematically possible?
   a. $\Delta S_{\text{sys}} < 0$, $\Delta S_{\text{surr}} > 0$, $\Delta S_{\text{univ}} > 0$
   b. $\Delta S_{\text{sys}} < 0$, $\Delta S_{\text{surr}} < 0$, $\Delta S_{\text{univ}} > 0$
   c. $\Delta S_{\text{sys}} < 0$, $\Delta S_{\text{surr}} < 0$, $\Delta S_{\text{univ}} < 0$

12.29. What are the signs of $\Delta S_{\text{sys}}$ and $\Delta S_{\text{univ}}$ for the photosynthesis of glucose from carbon dioxide and water?

12.30. What are the signs of $\Delta S_{\text{sys}}$, $\Delta S_{\text{surr}}$, and $\Delta S_{\text{univ}}$ for the complete combustion of propane in which the products include water vapor and carbon dioxide?

12.31. The nonspontaneous reaction $A + B \rightarrow C$ decreases the system entropy by 66.0 J/K. What is the minimum value of the entropy change of the surroundings?

12.32. The spontaneous reaction $D \rightarrow E + F$ increases the system entropy by 72.0 J/K. What is the maximum value of the entropy change of the surroundings?

Calculating Entropy Changes

CONCEPT REVIEW

12.33. Under standard conditions the products of a reaction have, overall, greater entropy than the reactants. What is the sign of $\Delta S_{\text{rxn}}^\circ$?

12.34. Do decomposition reactions tend to have $\Delta S_{\text{rxn}}^\circ$ values that are greater than zero or less than zero? Why?

12.35. Do precipitation reactions tend to have $\Delta S_{\text{rxn}}^\circ$ values that are greater than zero or less than zero? Why?

*12.36. Suppose compound $A(s)$ decomposes to substances $B(l)$ and $C(l)$ at moderately high temperatures. How would running the decomposition reaction at even higher temperatures (above the melting point of $A$, but still below the boiling points of $B$ and $C$) affect the value of $\Delta S_{\text{rxn}}^\circ$?

PROBLEMS

12.37. Smog Use the standard molar entropies in Appendix 4 to calculate $\Delta S^\circ$ values for each of the following atmospheric reactions that contribute to the formation of photochemical smog.
   a. $N_2(g) + O_2(g) \rightarrow 2$ NO(g)
   b. $2$ NO(g) + $O_2(g) \rightarrow 2$ NO$_2(g)$
   c. NO(g) + $\frac{1}{2}$ O$_2(g) \rightarrow$ NO$_2(g)$
12.38. Use the standard molar entropies in Appendix 4 to calculate the \( \Delta S^\circ \) value for each of the following reactions of sulfur compounds.

- a. \( \text{H}_2\text{S}(g) + \frac{3}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(g) + \text{SO}_2(g) \)
- b. \( 2 \text{SO}_2(g) + \text{O}_2(g) \rightarrow 2 \text{SO}_3(g) \)
- c. \( \text{SO}_3(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{SO}_4(aq) \)
- d. \( \text{S}(g) + \text{O}_2(g) \rightarrow \text{SO}_2(g) \)

12.39. Ozone Layer The following reaction plays a key role in the destruction of ozone in the atmosphere:

\[
\text{Cl}(g) + \text{O}_3(g) \rightarrow \text{ClO}(g) + \text{O}_2(g)
\]

The standard entropy change (\( \Delta S^\circ_{\text{rxn}} \)) is 19.9 J/(mol \cdot K). Use the standard molar entropies (\( S^\circ \)) in Appendix 4 to calculate the \( S^\circ \) value of \( \text{ClO}(g) \).

12.40. Calculate the \( \Delta S^\circ \) value for the conversion of ozone to oxygen

\[
2 \text{O}_3(g) \rightarrow 3 \text{O}_2(g)
\]

in the absence of Cl atoms, and compare it with the \( \Delta S^\circ \) value in Problem 12.39.

**Free Energy**

**CONCEPT REVIEW**

12.41. What does the sign of \( \Delta G \) tell you about the spontaneity of a process?

12.42. What does the sign of \( \Delta G \) tell you about the rate of a reaction?

12.43. Many 19th-century scientists believed that all exothermic reactions were spontaneous. Why did so many of them share this belief?

12.44. In which direction does a reaction proceed when:
   - a. \( \Delta G_{\text{rxn}} \equiv 0 \);
   - b. \( \Delta G_{\text{rxn}} = 0 \);
   - c. \( \Delta G_{\text{rxn}} > 0 \)?

12.45. What are the signs of \( \Delta S \), \( \Delta H \), and \( \Delta G \) for the sublimation of dry ice (solid CO\(_2\)) at 25°C?

12.46. What are the signs of \( \Delta S \), \( \Delta H \), and \( \Delta G \) for the formation of dew on a cool night?

12.47. Which of the following processes is/are spontaneous?
   - a. A tornado forms.
   - b. A broken cell phone fixes itself.
   - c. You get an A in this course.
   - d. Hot soup gets cold before it is served.

12.48. Which of the following processes is/are spontaneous?
   - a. Wood burns in air.
   - b. Water vapor condenses on the sides of a glass of ice tea.
   - c. Salt dissolves in water.
   - d. Photosynthesis.

**PROBLEMS**

12.49. Calculate the free-energy change for the dissolution in water of 1 mole of NaBr and 1 mole of NaI at 298 K from the values in the table below.

<table>
<thead>
<tr>
<th></th>
<th>( \Delta H^\circ_{\text{solution}} ) (kJ/mol)</th>
<th>( \Delta S^\circ_{\text{solution}} ) [J/(mol \cdot K)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBr</td>
<td>–1</td>
<td>57</td>
</tr>
<tr>
<td>NaI</td>
<td>–7</td>
<td>74</td>
</tr>
</tbody>
</table>

12.50. The values of \( \Delta H^\circ_{\text{rxn}} \) and \( \Delta S^\circ_{\text{rxn}} \) for the reaction

\[
2 \text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g)
\]

are –12 kJ and –146 J/K.

a. Use these values to calculate \( \Delta G^\circ_{\text{rxn}} \) at 298 K.

b. Explain why the value of \( \Delta S^\circ_{\text{rxn}} \) is negative.

12.51. A mixture of CO(g) and H\(_2\)(g) is produced by passing steam over hot charcoal:

\[
\text{H}_2\text{O}(g) + \text{C}(s) \rightarrow \text{H}_2(g) + \text{CO}(g)
\]

Calculate the \( \Delta G^\circ_{\text{rxn}} \) value for the reaction from the appropriate \( \Delta G^\circ_{\text{f}} \) data in Appendix 4.
12.52. Use the appropriate $\Delta G^\circ_T$ data in Appendix 4 to calculate $\Delta G^\circ_{\text{rxn}}$ for the complete combustion of methanol:

$$2 \text{CH}_3\text{OH(g)} + 3 \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) + 4 \text{H}_2\text{O(g)}$$

12.53. Photochemical Smog Use the appropriate $\Delta G^\circ_T$ data in Appendix 4 to calculate $\Delta G^\circ_{\text{rxn}}$ for the oxidation of NO to NO$_2$—a key reaction in the formation of photochemical smog:

$$\text{NO(g)} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{NO}_2(g)$$

12.54. Use the free energies of formation from Appendix 4 to calculate the standard free-energy change for the decomposition of ammonia in the following reaction:

$$2 \text{NH}_3(g) \rightarrow N_2(g) + 3 \text{H}_2(g)$$

Is the reaction spontaneous under standard conditions?

12.55. Acid Precipitation Aerosols (fine droplets) of sulfuric acid form in the atmosphere as a result of the reaction below. Use the appropriate $\Delta G^\circ_T$ data in Appendix 4 to calculate $\Delta G^\circ_{\text{rxn}}$ for the combination reaction

$$\text{SO}_3(g) + \text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{SO}_4(l)$$

12.56. One source of sulfuric acid aerosols in the atmosphere is combustion of high-sulfur fuels, which releases SO$_2$ gas that then is further oxidized to SO$_3$:

$$2 \text{SO}_2(g) + \text{O}_2(g) \rightarrow 2 \text{SO}_3(g)$$

Use the appropriate $\Delta G^\circ_T$ data in Appendix 4 to calculate $\Delta G^\circ_{\text{rxn}}$ for this combination reaction. Is it spontaneous under standard conditions?

Temperature and Spontaneity

CONCEPT REVIEW

12.57. Are exothermic reactions spontaneous only at low temperature? Explain your answer.

12.58. Are endothermic reactions never spontaneous at low temperature? Explain your answer.

PROBLEMS

12.59. What is the lowest temperature at which the following reaction (see Problem 12.51) is spontaneous?

$$\text{H}_2\text{O(g)} + \text{C(s)} \rightarrow \text{H}_2(g) + \text{CO(g)}$$

12.60. Above what temperature does nitrogen monoxide form from nitrogen and oxygen?

$$\text{N}_2(g) + \text{O}_2(g) \rightarrow 2 \text{NO(g)}$$

Assume that the values of $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ do not change appreciably with temperature.

12.61. Use the data in Appendix 4 to calculate $\Delta H^\circ$ and $\Delta S^\circ$ for the vaporization of hydrogen peroxide:

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

Assuming that the calculated values are independent of temperature, what is the boiling point of hydrogen peroxide at $P = 1.00$ atm?

12.62. Volcanoes Deposits of elemental sulfur are often seen near active volcanoes. Their presence there may be due to the following reaction of SO$_2$ with H$_2$S:

$$\text{SO}_2(g) + 2 \text{H}_2\text{S(g)} \rightarrow \frac{3}{8}\text{S}_8(s) + 2 \text{H}_2\text{O(g)}$$

Assuming the values of $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ do not change appreciably with temperature, over what temperature range is the reaction spontaneous?

12.63. Which of the following reactions is spontaneous: (i) only at low temperatures; (ii) only at high temperatures; (iii) at all temperatures?

a. $2 \text{NO(g)} + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g)$

b. $2 \text{NH}_3(g) + 2 \text{O}_2(g) \rightarrow \text{N}_2\text{O}_3(g) + 3 \text{H}_2\text{O(g)}$

c. $\text{NH}_2\text{NO}_3(s) \rightarrow 2 \text{H}_2\text{O(g)} + \text{N}_2\text{O}_3(g)$

12.64. Which of the following reactions is spontaneous: (i) only at low temperatures; (ii) only at high temperatures; (iii) at all temperatures?

a. $2 \text{H}_2\text{S(g)} + 3 \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O(g)} + 2 \text{SO}_2(g)$

b. $\text{SO}_2(g) + \text{H}_2\text{O}_2(l) \rightarrow \text{H}_2\text{SO}_4(l)$
Driving the Human Engine: Coupled Reactions

CONCEPT REVIEW

12.65. Describe the ways in which two chemical reactions must complement each other so that the decrease in free energy of the spontaneous one can drive the nonspontaneous reaction.

12.66. How do you calculate the value of $\Delta G^\circ$ for a reaction that is the result of coupling a spontaneous reaction ($\Delta G_{\text{spon}}^\circ \leq 0$) and a nonspontaneous reaction ($\Delta G_{\text{nonspon}}^\circ > 0$)?

12.67. Why is it important that at least some of the spontaneous steps in glycolysis convert ADP to ATP?

12.68. The second step in glycolysis converts glucose 6-phosphate into fructose 6-phosphate (Figure P12.68). Suggest a reason why $\Delta G^\circ$ for this reaction is close to zero.

PROBLEMS

12.69. The methane in natural gas is an important starting material, or feedstock, for producing industrial chemicals, including H₂ gas.

a. Use the appropriate $\Delta G^\circ_f$ value(s) from Appendix 4 to calculate $\Delta G^\circ_{\text{rxn}}$ for the reaction known as steam–methane reforming:

$$\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}(g) + 3 \text{H}_2(g)$$

b. To drive this nonspontaneous reaction the CO that is produced can be oxidized to CO₂ using more steam:

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

Use the appropriate $\Delta G^\circ_f$ value(s) from Appendix 4 to calculate $\Delta G^\circ_{\text{rxn}}$ for this reaction, which is known as the water–gas shift reaction.

c. Combine these two reactions and write the chemical equation of the overall reaction in which methane and steam combine to produce hydrogen gas and carbon dioxide.

d. Calculate the $\Delta G^\circ_{\text{rxn}}$ value of the overall reaction. Is it spontaneous under standard conditions?

12.70. In addition to the reactions described in Problem 12.69, methane can, in theory, be used to produce hydrogen gas by a process in which it decomposes into elemental carbon and hydrogen:

1. $\text{CH}_4(g) \rightarrow C(s) + 2 \text{H}_2(g)$

and the carbon produced in the first step is then oxidized to CO₂:

2. $C(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$

a. Calculate the $\Delta G^\circ_{\text{rxn}}$ values of the above two reactions.

b. Write a balanced chemical equation describing the overall reaction obtained by coupling the above two and calculate its $\Delta G^\circ_{\text{rxn}}$ value. Is the coupled reaction spontaneous under standard conditions?

Additional Problems

12.71. Chlorofluorocarbons (CFCs) are no longer used as refrigerants because they catalyze the decomposition of stratospheric ozone. Trichlorofluoromethane (CCl₃F) boils at 23.8 °C and its molar heat of vaporization is 24.8 kJ/mol. What is the molar entropy of evaporation of CCl₃F(ℓ)?

12.72. Methane-Producing Bacteria Methanogenic bacteria convert liquid acetic acid (CH₃COOH) into CO₂(g) and CH₄(g).

a. Is this process endothermic or exothermic under standard conditions?

b. Is the reaction spontaneous under standard conditions?

*12.73. At what temperature is the free-energy change for the following reaction equal to zero?
12.74. Consider the precipitation reactions described by the following net ionic equations:

\[
\text{Mg}^{2+}(aq) + 2 \text{OH}^-(aq) \rightarrow \text{Mg(OH)}_2(s)
\]
\[
\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s)
\]

a. Predict the sign of \( \Delta S_{\text{rxn}} \) for the reactions.
b. Using the values for \( S^\circ \) from Appendix 4, calculate \( \Delta S^\circ \) for these reactions.
c. Do your calculations support your prediction?

12.75. Calculate the standard free-energy change of the following reaction. Is it spontaneous?

\[
2 \text{NO}(g) + 2 \text{H}_2(g) \rightarrow \text{N}_2(g) + 2 \text{H}_2\text{O}(g)
\]

12.76. Which of these processes result in a decrease in entropy of the system?

a. Diluting hydrochloric acid with water
b. Boiling water
c. 2 \text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g)
d. Making ice cubes in the freezer

12.77. Show that hydrogen cyanide (HCN) is a gas at 25°C by estimating its normal boiling point from the following data:

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta H_f^\circ ) (kJ/mol)</th>
<th>( S^\circ ) [J/(mol \cdot K)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN(l)</td>
<td>108.9</td>
<td>113</td>
</tr>
<tr>
<td>HCN(g)</td>
<td>135.1</td>
<td>202</td>
</tr>
</tbody>
</table>

12.78. Estimate the free-energy change of the following reaction at 225°C:

\[
\text{C}_2\text{H}_4(g) + 3 \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) + 2 \text{H}_2\text{O}(g)
\]

12.79. Lightbulb Filaments Tungsten (W) is the favored metal for lightbulb filaments, in part because of its high melting point of 3422°C. The enthalpy of fusion of tungsten is 35.4 kJ/mol. What is its entropy of fusion?

12.80. Making Methanol The element hydrogen (H\textsubscript{2}) is not abundant in nature, but it is a useful reagent in, for example, the potential synthesis of the liquid fuel methanol from gaseous carbon monoxide:

\[
2 \text{H}_2(g) + \text{CO}(g) \rightarrow \text{CH}_3\text{OH}(l)
\]

Under what temperature conditions is this reaction spontaneous?

12.81. Two allotropes (A and B) of sulfur interconvert at 369 K and 1 atm pressure:

\[
S(s, A) \rightarrow S(s, B)
\]

The enthalpy change in this transition is 297 J/mol. What is the entropy change?

12.82. Over what temperature range is the reduction of tungsten(VI) oxide by hydrogen to give metallic tungsten and water spontaneous? The standard heat of formation of WO\textsubscript{3}(s) is –843 kJ/mol, and its standard molar entropy is 76 J/(mol \cdot K)

12.83. Lime Enormous amounts of lime (CaO) are used in steel industry blast furnaces to remove impurities from iron. Lime is made by heating limestone and other solid forms of CaCO\textsubscript{3}(s). Why is the standard molar entropy of CaCO\textsubscript{3}(s) higher than that of CaO(s)? At what temperature is the pressure of CO\textsubscript{2}(g) over CaCO\textsubscript{3}(s) equal to 1.0 atm?

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta H_f^\circ ) (kJ/mol)</th>
<th>( S^\circ ) [J/(mol \cdot K)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO\textsubscript{3}(s)</td>
<td>–1207</td>
<td>93</td>
</tr>
<tr>
<td>CaO(s)</td>
<td>–636</td>
<td>40</td>
</tr>
<tr>
<td>CO\textsubscript{2}(g)</td>
<td>–394</td>
<td>214</td>
</tr>
</tbody>
</table>

12.84. Copper forms two oxides, Cu\textsubscript{2}O and CuO.

a. Name these oxides.
b. Predict over what temperature range this reaction is spontaneous using the following thermodynamic data:

\[ \text{Cu}_2\text{O}(s) \rightarrow \text{CuO}(s) + \text{Cu}(s) \]

<table>
<thead>
<tr>
<th></th>
<th>( \Delta H^\circ_f ) (kJ/mol)</th>
<th>( S^\circ ) [J/(mol \cdot K)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{Cu}_2\text{O}(s)</td>
<td>-170.7</td>
<td>92.4</td>
</tr>
<tr>
<td>\text{CuO}(s)</td>
<td>-156.1</td>
<td>42.6</td>
</tr>
</tbody>
</table>

c. Why is the standard molar entropy of \text{Cu}_2\text{O}(s) larger than that of \text{CuO}(s)?

*12.85. Melting Organic Compounds When dicarboxylic acids (compounds with two \(-\text{COOH}\) groups in their structures) melt, they frequently decompose to produce 1 mole of \( \text{CO}_2 \) gas for every 1 mole of dicarboxylic acid melted (shown in Figure P12.85).

a. What are the signs of \( \Delta H \) and \( \Delta S \) for the process as written?

b. Do you think the dicarboxylic acid will re-form when the melted material cools? Why or why not?

\[
\text{C}(\text{CH}_2)_n\text{C}(\text{CH}_2)_n \rightarrow \text{H}(\text{CH}_2)_n\text{C} \rightarrow \text{CO}_2(g)
\]

\*FIGURE P12.85

*12.86. Melting DNA When a solution of DNA in water is heated, the DNA double helix separates into two single strands.

a. What is the sign of \( \Delta S \) for the separation process?

b. The DNA double helix re-forms as the system cools. What is the sign of \( \Delta S \) for the process by which two single strands re-form the double helix?

c. The melting point of DNA is defined as the temperature at which \( \Delta G^\circ = 0 \). At that temperature, the melting reaction produces two single strands as fast as two single strands recombine to form the double helix. Write an equation that defines the melting temperature \( T \) of DNA in terms of \( \Delta H \) and \( \Delta S \).
VISUAL PROBLEMS

(Answers to boldface end-of-chapter questions and problems are in the back of the book.)

13.1. Nitrous oxide decomposes to nitrogen and oxygen in the following reaction:

\[ 2 \text{N}_2\text{O}(g) \rightarrow 2 \text{N}_2(g) + \text{O}_2(g) \]

In Figure P13.1, which curve represents \([\text{N}_2\text{O}]\) and which curve represents \([\text{O}_2]\)?

![Figure P13.1](image)

13.2. Sulfur trioxide is formed in the reaction

\[ \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{SO}_3(g) \]

In Figure P13.2, which curve represents \([\text{SO}_2]\) and which curve represents \([\text{O}_2]\)? All three gases are present initially.

![Figure P13.2](image)

13.3. The rate law for the reaction \(2 \text{A} \rightarrow \text{B}\) is second order in \(\text{A}\). Figure P13.3 represents samples with different concentrations of \(\text{A}\); the red spheres represent molecules of \(\text{A}\). In which sample will the reaction \(\text{A} \rightarrow \text{B}\) proceed most rapidly?

![Figure P13.3](image)

13.4. The rate law for the reaction \(\text{A} + \text{B} \rightarrow \text{C}\) is first order in both \(\text{A}\) and \(\text{B}\). Figure P13.4 represents samples with different concentrations of \(\text{A}\) (red spheres) and \(\text{B}\) (blue spheres). In which sample will the reaction \(\text{A} + \text{B} \rightarrow \text{C}\) proceed most rapidly?
13.5. Using the numbers 1–5 on the reaction profile (Figure P13.5), identify the following:
   a. The energy of the reactants
   b. The energy of the products
   c. The activation energy of the forward reaction
   d. The activation energy of the reverse reaction
   e. The energy change of the reaction

13.6. Select the diagram from those given in Figure P13.6 that best corresponds to the following:
   a. A highly exothermic reaction with a large activation energy
   b. A highly endothermic reaction with a small activation energy
   c. A reaction involving a stable intermediate

13.7. Which of the reaction profiles in Figure P13.7 represents the reaction with the smallest rate constant at constant $T$?
13.8. Which of the reaction profiles in Figure P13.8 represents the reaction with the largest rate constant at constant $T$?

13.9. Which of the following mechanisms is consistent with the reaction profile shown in Figure P13.9?

- a. $2 \text{A} \underset{\text{slow}}{\xrightarrow{\text{fast}}} \text{B}$
  
  $\text{B} \underset{\text{fast}}{\xrightarrow{\text{slow}}} \text{C}$

- b. $\text{A} + \text{B} \rightarrow \text{C}$

- c. $2 \text{A} \underset{\text{fast}}{\xrightarrow{\text{slow}}} \text{B}$
  
  $\text{B} \underset{\text{slow}}{\xrightarrow{\text{fast}}} \text{C}$

13.10. Which of the following mechanisms is consistent with the reaction profile shown in Figure P13.10?

- a. $\text{A} + \text{B} \underset{\text{slow}}{\xrightarrow{\text{fast}}} \text{C}$
  
  $\text{C} \underset{\text{fast}}{\xrightarrow{\text{slow}}} \text{D}$

- b. $\text{A} + \text{B} \rightarrow \text{C}$

- c. $2 \text{A} \underset{\text{fast}}{\xrightarrow{\text{slow}}} \text{B}$
  
  $\text{B} + \text{C} \underset{\text{slow}}{\xrightarrow{\text{fast}}} \text{D}$
13.11. Which of the reaction profiles in Figure P13.11 represents the effect of a catalyst on the rate of a reaction?

![Energy vs Progress of reaction graphs]

(a) Uncatalyzed reaction
(b) Uncatalyzed reaction
(c) Uncatalyzed reaction

*13.12. Which of the reaction profiles in Figure P13.12 represents the effect of a catalyst on the rate of a reaction?

![Energy vs Progress of reaction graphs]

(a) Uncatalyzed reaction
(b) Uncatalyzed reaction
(c) Uncatalyzed reaction

13.13. Which of the highlighted elements in Figure P13.13 forms volatile oxides associated with photochemical smog formation?

![Periodic Table]

13.14. Which of the highlighted elements in Figure P13.13 forms noxious oxides that are removed from
automobile exhaust as it passes through a catalytic converter?

13.15. Which of the highlighted elements in Figure P13.15 are widely used as heterogeneous catalysts?

![Figure P13.15]

13.16. Which of the highlighted elements in Figure P13.16 forms volatile, odd-electron oxides that catalyze the destruction of stratospheric ozone?

![Figure P13.16]

QUESTIONS AND PROBLEMS

Cars, Trucks, and Air Quality

CONCEPT REVIEW

13.17. Why does the maximum concentration of ozone in Figure 13.2 occur much later in the day than the maximum concentration of NO and NO₂?

13.18. If we plot the concentration of reactants and products as a function of time for any sequence of two spontaneous chemical reactions, such as

\[ \text{A} \rightarrow \text{B} \rightarrow \text{C} \]

will the maximum concentration of final product C always appear after the maximum concentration of B?

13.19. Why isn’t there an increase in NO concentration after the evening rush hour?

13.20. If ozone can react with NO to form NO₂, why does the ozone concentration reach a maximum in the early afternoon?

PROBLEMS

13.21. Using data in Appendix 4, calculate \( \Delta H^\circ \) for the reaction

\[ 2 \text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g) \]

13.22. Using data in Appendix 4, calculate \( \Delta H^\circ \) for the reaction

\[ \text{O}_3(g) + \text{NO}(g) \rightarrow \text{O}_2(g) + \text{NO}_2(g) \]

13.23. Nitrogen and oxygen can combine to form different nitrogen oxides that play a minor role in the chemistry of smog. Write balanced chemical equations for the reactions of N₂ and O₂ that produce (a) N₂O and (b) N₂O₅.

13.24. Nitrogen oxides such as N₂O and N₂O₅ are present in the air in low concentrations, in part because of their reactivity. Write balanced chemical equations for these reactions:

a. The conversion of N₂O to NO₂ in the presence of oxygen
b. The decomposition of N₂O₅ to NO₂ and O₂
### Reaction Rates

**CONCEPT REVIEW**

**13.25.** Explain the difference between the average rate and the instantaneous rate of a chemical reaction.

**13.26.** Can the average rate and instantaneous rate of a chemical reaction ever be the same?

**13.27.** Why do the average rates of most reactions change with time?

**13.28.** Does the instantaneous rate of a chemical reaction change with time?

### PROBLEMS

**13.29.** Bacterial Degradation of Ammonia *Nitrosomonas* bacteria convert ammonia into nitrite in the presence of oxygen by the following reaction:

\[
2 \text{NH}_3(aq) + 3 \text{O}_2(g) \rightarrow 2 \text{H}^+(aq) + 2 \text{NO}_2^-(aq) + 2 \text{H}_2\text{O}(l)
\]

a. How are the rates of formation of \(\text{H}^+\) and \(\text{NO}_2^-\) related to the rate of consumption of \(\text{NH}_3\)?

b. How is the rate of formation of \(\text{NO}_2^-\) related to the rate of consumption of \(\text{O}_2\)?

c. How is the rate of consumption of \(\text{NH}_3\) related to the rate of consumption of \(\text{O}_2\)?

**13.30.** Catalytic Converters and Combustion Catalytic converters in automobiles combat air pollution by converting NO and CO into \(\text{N}_2\) and \(\text{CO}_2\):

\[
2 \text{CO}(g) + 2 \text{NO}(g) \rightarrow \text{N}_2(g) + 2 \text{CO}_2(g)
\]

a. How is the rate of formation of \(\text{N}_2\) related to the rate of consumption of \(\text{CO}\)?

b. How is the rate of formation of \(\text{CO}_2\) related to the rate of consumption of \(\text{NO}\)?

c. How is the rate of consumption of \(\text{CO}\) related to the rate of consumption of \(\text{NO}\)?

**13.31.** Write expressions for the rate of formation of products and the rate of consumption of reactants in each of the following reactions:

a. \(\text{H}_2\text{O}_2(g) \rightarrow 2 \text{OH}(g)\)

b. \(\text{ClO}(g) + \text{O}_2(g) \rightarrow \text{ClO}_2(g)\)

c. \(\text{N}_2\text{O}_3(g) + \text{H}_2\text{O}(g) \rightarrow 2 \text{HNO}_2(g)\)

**13.32.** Write expressions for the rate of formation of products and the rate of consumption of reactants in each of the following reactions:

a. \(\text{Cl}_2\text{O}_2(g) \rightarrow 2 \text{ClO}(g)\)

b. \(\text{N}_2\text{O}_3(g) \rightarrow \text{NO}_2(g) + \text{NO}(g)\)

c. \(2 \text{INO}(g) \rightarrow \text{I}_2(g) + 2 \text{NO}(g)\)

**13.33.** Power-Plant Emissions Sulfur dioxide emissions in power-plant stack gases may react with carbon monoxide as follows:

\[
\text{SO}_2(g) + 3 \text{CO}(g) \rightarrow 2 \text{CO}_2(g) + \text{COS}(g)
\]

Write an equation relating each of the following pairs of rates:

a. The rate of formation of \(\text{CO}_2\) to the rate of consumption of \(\text{CO}\)

b. The rate of formation of \(\text{COS}\) to the rate of consumption of \(\text{SO}_2\)

c. The rate of consumption of \(\text{CO}\) to the rate of consumption of \(\text{SO}_2\)

**13.34.** Reducing Nitric Oxide Emissions from Power Plants Nitric oxide (NO) can be removed from gas-fired power-plant emissions by reaction with methane as follows:

\[
\text{CH}_4(g) + 4 \text{NO}(g) \rightarrow 2 \text{N}_2(g) + \text{CO}_2(g) + 2 \text{H}_2\text{O}(g)
\]

Write an equation relating each of the following pairs of rates:

a. The rate of formation of \(\text{N}_2\) to the rate of formation of \(\text{CO}_2\)

b. The rate of formation of \(\text{CO}_2\) to the rate of consumption of \(\text{NO}\)

c. The rate of consumption of \(\text{CH}_4\) to the rate of formation of \(\text{H}_2\text{O}\)

**13.35.** Stratospheric Ozone Depletion Chlorine monoxide (ClO) plays a major role in the creation of the ozone holes in the stratosphere over Earth’s polar regions.

a. If \(\Delta[\text{ClO}] / \Delta t\) at 298 K is \(-2.3 \times 10^7 \text{ M/s}\), what is the rate of change in \(\Delta[\text{Cl}_2]\) and \([\text{O}_2]\) in the following reaction?

\[
2 \text{ClO}(g) \rightarrow \text{Cl}_2(g) + \text{O}_2(g)
\]

b. If \(\Delta[\text{ClO}] / \Delta t\) is \(-2.9 \times 10^4 \text{ M/s}\), what is the rate of formation of oxygen and \(\text{ClO}_2\) in the following reaction?
ClO(g) + O₃(g) → O₂(g) + ClO₂(g)

13.36. The chemistry of smog formation includes NO₃ as an intermediate in several reactions.
a. If Δ[NO₃]/Δt is $-2.2 \times 10^5$ mM/min in the following reaction, what is the rate of formation of NO₂?

\[
\text{NO}_3(g) + \text{NO}(g) \rightarrow 2 \text{NO}_2(g)
\]

b. What is the rate of change of [NO₂] in the following reaction if Δ[NO₃]/Δt is $-2.3$ mM/min?

\[
2 \text{NO}_3(g) \rightarrow 2 \text{NO}_2(g) + \text{O}_2(g)
\]

13.37. Nitrite ion reacts with ozone in aqueous solution, producing nitrate ion and oxygen:

\[
\text{NO}_2^-(aq) + \text{O}_3(g) \rightarrow \text{NO}_3^-(aq) + \text{O}_2(g)
\]

The following data were collected for this reaction at 298 K. Calculate the average reaction rate between 0 and 100 µs (microseconds) and between 200 and 300 µs.

<table>
<thead>
<tr>
<th>Time (µs)</th>
<th>[O₃] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$1.13 \times 10^{-2}$</td>
</tr>
<tr>
<td>100</td>
<td>$9.93 \times 10^{-3}$</td>
</tr>
<tr>
<td>200</td>
<td>$8.70 \times 10^{-3}$</td>
</tr>
<tr>
<td>300</td>
<td>$8.15 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

13.38. Dinitrogen pentoxide (N₂O₅) decomposes as follows to nitrogen dioxide and nitrogen trioxide:

\[
\text{N}_2\text{O}_5(g) \rightarrow \text{NO}_2(g) + \text{NO}_3(g)
\]

Calculate the average rate of this reaction between consecutive measurement times listed in the following table.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[N₂O₅] (molecules/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$1.500 \times 10^{12}$</td>
</tr>
<tr>
<td>1.45</td>
<td>$1.357 \times 10^{12}$</td>
</tr>
<tr>
<td>2.90</td>
<td>$1.228 \times 10^{12}$</td>
</tr>
<tr>
<td>4.35</td>
<td>$1.111 \times 10^{12}$</td>
</tr>
<tr>
<td>5.80</td>
<td>$1.005 \times 10^{12}$</td>
</tr>
</tbody>
</table>

13.39. The following data were collected for the dimerization of ClO to Cl₂O₂ at 298 K.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[ClO] (molecules/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$2.60 \times 10^{11}$</td>
</tr>
<tr>
<td>1</td>
<td>$1.08 \times 10^{11}$</td>
</tr>
<tr>
<td>2</td>
<td>$6.83 \times 10^{10}$</td>
</tr>
<tr>
<td>3</td>
<td>$4.99 \times 10^{10}$</td>
</tr>
<tr>
<td>4</td>
<td>$3.93 \times 10^{10}$</td>
</tr>
<tr>
<td>5</td>
<td>$3.24 \times 10^{10}$</td>
</tr>
<tr>
<td>6</td>
<td>$2.76 \times 10^{10}$</td>
</tr>
</tbody>
</table>
Plot \([\text{ClO}]\) and \([\text{Cl}_2\text{O}_2]\) as a function of time and determine the instantaneous rates of change in both at 1 s.

13.40. Tropospheric Ozone  Tropospheric (lower atmosphere) ozone is rapidly consumed in many reactions, including

\[
\text{O}_3(g) + \text{NO}(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g)
\]

Use the following data to calculate the instantaneous rate of the reaction at \(t = 0.000\) s and \(t = 0.052\) s.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[NO] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>2.0 \times 10^{-8}</td>
</tr>
<tr>
<td>0.011</td>
<td>1.8 \times 10^{-8}</td>
</tr>
<tr>
<td>0.027</td>
<td>1.6 \times 10^{-8}</td>
</tr>
<tr>
<td>0.052</td>
<td>1.4 \times 10^{-8}</td>
</tr>
<tr>
<td>0.102</td>
<td>1.2 \times 10^{-8}</td>
</tr>
</tbody>
</table>

**Effect of Concentration on Reaction Rate**

**CONCEPT REVIEW**

13.41. Can two different chemical reactions have the same rate law?
13.42. Why are the units of the rate constants different for reactions of different order?
13.43. Does the half-life of a second-order reaction have the same units as the half-life for a first-order reaction?
13.44. Does the half-life of a first-order reaction depend on the concentration of the reactants?
13.45. What effect does doubling the initial concentration of a reactant have on the half-life of a reaction that is second order in the reactant?
13.46. Two first-order decomposition reactions of the form \(A \rightarrow B + C\) have the same rate constant at a given temperature. Do the reactants in the two reactions have the same half-lives at this temperature?

**PROBLEMS**

13.47. For each of the following rate laws, determine the order with respect to each reactant and the overall reaction order.
   a. Rate = \(k[A][B]\)
   b. Rate = \(k[A]^2[B]\)
   c. Rate = \(k[A][B]^3\)

13.48. Determine the overall order of the following rate laws and the order with respect to each reactant.
   a. Rate = \(k[A]^2[B]^{1/2}\)
   b. Rate = \(k[A]^2[B][C]\)
   c. Rate = \(k[A][B]^{1/2}[C]\^{1/2}\)

13.49. Write rate laws and determine the units of the rate constant (by using the units \(M\) for concentration and \(s\) for time) for the following reactions:
   a. The reaction of oxygen atoms with \(\text{NO}_2\) is first order in both reactants.
   b. The reaction between \(\text{NO}\) and \(\text{Cl}_2\) is second order in \(\text{NO}\) and first order in \(\text{Cl}_2\).
   c. The reaction between \(\text{Cl}_2\) and chloroform (\(\text{CHCl}_3\)) is first order in \(\text{CHCl}_3\) and one-half order in \(\text{Cl}_2\).
   d. The decomposition of ozone (\(\text{O}_3\)) to \(\text{O}_2\) is second order in \(\text{O}_3\) and an order of \(-1\) in \(\text{O}\) atoms.

13.50. Compounds \(A\) and \(B\) react to give a single product, \(C\). Write the rate law for each of the following cases and determine the units of the rate constant by using the units \(M\) for concentration and \(s\) for time:
   a. The reaction is first order in \(A\) and second order in \(B\).
   b. The reaction is first order in \(A\) and second order overall.
   c. The reaction is independent of the concentration of \(A\) and second order overall.
   d. The reaction is second order in both \(A\) and \(B\).
13.51. Predict the rate law for the reaction 2 BrO(g) → Br\(_2\)(g) + O\(_2\)(g) under each of the following conditions:
   a. The rate doubles when [BrO] doubles.
   b. The rate quadruples when [BrO] doubles.
   c. The rate is halved when [BrO] is halved.
   d. The rate is unchanged when [BrO] is doubled.

13.52. Predict the rate law for the reaction NO(g) + Br\(_2\)(g) → NOBr\(_2\)(g) under each of the following conditions:
   a. The rate doubles when [NO] is doubled and [Br\(_2\)] remains constant.
   b. The rate doubles when [Br\(_2\)] is doubled and [NO] remains constant.
   c. The rate increases by 1.56 times when [NO] is increased 1.25 times and [Br\(_2\)] remains constant.
   d. The rate is halved when [NO] is doubled and [Br\(_2\)] remains constant.

13.53. In the reaction of NO with ClO,
   \[ \text{NO(g)} + \text{ClO(g)} \rightarrow \text{NO}_2(g) + \text{Cl(g)} \]
   the initial rate of reaction quadruples when the concentrations of both reactants are doubled. What additional information do we need to determine whether the reaction is first order in each reactant?

13.54. The reaction between chlorine monoxide and nitrogen dioxide
   \[ \text{ClO(g)} + \text{NO}_2(g) + \text{M(g)} \rightarrow \text{ClONO}_2(g) + \text{M(g)} \]
   produces chlorine nitrate (ClONO\(_2\)). A third molecule (M) takes part in the reaction but is unchanged by it. The reaction is first order in NO\(_2\) and in ClO.
   a. Write the rate law for this reaction.
   b. What is the reaction order with respect to M?

13.55. Rate Laws for Destruction of Tropospheric Ozone The reaction of NO\(_2\) with ozone produces NO\(_3\) in a second-order reaction overall:
   \[ \text{NO}_2(g) + O_3(g) \rightarrow \text{NO}_3(g) + O_2(g) \]
   a. Write the rate law for the reaction if the reaction is first order in each reactant.
   b. The rate constant for the reaction is \(1.93 \times 10^4\) M\(^{-1}\) s\(^{-1}\) at 298 K. What is the rate of the reaction when
      \[ [\text{NO}_2] = 1.8 \times 10^{-8} \text{ M} \text{ and } [\text{O}_3] = 1.4 \times 10^{-7} \text{ M} \text{?} \]
   c. What is the rate of formation of NO\(_3\) under these conditions?
   d. What happens to the rate of the reaction if the concentration of O\(_2\)(g) is doubled?

13.56. Sources of Nitric Acid in the Atmosphere The reaction between N\(_2\)O\(_3\) and water is a source of nitric acid in the atmosphere:
   \[ \text{N}_2\text{O}_3(g) + \text{H}_2\text{O}(g) \rightarrow 2 \text{HNO}_3(g) \]
   a. The reaction is first order in each reactant. Write the rate law for the reaction.
   b. When [N\(_2\)O\(_3\)] is 0.132 mM and [H\(_2\)O] is 230 mM, the rate of the reaction is \(4.55 \times 10^{-4}\) mM/min\(^{-1}\). What is the rate constant for the reaction?

13.57. Each of the following reactions is first order in the reactants and second order overall. Which reaction is fastest if the initial concentrations of the reactants are the same? All reactions are at 298 K.
   a. ClO\(_2\)(g) + O\(_3\)(g) → ClO\(_3\)(g) + O\(_2\)(g)  \( k = 3.0 \times 10^{-19}\) cm\(^3\)/(molecule ∙ s)
   b. ClO\(_2\)(g) + NO\(_2\)(g) → NO\(_3\)(g) + ClO(g)  \( k = 3.4 \times 10^{-13}\) cm\(^3\)/(molecule ∙ s)
   c. ClO\(_3\)(g) + NO\(_2\)(g) → Cl(g) + NO\(_3\)(g)  \( k = 1.7 \times 10^{-11}\) cm\(^3\)/(molecule ∙ s)
   d. ClO\(_2\)(g) + O\(_2\)(g) → ClO\(_3\)(g) + O\(_2\)(g)  \( k = 1.5 \times 10^{-17}\) cm\(^3\)/(molecule ∙ s)

13.58. Two reactions in which there is a single reactant have nearly the same magnitude rate constant. One is first order; the other is second order.
   a. If the initial concentrations of the reactants are both 1.0 mM, which reaction will proceed at the higher rate?
b. If the initial concentrations of the reactants are both 2.0 M, which reaction will proceed at the higher rate?

13.59. In the presence of water, the species NO and NO$_2$ react to form nitrous acid (HNO$_2$) by the following reaction:

$$\text{NO}(g) + \text{NO}_2(g) + \text{H}_2\text{O}(l) \rightarrow 2 \text{HNO}_2(aq)$$

When the concentration of NO or NO$_2$ is doubled, the initial rate of reaction doubles. If the rate of the reaction does not depend on [H$_2$O], what is the rate law for this reaction?

13.60. Hydroperoxyl Radicals in the Atmosphere During a smog event, trace amounts of many highly reactive substances are present in the atmosphere. One of these is the hydroperoxyl radical, HO$_2$, which reacts with sulfur trioxide, SO$_3$. The rate constant for the reaction

$$2 \text{HO}_2(g) + \text{SO}_3(g) \rightarrow \text{H}_2\text{SO}_3(g) + 2 \text{O}_2(g)$$

at 298 K is $2.6 \times 10^{11}$ M$^{-1}$ s$^{-1}$. The initial rate of the reaction doubles when the concentration of SO$_3$ or HO$_2$ is doubled. What is the rate law for the reaction?

13.61. Disinfecting Municipal Water Supplies Chlorine dioxide (ClO$_2$) is a disinfectant used in municipal water-treatment plants (Figure P13.61). It dissolves in basic solution, producing ClO$_3^-$ and ClO$_2^-$:  

$$2 \text{ClO}_2(g) + 2 \text{OH}^-(aq) \rightarrow \text{ClO}_3^-(aq) + \text{ClO}_2^-(aq) + \text{H}_2\text{O}(l)$$

The following kinetic data were obtained at 298 K for the reaction:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[ClO$_2$]$_0$ (M)</th>
<th>[OH$^-$]$_0$ (M)</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.060</td>
<td>0.030</td>
<td>0.0248</td>
</tr>
<tr>
<td>2</td>
<td>0.020</td>
<td>0.030</td>
<td>0.00827</td>
</tr>
<tr>
<td>3</td>
<td>0.020</td>
<td>0.090</td>
<td>0.0247</td>
</tr>
</tbody>
</table>

Determine the rate law and the rate constant for this reaction at 298 K.

13.62. The following kinetic data were collected at 298 K for the reaction of ozone with nitrite ion, producing nitrate and oxygen:

$$\text{NO}_2^-(aq) + \text{O}_3(g) \rightarrow \text{NO}_3^-(aq) + \text{O}_2(g)$$

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[NO$_2^-$]$_0$ (M)</th>
<th>[O$_3$]$_0$ (M)</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0100</td>
<td>0.0050</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>0.0150</td>
<td>0.0050</td>
<td>37.5</td>
</tr>
<tr>
<td>3</td>
<td>0.0200</td>
<td>0.0050</td>
<td>50.0</td>
</tr>
<tr>
<td>4</td>
<td>0.0200</td>
<td>0.0200</td>
<td>200.0</td>
</tr>
</tbody>
</table>
13.63. Hydrogen gas reduces NO to N\textsubscript{2} in the following reaction:
\[ 2 \text{H}_2(\text{g}) + 2 \text{NO}(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g}) \]

The initial reaction rates of four mixtures of H\textsubscript{2} and NO were measured at 900°C with the following results:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[H\textsubscript{2}\textsubscript{0}] (M)</th>
<th>[NO\textsubscript{0}] (M)</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.212</td>
<td>0.136</td>
<td>0.0248</td>
</tr>
<tr>
<td>2</td>
<td>0.212</td>
<td>0.272</td>
<td>0.0991</td>
</tr>
<tr>
<td>3</td>
<td>0.424</td>
<td>0.544</td>
<td>0.793</td>
</tr>
<tr>
<td>4</td>
<td>0.848</td>
<td>0.544</td>
<td>1.59</td>
</tr>
</tbody>
</table>

Determine the rate law and the rate constant for the reaction at 900°C.

13.64. The rate of the reaction
\[ \text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g}) \]
was determined in three experiments at 225°C. The results are given in the following table:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[NO\textsubscript{2}\textsubscript{0}] (M)</th>
<th>[CO\textsubscript{0}] (M)</th>
<th>Initial Rate $\Delta[\text{NO}_2]/\Delta t$ (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.263</td>
<td>0.826</td>
<td>$1.44 \times 10^{-5}$</td>
</tr>
<tr>
<td>2</td>
<td>0.263</td>
<td>0.413</td>
<td>$1.44 \times 10^{-5}$</td>
</tr>
<tr>
<td>3</td>
<td>0.526</td>
<td>0.413</td>
<td>$5.76 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

a. Determine the rate law for the reaction.
b. Calculate the value of the rate constant at 225°C.
c. Calculate the rate of appearance of CO\textsubscript{2} when [NO\textsubscript{2}] = [CO] = 0.500 \text{ M}.

13.65. Nitrogen trioxide decomposes to NO\textsubscript{2} and O\textsubscript{2} in the following reaction:
\[ 2 \text{NO}_3(\text{g}) \rightarrow 2 \text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \]

The following data were collected at 298 K:

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>[NO\textsubscript{3}] (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$1.470 \times 10^{-3}$</td>
</tr>
<tr>
<td>10</td>
<td>$1.463 \times 10^{-3}$</td>
</tr>
<tr>
<td>100</td>
<td>$1.404 \times 10^{-3}$</td>
</tr>
<tr>
<td>200</td>
<td>$1.344 \times 10^{-3}$</td>
</tr>
<tr>
<td>300</td>
<td>$1.288 \times 10^{-3}$</td>
</tr>
<tr>
<td>400</td>
<td>$1.237 \times 10^{-3}$</td>
</tr>
<tr>
<td>500</td>
<td>$1.190 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Calculate the value of the second-order rate constant.
at 298 K.

13.66. Two structural isomers of ClO₂ are shown in Figure P13.66.

\[
\text{Cl} - \text{O} - \text{O} \quad \text{Cl} - \text{O} - \text{C}
\]

FIGURE P13.66

The isomer with the Cl—O—O skeletal arrangement is unstable and rapidly decomposes according to the reaction \(2 \text{ClOO}(g) \rightarrow \text{Cl}_2(g) + 2 \text{O}_2(g)\). The following data were collected for the decomposition of ClOO at 298 K:

<table>
<thead>
<tr>
<th>Time (µs)</th>
<th>[ClOO] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.76 × 10⁻⁶</td>
</tr>
<tr>
<td>0.7</td>
<td>2.36 × 10⁻⁷</td>
</tr>
<tr>
<td>1.3</td>
<td>3.56 × 10⁻⁸</td>
</tr>
<tr>
<td>2.1</td>
<td>3.23 × 10⁻⁹</td>
</tr>
<tr>
<td>2.8</td>
<td>3.96 × 10⁻¹⁰</td>
</tr>
</tbody>
</table>

Determine the rate law and the rate constant for the reaction at 298 K.

13.67. At high temperatures, ammonia spontaneously decomposes into \(\text{N}_2\) and \(\text{H}_2\). The following data were collected at one such temperature:

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[NH₃] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.56 × 10⁻²</td>
</tr>
<tr>
<td>12</td>
<td>2.47 × 10⁻²</td>
</tr>
<tr>
<td>56</td>
<td>2.16 × 10⁻²</td>
</tr>
<tr>
<td>224</td>
<td>1.31 × 10⁻²</td>
</tr>
<tr>
<td>532</td>
<td>5.19 × 10⁻³</td>
</tr>
<tr>
<td>746</td>
<td>2.73 × 10⁻³</td>
</tr>
</tbody>
</table>

Determine the rate law for the decomposition of ammonia and the value of the rate constant at the temperature of the experiment.

13.68. Atmospheric Chemistry of Hydroperoxyl Radicals

Atmospheric chemistry involves highly reactive, odd-electron molecules such as the hydroperoxyl radical \(\text{HO}_2\), which decomposes into \(\text{H}_2\text{O}_2\) and \(\text{O}_2\). Determine the rate law for the reaction and the value of the rate constant at 298 K by using the following data obtained at 298 K:

<table>
<thead>
<tr>
<th>Time (µs)</th>
<th>[HO₂] (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.5</td>
</tr>
<tr>
<td>0.6</td>
<td>5.1</td>
</tr>
<tr>
<td>1.0</td>
<td>3.6</td>
</tr>
<tr>
<td>1.4</td>
<td>2.6</td>
</tr>
<tr>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>2.4</td>
<td>1.1</td>
</tr>
</tbody>
</table>

13.69. In addition to being studied in the gas phase, the decomposition of \(\text{N}_2\text{O}_5\) has been evaluated in
is a first-order reaction and \( k = 6.32 \times 10^{-4} \text{ s}^{-1} \). How much \( \text{N}_2\text{O}_5 \) remains in solution after 1 hr if the initial concentration of \( \text{N}_2\text{O}_5 \) was 0.50 mol/L? What percent of the \( \text{N}_2\text{O}_5 \) has reacted at that point?

13.70. Because the units of concentration in the term \( \ln[X]/[X]_0 \) cancel out in the integrated rate law for first-order reactions (Equation 13.17), molar concentration can be replaced by any concentration term that is proportional to mol/L. With gases, for example, partial pressures may be used. The decomposition of phosphine gas \((\text{PH}_3)\) at 600°C is first order in \( \text{PH}_3 \), and \( k = 0.023 \text{ s}^{-1} \).

\[
4 \text{PH}_3(g) \rightarrow \text{P}_4(g) + 6 \text{H}_2(g)
\]

If the initial partial pressure of \( \text{PH}_3 \) is 375 torr, what percent of \( \text{PH}_3 \) reacts in 1 min?

13.71. Laughing Gas Nitrous oxide \((\text{N}_2\text{O})\) is used as an anesthetic (laughing gas) and in aerosol cans to produce whipped cream. It is a potent greenhouse gas and decomposes slowly to \( \text{N}_2 \) and \( \text{O}_2 \):  

\[
2 \text{N}_2\text{O}(g) \rightarrow 2 \text{N}_2(g) + \text{O}_2(g)
\]

a. If the plot of \( \ln[\text{N}_2\text{O}] \) as a function of time is linear, what is the rate law for the reaction?

b. How many half-lives will it take for the concentration of \( \text{N}_2\text{O} \) to reach 6.25% of its original concentration?

[Hint: The amount of reactant remaining after time \( t \) \((A_t)\) is related to the amount initially present \((A_0)\) by the equation \( A_t/A_0 = (0.5)^n \), where \( n \) is the number of half-lives in time \( t \).]

13.72. The unsaturated hydrocarbon butadiene \(( \text{C}_4\text{H}_6)\) dimerizes to 4-vinylcyclohexene \(( \text{C}_8\text{H}_{12})\). When data collected in studies of the kinetics of this reaction were plotted against reaction time, plots of \([\text{C}_4\text{H}_6]\) or \(\ln[\text{C}_4\text{H}_6]\) produced curved lines, but the plot of \(1/[\text{C}_4\text{H}_6]\) was linear.

a. What is the rate law for the reaction?

b. How many half-lives will it take for the \([\text{C}_4\text{H}_6]\) to decrease to 3.1% of its original concentration?

13.73. Tracing Phosphorus in Organisms Radioactive isotopes such as \(^{32}\text{P}\) are used to follow biological processes. The following radioactivity data (in relative radioactivity values) were collected for a sample containing \(^{32}\text{P}\):

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Relative Radioactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.00</td>
</tr>
<tr>
<td>1</td>
<td>9.53</td>
</tr>
<tr>
<td>2</td>
<td>9.08</td>
</tr>
<tr>
<td>5</td>
<td>7.85</td>
</tr>
<tr>
<td>10</td>
<td>6.16</td>
</tr>
<tr>
<td>20</td>
<td>3.79</td>
</tr>
</tbody>
</table>

a. Write the rate law for the decay of \(^{32}\text{P}\).

b. Determine the value of the rate constant.

c. Determine the half-life of \(^{32}\text{P}\).

13.74. Nitrous acid slowly decomposes to \( \text{NO}, \text{NO}_2 \), and water in the following second-order reaction:

\[
2 \text{HNO}_2(aq) \rightarrow \text{NO(g)} + \text{NO}_2(g) + \text{H}_2\text{O(l)}
\]

a. Use the data below to determine the rate constant for this reaction at 298 K:

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>[HNO2] (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1560</td>
</tr>
<tr>
<td>1000</td>
<td>0.1466</td>
</tr>
<tr>
<td>1500</td>
<td>0.1424</td>
</tr>
<tr>
<td>2000</td>
<td>0.1383</td>
</tr>
</tbody>
</table>
b. Determine the half-life for the decomposition of HNO$_2$.

13.75. The dimerization of ClO.

2 ClO(g) → Cl$_2$O$_2$(g)

is second order in ClO. Use the following data to determine the value of $k$ at 298 K.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[ClO] (molecules/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.60 × 10$^{11}$</td>
</tr>
<tr>
<td>1</td>
<td>1.08 × 10$^{11}$</td>
</tr>
<tr>
<td>2</td>
<td>6.83 × 10$^{10}$</td>
</tr>
<tr>
<td>3</td>
<td>4.99 × 10$^{10}$</td>
</tr>
<tr>
<td>4</td>
<td>3.93 × 10$^{10}$</td>
</tr>
</tbody>
</table>

Determine the half-life for the dimerization of ClO.

13.76. Kinetic data for the reaction Cl$_2$O$_2$(g) → 2 ClO(g) are summarized in the following table. Determine the value of the rate constant.

<table>
<thead>
<tr>
<th>Time (µs)</th>
<th>[Cl$_2$O$_2$] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.60 × 10$^{-8}$</td>
</tr>
<tr>
<td>172</td>
<td>5.68 × 10$^{-8}$</td>
</tr>
<tr>
<td>345</td>
<td>4.89 × 10$^{-8}$</td>
</tr>
<tr>
<td>517</td>
<td>4.21 × 10$^{-8}$</td>
</tr>
<tr>
<td>690</td>
<td>3.62 × 10$^{-8}$</td>
</tr>
<tr>
<td>862</td>
<td>3.12 × 10$^{-8}$</td>
</tr>
</tbody>
</table>

Determine the half-life for the decomposition of Cl$_2$O$_2$.

13.77. Kinetics of Sucrose Hydrolysis The metabolism of table sugar (sucrose, C$_{12}$H$_{22}$O$_{11}$) begins with the hydrolysis of the disaccharide to glucose and fructose (both C$_6$H$_{12}$O$_6$):

C$_{12}$H$_{22}$O$_{11}$(aq) + H$_2$O(l) → 2 C$_6$H$_{12}$O$_6$(aq)

The kinetics of the reaction were studied at 24°C in a reaction system with a large excess of water, so the reaction was pseudo-first-order in sucrose. Determine the rate law and the pseudo-first-order rate constant for the reaction from the following data:

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[C$<em>6$H$</em>{12}$O$_{11}$] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.562</td>
</tr>
<tr>
<td>612</td>
<td>0.541</td>
</tr>
<tr>
<td>1600</td>
<td>0.509</td>
</tr>
<tr>
<td>2420</td>
<td>0.484</td>
</tr>
<tr>
<td>3160</td>
<td>0.462</td>
</tr>
</tbody>
</table>
13.78. Hydroperoxyl radicals react rapidly with ozone to produce oxygen and OH radicals:

\[
\text{HO}_2(g) + \text{O}_3(g) \rightarrow \text{OH}(g) + 2 \text{O}_2(g)
\]

The rate of this reaction was studied in the presence of a large excess of ozone. Determine the pseudo-first-order rate constant and the second-order rate constant for the reaction from the following data:

<table>
<thead>
<tr>
<th>Time (ms)</th>
<th>[HO(_2)] (M)</th>
<th>[O(_3)] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.2 × 10(^{-6})</td>
<td>1.0 × 10(^{-3})</td>
</tr>
<tr>
<td>10</td>
<td>2.9 × 10(^{-6})</td>
<td>1.0 × 10(^{-3})</td>
</tr>
<tr>
<td>20</td>
<td>2.6 × 10(^{-6})</td>
<td>1.0 × 10(^{-3})</td>
</tr>
<tr>
<td>30</td>
<td>2.4 × 10(^{-6})</td>
<td>1.0 × 10(^{-3})</td>
</tr>
<tr>
<td>80</td>
<td>1.4 × 10(^{-6})</td>
<td>1.0 × 10(^{-3})</td>
</tr>
</tbody>
</table>

### Reaction Rates, Temperature, and the Arrhenius Equation

**CONCEPT REVIEW**

13.79. How does the size of a reaction’s activation energy influence the rate of a reaction?

13.80. Do all spontaneous reactions happen instantaneously at room temperature?

13.81. Under what circumstances is the activation energy of a reaction proceeding in the forward direction less than the activation energy of it happening in reverse?

13.82. Under what circumstances is the activation energy of a reaction proceeding in the forward direction greater than the activation energy of it happening in reverse?

*13.83. The order of a reaction is independent of temperature, but the value of the rate constant varies with temperature. Why?

13.84. Does reducing the activation energy of a reaction by \(1/2\) increase its rate constant by a factor of 2?

*13.85. Two first-order reactions have activation energies of 15 and 150 kJ/mol. Which reaction will show the larger increase in rate as temperature is increased?

13.86. According to the Arrhenius equation, does the activation energy of a chemical reaction depend on temperature? Explain your answer.

**PROBLEMS**

13.87. The rate constant for the reaction of ozone with oxygen atoms was determined at four temperatures. Calculate the activation energy and frequency factor \(A\) for the reaction

\[
\text{O}(g) + \text{O}_3(g) \rightarrow 2 \text{O}_2(g)
\]

given the following data:

<table>
<thead>
<tr>
<th>(T) (K)</th>
<th>(k) [cm(^3)/molecule (\cdot) s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>2.64 \times 10^{-4}</td>
</tr>
<tr>
<td>275</td>
<td>5.58 \times 10^{-4}</td>
</tr>
<tr>
<td>300</td>
<td>1.04 \times 10^{-3}</td>
</tr>
<tr>
<td>325</td>
<td>1.77 \times 10^{-3}</td>
</tr>
</tbody>
</table>

13.88. The rate constant for the reaction

\[
\text{NO}_2(g) + \text{O}_3(g) \rightarrow \text{NO}_3(g) + \text{O}_2(g)
\]

was determined over a temperature range of 40 K, with the following results:
### 13.89. Activation Energy of Smog-Forming Reactions

The initial step in the formation of smog is the reaction between nitrogen and oxygen. The activation energy of the reaction can be determined from the temperature dependence of the rate constants. At the temperatures indicated, values of the rate constant of the reaction

\[ \text{N}_2(g) + \text{O}_2(g) \rightarrow 2 \text{NO}(g) \]

are as follows:

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( k ) (M(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>318</td>
</tr>
<tr>
<td>2100</td>
<td>782</td>
</tr>
<tr>
<td>2200</td>
<td>1770</td>
</tr>
<tr>
<td>2300</td>
<td>3733</td>
</tr>
<tr>
<td>2400</td>
<td>7396</td>
</tr>
</tbody>
</table>

a. Calculate the activation energy of the reaction.
b. Calculate the frequency factor for the reaction.
c. Calculate the value of the rate constant at ambient temperature, \( T = 300 \) K.

### 13.90. Activation Energy of Stratospheric Ozone Destruction Reactions

The kinetics of the reaction between chlorine dioxide and ozone are relevant to the study of atmospheric ozone destruction. The activation energy of the reaction can be determined from the temperature dependence of the rate constant. The value of the rate constant for the reaction between chlorine dioxide and ozone was measured at four temperatures between 193 and 208 K. The results were as follows:

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( k ) (M(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>658</td>
<td>2.14 \times 10^3</td>
</tr>
<tr>
<td>673</td>
<td>3.23 \times 10^3</td>
</tr>
<tr>
<td>688</td>
<td>4.81 \times 10^3</td>
</tr>
<tr>
<td>703</td>
<td>7.03 \times 10^3</td>
</tr>
</tbody>
</table>

a. Determine the activation energy of the decomposition reaction.
b. Calculate the value of the rate constant at 300 K.
Calculate the values of the activation energy and the frequency factor for the reaction.

13.92. Chlorine atoms react with methane, forming HCl and CH₃. The rate constant for the reaction is $6.0 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$ at 298 K. When the experiment was repeated at three other temperatures, the following data were collected:

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$k$ (M$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>$6.5 \times 10^7$</td>
</tr>
<tr>
<td>308</td>
<td>$7.0 \times 10^7$</td>
</tr>
<tr>
<td>313</td>
<td>$7.5 \times 10^7$</td>
</tr>
</tbody>
</table>

Calculate the values of the activation energy and the frequency factor for the reaction.

13.93. A rule of thumb states that a reaction rate doubles for every 10°C rise in temperature. This is not always the case, but it is a convenient concept to apply when making estimations. Azomethane (CH$_3$NNCH$_3$) is a heat-sensitive explosive that decomposes to yield nitrogen gas and methyl radicals:

$$\text{CH}_3\text{NNCH}_3(g) \rightarrow \text{N}_2(g) + 2 \text{CH}_3(g)$$

At 600°C, the reaction has an activation energy of $2.14 \times 10^4 \text{ J/mol}$ and $k = 2.00 \times 10^8 \text{ s}^{-1}$. Does the rule of thumb hold for this reaction?

13.94. The compound 1,1-difluoroethane decomposes at elevated temperatures to give fluoroethylene and hydrogen fluoride:

$$\text{CH}_3\text{CHF}_2(g) \rightarrow \text{CH}_2\text{CHF}(g) + \text{HF}(g)$$

At 460°C, $k = 5.8 \times 10^{-6} \text{ s}^{-1}$ and $E_a = 265 \text{ kJ/mol}$. To what temperature would you have to raise the reaction to make it go four times as fast?

**Reaction Mechanisms**

**CONCEPT REVIEW**

13.95. The rate law for the reaction between NO and H$_2$ is second order in NO and third order overall, whereas the reaction of NO with Cl$_2$ is first order in each reactant and second order overall. Do these reactions proceed by similar mechanisms?

13.96. The rate law for the reaction of NO with Cl$_2$ (Rate = $k[\text{NO}][\text{Cl}_2]$) is the same as that for the reaction of NO$_2$ with F$_2$ (Rate = $k[\text{NO}_2][\text{F}_2]$). Is it possible that these reactions have similar mechanisms?

*13.97. Under what reaction conditions does a bimolecular reaction obey pseudo-first-order reaction kinetics?

*13.98. If a reaction is zero order in a reactant, does that mean the reactant is never involved in collisions with other reactants? Explain your answer.

**PROBLEMS**

13.99. The hypothetical reaction A $\rightarrow$ B has an activation energy of 50.0 kJ/mol. Draw a reaction profile for each of the following mechanisms:
   a. A single elementary step.
   b. A two-step reaction in which the activation energy of the second step is 15 kJ/mol.
   c. A two-step reaction in which the activation energy of the second step is the rate-determining barrier.

13.100. For the spontaneous reaction A + B $\rightarrow$ C $\rightarrow$ D + E, draw three reaction profiles, one for each of the following mechanisms:
   a. C is an activated complex.
13.101. Write the rate laws for the following elementary steps and identify them as uni-, bi-, or termolecular steps:
   a. \( \text{SO}_2\text{Cl}_2(g) \rightarrow \text{SO}_2(g) + \text{Cl}_2(g) \)
   b. \( \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g) \)
   c. \( 2 \text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{NO}(g) \)

13.102. Write the rate laws for the following elementary steps and identify them as uni-, bi-, or termolecular steps:
   a. \( \text{Cl}(g) + \text{O}_3(g) \rightarrow \text{ClO}(g) + \text{O}_2(g) \)
   b. \( 2 \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g) \)

13.103. Write the overall reaction that consists of the following elementary steps:

\[
\text{N}_2\text{O}_3(g) \rightarrow \text{NO}_3(g) + \text{NO}_2(g)
\]

\[
\text{NO}_3(g) \rightarrow \text{NO}_2(g) + \text{O}(g)
\]

\[
2 \text{O}(g) \rightarrow \text{O}_2(g)
\]

13.104. What overall reaction consists of the following elementary steps?

\[
\text{ClO}^{-}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{HClO}(aq) + \text{OH}^{-}(aq)
\]

\[
\Gamma^{-}(aq) + \text{HClO}(aq) \rightarrow \text{HIO}(aq) + \text{Cl}^{-}(aq)
\]

\[
\text{OH}^{-}(aq) + \text{HIO}(aq) \rightarrow \text{H}_2\text{O}(l) + \text{IO}^{-}(aq)
\]

*13.105. In the following mechanism for NO formation, oxygen atoms are produced by breaking O-O bonds at high temperature in a fast reversible reaction. If \( \Delta[\text{NO}]/\Delta t = k[\text{N}_2][\text{O}_2]^{1/2} \), which step in the mechanism is the rate-determining step?

\[
\begin{align*}
    (1) & \quad \text{O}_2(g) \rightarrow 2 \text{O}(g) \\
    (2) & \quad \text{O}(g) + \text{N}_2(g) \rightarrow \text{NO}(g) + \text{N}(g) \\
    (3) & \quad \text{N}(g) + \text{O}(g) \rightarrow \text{NO}(g)
\end{align*}
\]

Overall:

\[ \text{N}_2(g) + \text{O}_2(g) \rightarrow 2 \text{NO}(g) \]

13.106. A proposed mechanism for the decomposition of hydrogen peroxide consists of three elementary steps:

\[
\text{H}_2\text{O}_2(g) \rightarrow 2 \text{OH}(g)
\]

\[
\text{H}_2\text{O}_2(g) + \text{OH}(g) \rightarrow \text{H}_2\text{O}(g) + \text{HO}_2(g)
\]

\[
\text{HO}_2(g) + \text{OH}(g) \rightarrow \text{H}_2\text{O}(g) + \text{O}_2(g)
\]

If the rate law for the reaction is first order in \( \text{H}_2\text{O}_2 \), which step in the mechanism is the rate-determining step?

13.107. At a given temperature, the rate of the reaction between NO and Cl\(_2\) is proportional to the product of the concentrations of the two gases: \( [\text{NO}][\text{Cl}_2] \). The following two-step mechanism has been proposed for the reaction:

\[
(1) \quad \text{NO}(g) + \text{Cl}_2(g) \rightarrow \text{NOCl}_2(g)
\]

\[
(2) \quad \text{NOCl}_2(g) + \text{NO}(g) \rightarrow 2 \text{NOCl}(g)
\]

Overall:

\[
2 \text{NO}(g) + \text{Cl}_2(g) \rightarrow 2 \text{NOCl}(g)
\]

Which step must be the rate-determining step if this mechanism is correct?

13.108. Mechanism of Ozone Destruction. Ozone decomposes thermally to oxygen in the following reaction:

\[ 2 \text{O}_3(g) \rightarrow 3 \text{O}_2(g) \]

The following mechanism has been proposed:

\[ \text{O}_3(g) \rightarrow \text{O}(g) + \text{O}_2(g) \]
The reaction is second order in ozone. What properties of the two elementary steps (specifically, relative rate and reversibility) are consistent with this mechanism?

13.109. **Mechanism of NO₂ Destruction**

The rate laws for the thermal and photochemical decomposition of NO₂ are different. Which of the following mechanisms are possible for the thermal decomposition of NO₂, and which are possible for the photochemical decomposition of NO₂? For thermal decomposition, Rate = \( k[NO₂]^2 \), and for photochemical decomposition, Rate = \( k[NO₂] \).

a. \( NO₂(g) \xrightarrow{\text{slow}} NO(g) + O(g) \)
   \( O(g) + NO₂(g) \xrightarrow{\text{fast}} NO(g) + O₂(g) \)

b. \( NO₂(g) + NO₂(g) \xrightarrow{\text{fast}} N₂O₄(g) \)
   \( N₂O₄(g) \xrightarrow{\text{slow}} NO(g) + NO₃(g) \)
   \( NO₃(g) \xrightarrow{\text{fast}} NO(g) + O₂(g) \)

c. \( NO₂(g) + NO₂(g) \xrightarrow{\text{slow}} NO(g) + NO₃(g) \)
   \( NO₃(g) \xrightarrow{\text{fast}} NO(g) + O₂(g) \)

13.110. The rate laws for the thermal and photochemical decomposition of NO₂ are different. Which of the following mechanisms are possible for the thermal decomposition of NO₂, and which are possible for the photochemical decomposition of NO₂? For thermal decomposition, Rate = \( k[NO₂]^2 \), and for photochemical decomposition, Rate = \( k[NO₂] \).

a. \( NO₂(g) + NO₂(g) \xrightarrow{\text{slow}} N₂O₄(g) \)
   \( N₂O₄(g) \xrightarrow{\text{fast}} N₂O₃(g) + O(g) \)
   \( N₂O₃(g) + O(g) \xrightarrow{\text{fast}} N₂O₄(g) + O₂(g) \)
   \( N₂O₄(g) \xrightarrow{\text{fast}} 2 NO(g) \)

b. \( NO₂(g) + NO₂(g) \xrightarrow{\text{slow}} NO(g) + NO₃(g) \)
   \( NO₃(g) \xrightarrow{\text{fast}} NO(g) + O₂(g) \)

c. \( NO₂(g) \xrightarrow{\text{slow}} N(g) + O₂(g) \)
   \( N(g) + NO₂(g) \xrightarrow{\text{fast}} N₂O₄(g) \)
   \( N₂O₄(g) \xrightarrow{\text{slow}} 2 NO(g) \)

**Catalysts**

**CONCEPT REVIEW**

13.111. Does a catalyst affect both the rate and the rate constant of a reaction?

13.112. Is the rate law for a catalyzed reaction the same as that for the uncatalyzed reaction?

13.113. Does a substance that increases the rate of a reaction also increase the rate of the reverse reaction?

13.114. The rate of the reaction between NO₂ and CO is independent of [CO]. Does this mean that CO is a catalyst for the reaction?

13.115. Why doesn’t the concentration of a homogeneous catalyst appear in the rate law for the reaction it catalyzes?

*13.116. The rate of a chemical reaction is too slow to measure at room temperature. We could either raise the temperature or add a catalyst. Which would be a better solution for making an accurate determination of the rate constant?
PROBLEMS

13.117. Is NO a catalyst for the decomposition of N₂O in the following two-step reaction mechanism, or is N₂O a catalyst for the conversion of NO to NO₂?

\[ \text{(1)} \quad \text{NO}(g) + \text{N}_2\text{O}(g) \rightarrow \text{N}_2(g) + \text{NO}_2(g) \]
\[ \text{(2)} \quad 2 \text{NO}_2(g) \rightarrow 2 \text{NO}(g) + \text{O}_2(g) \]

13.118. NO as a Catalyst for Ozone Destruction Explain why NO is a catalyst in the following two-step process that results in the depletion of ozone in the stratosphere:

\[ \text{(1)} \quad \text{NO}(g) + \text{O}_3(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g) \]
\[ \text{(2)} \quad \text{O}(g) + \text{NO}_2(g) \rightarrow \text{NO}(g) + \text{O}_2(g) \]
Overall: \quad \text{O}(g) + \text{O}_3(g) \rightarrow 2 \text{O}_2(g) \]

13.119. On the basis of the frequency factors and activation energy values of the following two reactions, determine which one will have the larger rate constant at room temperature (298 K).

\[ \text{O}_3(g) + \text{O}(g) \rightarrow \text{O}_2(g) + \text{O}_2(g) \]
\[ A = 8.0 \times 10^{-12} \text{ cm}^3/(\text{molecules} \cdot \text{s}) \quad E_a = 17.1 \text{ kJ/mol} \]

\[ \text{O}_3(g) + \text{Cl}(g) \rightarrow \text{ClO}(g) + \text{O}_2(g) \]
\[ A = 2.9 \times 10^{-11} \text{ cm}^3/(\text{molecules} \cdot \text{s}) \quad E_a = 2.16 \text{ kJ/mol} \]

13.120. On the basis of the frequency factors and activation energy values of the following two reactions, determine which one will have the larger rate constant at room temperature (298 K).

\[ \text{O}_3(g) + \text{Cl}(g) \rightarrow \text{ClO}(g) + \text{O}_2(g) \]
\[ A = 2.9 \times 10^{-11} \text{ cm}^3/(\text{molecules} \cdot \text{s}) \quad E_a = 2.16 \text{ kJ/mol} \]
\[ \text{O}_3(g) + \text{NO}(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g) \]
\[ A = 2.0 \times 10^{-12} \text{ cm}^3/(\text{molecules} \cdot \text{s}) \quad E_a = 11.6 \text{ kJ/mol} \]

Additional Problems

13.121. A student inserts a glowing wood splint into a test tube filled with O₂. The splint quickly catches on fire (Figure P13.121). Why does the splint burn so much faster in pure O₂ than in air?

![Figure P13.121](image-url)

*13.122. A backyard chef turns on the propane gas to a barbecue grill. Even though the reaction between propane and oxygen is spontaneous, the gas does not begin to burn until the chef pushes an igniter button to produce a spark. Why is the spark needed?

13.123. On average, someone who falls through the ice covering a frozen lake is less likely to experience anoxia (lack of oxygen) than someone who falls into a warm pool and is underwater for the same length of time. Why?

*13.124. Why doesn’t a quadrupling of the rate correspond to a reaction order of 4, for example, Rate \( \propto [\text{NO}]^4 \)?

13.125. If the rate of the reverse reaction is much slower than the rate of the forward reaction, does the method used to determine a rate law from initial concentrations and initial rates also work at some
other time \( t \)? What concentrations would we use in the case where we use the rate when \( t \neq 0 \)?

13.126. Identify what is wrong with the following statement: The reaction rate and the rate constant for a reaction both depend on the number of collisions and on the concentrations of the reactants.

13.127. How do we find \( k \) if we plot \( 1/[X] - 1/[X]_0 \) as a function of \( t \)?

13.128. Many reactions are first order, fewer are second order in a single reactant, and third-order reactions in a single reactant are practically nonexistent. Can you suggest why?

13.129. Why can’t an elementary step in a mechanism have a rate law that is zero order in a reactant?

13.130. During the decomposition of dinitrogen pentoxide,

\[
2 \text{N}_2\text{O}_5(g) \rightarrow 4 \text{NO}_2(g) + \text{O}_2(g)
\]

how is the rate of consumption of \( \text{N}_2\text{O}_5 \) related to the rate of formation of \( \text{NO}_2 \) and \( \text{O}_2 \)?

13.131. In the reaction between nitrogen dioxide and ozone,

\[
2 \text{NO}_2(g) + \text{O}_3(g) \rightarrow \text{N}_2\text{O}_5(g) + \text{O}_2(g)
\]

how are the rates of change in the concentrations of the reactants and products related?

13.132. Determine the order of the decomposition reaction of \( \text{N}_2\text{O}_5 \), by using the initial rate data from the following table:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>([\text{N}_2\text{O}_5]_0 ) (M)</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.050</td>
<td>1.8 \times 10^{-5}</td>
</tr>
<tr>
<td>2</td>
<td>0.100</td>
<td>3.6 \times 10^{-5}</td>
</tr>
</tbody>
</table>

13.133. At the temperature at which the experiments were carried out in the previous problem, what is the rate constant for the decomposition of \( \text{N}_2\text{O}_5 \)? Write the complete rate law for the decomposition reaction.

13.134. The table below contains kinetics data for the reaction

\[
2 \text{NO}(g) + \text{Cl}_2(g) \rightarrow 2 \text{NOCl}(g)
\]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[\text{NO}]_0 (M)</th>
<th>[\text{Cl}_2]_0 (M)</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.20</td>
<td>0.10</td>
<td>0.63</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>0.30</td>
<td>5.70</td>
</tr>
<tr>
<td>3</td>
<td>0.80</td>
<td>0.10</td>
<td>2.58</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.20</td>
<td>?</td>
</tr>
</tbody>
</table>

Predict the initial rate of reaction in experiment 4.

13.135. An important reaction in the formation of photochemical smog is the reaction between ozone and NO:

\[
\text{NO}(g) + \text{O}_3(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g)
\]

The reaction is first order in NO and \( \text{O}_3 \). The rate constant of the reaction is 80 M\(^{-1}\) s\(^{-1}\) at 25°C and 3000 M\(^{-1}\) s\(^{-1}\) at 75°C.

a. If this reaction were to occur in a single step, would the rate law be consistent with the observed order of the reaction for NO and \( \text{O}_3 \)?

b. What is the value of the activation energy of the reaction?

c. What is the rate of the reaction at 25°C when \([\text{NO}] = 3 \times 10^{-6} \) M and \([\text{O}_3] = 5 \times 10^{-9} \) M?

d. Predict the values of the rate constant at 10°C and 35°C.

13.136. Ammonia reacts with nitrous acid to form an intermediate, ammonium nitrite (\( \text{NH}_4\text{NO}_2 \)), which decomposes to \( \text{N}_2 \) and \( \text{H}_2\text{O} \):

\[
\text{NH}_3(g) + \text{HNO}_2(aq) \rightarrow \text{NH}_4\text{NO}_2(aq) \rightarrow \text{N}_2(g) + 2 \text{H}_2\text{O}(l)
\]
a. The reaction is first order in ammonia and second order in nitrous acid. What is the rate law for the reaction? What are the units on the rate constant if concentrations are expressed in molarity and time in seconds?
b. The rate law for the reaction has also been written as

\[ \text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-][\text{HNO}_3] \]

Is this expression equivalent to the one you wrote in part a?
c. With the data in Appendix 4, calculate the value of \( \Delta H_{\text{rxn}} \) of the overall reaction (\( \Delta H_{\text{HNO}_3} = -43.1 \text{ kJ/mol} \)).
d. Draw a reaction-energy profile for the process with the assumption that \( E_a \) of the first step is lower than \( E_a \) of the second step.

*13.137. When ionic compounds such as NaCl dissolve in water, the sodium ions are surrounded by six water molecules. The bound water molecules exchange with those in bulk solution as described by the reaction involving \(^{18}\text{O}-\text{enriched water}:

\[ \text{Na(H}_2\text{O)}_6^{+}(aq) + \text{H}_2^{18}\text{O}(l) \rightarrow \text{Na(H}_2\text{O)}_6(\text{H}_2^{18}\text{O})(aq) + \text{H}_2\text{O}(l) \]

a. The following reaction mechanism has been proposed:

1. \( \text{Na(H}_2\text{O)}_6^{+}(aq) \rightarrow \text{Na(H}_2\text{O)}_6^{+}(aq) + \text{H}_2\text{O}(l) \)
2. \( \text{Na(H}_2\text{O)}_6^{+}(aq) + \text{H}_2^{18}\text{O}(l) \rightarrow \text{Na(H}_2\text{O)}_6(\text{H}_2^{18}\text{O})(aq) \)

What is the rate law if the first step is the rate-determining step?
b. If you were to sketch a reaction-energy profile, which would you draw with the higher energy, the reactants or the products?

13.138. Lachrymators in Smog The combination of ozone, volatile hydrocarbons, nitrogen oxide, and sunlight in urban environments produces peroxyacetyl nitrate (PAN), a potent lachrymator (a substance that causes eyes to tear). PAN decomposes to acetyl radicals and nitrogen dioxide in a process that is second order in PAN, as shown in Figure P13.138:

\[ \text{PAN} \rightarrow \text{CH}_3\text{CO}^- + \text{NO}_2 \]

a. The half-life of the reaction, at 23°C and \( P_{\text{CH}_3\text{CO}_2\text{NO}_2} = 10.5 \text{ torr} \), is 100 hr. Calculate the rate constant for the reaction.
b. Determine the rate of the reaction at 23°C and \( P_{\text{CH}_3\text{CO}_2\text{NO}_2} = 10.5 \text{ torr} \).
c. Draw a graph showing \( P_{\text{PAN}} \) as a function of time from 0 to 200 hr starting with \( P_{\text{CH}_3\text{CO}_2\text{NO}_2} = 10.5 \text{ torr} \).

13.139. Nitric Oxide in the Human Body Nitric oxide (NO) is a gaseous free radical that plays many biological roles including regulating neurotransmission and the human immune system. One of its many reactions involves the peroxynitrite ion (\( \text{ONOO}^- \)):

\[ \text{NO}(g) + \text{ONOO}^- (aq) \rightarrow \text{NO}_2(g) + \text{NO}_2^- (aq) \]

a. Use the following data to determine the rate law and rate constant of the reaction at the experimental temperature at which these data were generated.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[NO]_0 (M)</th>
<th>[ONOO^-]_0 (M)</th>
<th>Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.25 \times 10^{-4}</td>
<td>1.25 \times 10^{-4}</td>
<td>2.03 \times 10^{-11}</td>
</tr>
<tr>
<td>2</td>
<td>1.25 \times 10^{-4}</td>
<td>0.625 \times 10^{-4}</td>
<td>1.02 \times 10^{-11}</td>
</tr>
<tr>
<td>3</td>
<td>0.625 \times 10^{-4}</td>
<td>2.50 \times 10^{-4}</td>
<td>2.03 \times 10^{-11}</td>
</tr>
<tr>
<td>4</td>
<td>0.625 \times 10^{-4}</td>
<td>3.75 \times 10^{-4}</td>
<td>3.05 \times 10^{-11}</td>
</tr>
</tbody>
</table>

b. Draw the Lewis structure of peroxynitrite ion (including all resonance forms) and assign formal charges. Note which form is preferred.
c. Use the average bond energies in Appendix Table A4.1 to estimate the value of \( \Delta H_{\text{rxn}} \) using the preferred structure from part b.

13.140. Kinetics of Protein Chemistry In the presence of O2, NO reacts with sulfur-containing proteins to form S-nitrosothiolis, such as C6H5SNO. This compound decomposes to form a disulfide and NO:
2 C₆H₁₃SNO(aq) → 2 NO(g) + C₁₂H₂₆S₂(aq)

The following data were collected for the decomposition reaction at 69°C.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>[C₆H₁₃SNO] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.05 × 10⁻³</td>
</tr>
<tr>
<td>10</td>
<td>9.84 × 10⁻⁴</td>
</tr>
<tr>
<td>20</td>
<td>9.22 × 10⁻⁴</td>
</tr>
<tr>
<td>30</td>
<td>8.64 × 10⁻⁴</td>
</tr>
<tr>
<td>60</td>
<td>7.11 × 10⁻⁴</td>
</tr>
</tbody>
</table>

Calculate the value of the first-order rate constant for the reaction.

13.141. Solutions of nitrous acid, HNO₂, in ¹⁸O-labeled water undergo isotope exchange:

\[ \text{HNO}_2(\text{aq}) + \text{H}_2^{18}\text{O}(\ell) \rightarrow \text{HN}^{18}\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\ell) \]

a. Use the following data at 24°C to determine the dependence of the reaction rate on the concentration of HNO₂.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>[HN¹⁸O₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.4 × 10⁻²</td>
</tr>
<tr>
<td>20</td>
<td>1.5 × 10⁻³</td>
</tr>
<tr>
<td>40</td>
<td>7.7 × 10⁻⁴</td>
</tr>
<tr>
<td>60</td>
<td>5.2 × 10⁻⁴</td>
</tr>
</tbody>
</table>

b. Does the reaction rate depend on the concentration of H₂¹⁸O?

13.142. Ethylene (C₂H₄) reacts with ozone to form 2 mol of formaldehyde (a probable human carcinogen) per mole of ethylene as shown in Figure P13.142. The following kinetic data were collected at 298 K.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[O₃]₀ (M)</th>
<th>[C₂H₄]₀ (M)</th>
<th>Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.86 × 10⁻²</td>
<td>1.00 × 10⁻²</td>
<td>0.0877</td>
</tr>
<tr>
<td>2</td>
<td>0.43 × 10⁻²</td>
<td>1.00 × 10⁻²</td>
<td>0.0439</td>
</tr>
<tr>
<td>3</td>
<td>0.22 × 10⁻²</td>
<td>0.50 × 10⁻²</td>
<td>0.0110</td>
</tr>
</tbody>
</table>

a. Determine the rate law and the value of the rate constant of the reaction at 298 K.

b. The rate constant was determined at several additional temperatures. Calculate the activation energy of the reaction from the following data.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>k (M⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>263</td>
<td>3.28 × 10²</td>
</tr>
<tr>
<td>273</td>
<td>4.73 × 10²</td>
</tr>
</tbody>
</table>
13.143. Reducing NO Emissions  
Adding NH$_3$ to the stack gases at an electric power generating plant can reduce NO$_x$ emissions. This selective noncatalytic reduction (SNR) process depends on the reaction between NH$_2$ (an odd-electron compound) and NO:

$$\text{NH}_2(g) + \text{NO}(g) \rightarrow \text{N}_2(g) + \text{H}_2\text{O}(g)$$

The following kinetic data were collected at 1200 K.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[NH$_2$]$_0$ (M)</th>
<th>[NO]$_0$ (M)</th>
<th>Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.00 \times 10^{-5}$</td>
<td>$1.00 \times 10^{-5}$</td>
<td>0.12</td>
</tr>
<tr>
<td>2</td>
<td>$2.00 \times 10^{-5}$</td>
<td>$1.00 \times 10^{-5}$</td>
<td>0.24</td>
</tr>
<tr>
<td>3</td>
<td>$2.00 \times 10^{-5}$</td>
<td>$1.50 \times 10^{-5}$</td>
<td>0.36</td>
</tr>
<tr>
<td>4</td>
<td>$2.50 \times 10^{-5}$</td>
<td>$1.50 \times 10^{-5}$</td>
<td>0.45</td>
</tr>
</tbody>
</table>

a. What is the rate law for the reaction?
b. What is the value of the rate constant at 1200 K?
VISUAL PROBLEMS

(Answers to boldface end-of-chapter questions and problems are in the back of the book.)

14.1. Figure P14.1 shows the energy profiles of reactions A \( \rightleftharpoons \) B and C \( \rightleftharpoons \) D, respectively. Which reaction has the larger forward rate constant? Which reaction has the smaller reverse rate constant? Which reaction has the larger equilibrium constant \( K_c \)?

![Figure P14.1](image1.png)

**FIGURE P14.1**

14.2. The progress with time of a reaction system is depicted in Figure P14.2. Red spheres represent the molar concentration of substance A and blue spheres represent the molar concentration of substance B.

a. Does the system reach equilibrium?

b. In which direction (A \( \rightarrow \) B or B \( \rightarrow \) A) is equilibrium attained?

c. What is the value of the equilibrium constant \( K_c \)?

![Figure P14.2](image2.png)

**FIGURE P14.2**

14.3. In Figure P14.3 the red spheres represent reactant A and the blue spheres represent product B in equilibrium with A.

a. Write a chemical equation that describes the equilibrium.

b. What is the value of the equilibrium constant \( K_c \)?

![Figure P14.3](image3.png)

**FIGURE P14.3**

14.4. The equilibrium constant \( K_c \) for the reaction

\[
A \text{ (red spheres)} + B \text{ (blue spheres)} \rightleftharpoons AB
\]

is 3.0 at 300.0 K. Does the situation depicted in Figure P14.4 correspond to equilibrium? If not, in what direction (to the left or to the right) will the system shift to attain equilibrium?

![Figure P14.4](image4.png)
14.5. The left and right diagrams in Figure P14.5 represent equilibrium states of the reaction

\[ A \text{ (red spheres)} + B \text{ (blue spheres)} \rightleftharpoons AB \]

at 300 K and 400 K, respectively. Is this reaction endothermic or exothermic? Explain.

14.6. Figure P14.6 shows a plot of \( \ln K_c \) versus \( 1/T \) for the reaction \( A + 2 B \rightleftharpoons AB_2 \). Is the reaction endothermic or exothermic?

14.7. Does the reaction \( A \rightarrow 2 B \) represented in Figure P14.7 reach equilibrium in 20 \( \mu \)s? Explain your answer.

14.8. How are forward and reverse reaction rates in Figure P14.7 related at 30 \( \mu \)s?
The Dynamics of Chemical Equilibrium

CONCEPT REVIEW

14.9. Describe an example of a dynamic equilibrium that you experienced today.

14.10. At equilibrium, is the sum of the concentrations of all the reactants always equal to the sum of the concentrations of the products? Explain.

14.11. Suppose the forward rate constant of the reaction \( A \rightleftharpoons B \) is greater than the rate constant of the reverse reaction at a given temperature. Is the value of the equilibrium constant less than, greater than, or equal to 1?

14.12. Explain how it is possible for a reaction to have a large equilibrium constant but small forward and reverse rate constants.

PROBLEMS

14.13. In a study of the reaction

\[
\text{2 N}_2\text{O}(\text{g}) \rightleftharpoons \text{2 N}_2(\text{g}) + \text{O}_2(\text{g})
\]

quantities of all three gases were injected into a reaction vessel. The N\(_2\)O consisted entirely of isotopically labeled \(^{15}\text{N}_2\)O. Analysis of the reaction mixture after 1 day revealed the presence of compounds with molar masses 28, 29, 30, 32, 44, 45, and 46 g/mol. Identify the compounds and account for their presence.

14.14. A mixture of \(^{13}\text{CO}, ^{12}\text{CO}_2, \) and \( \text{O}_2 \) in a sealed reaction vessel was used to follow the reaction

\[
\text{2 CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{2 CO}_2(\text{g})
\]

Analysis of the reaction mixture after 1 day revealed the presence of compounds with molar masses 28, 29, 32, 44, and 45 g/mol. Identify the compounds and account for their presence.

14.15. Suppose the reaction \( A \rightleftharpoons B \) in the forward direction is first order in \( A \) and the rate constant is \( 1.50 \times 10^{-2} \text{ s}^{-1} \). The reverse reaction is first order in \( B \) and the rate constant is \( 4.50 \times 10^{-2} \text{ s}^{-1} \) at the same temperature. What is the value of the equilibrium constant for the reaction \( A \rightleftharpoons B \) at this temperature?

14.16. At 700 K the equilibrium constant \( K_c \) for the gas-phase reaction between NO and \( \text{O}_2 \) forming \( \text{NO}_2 \) is \( 8.7 \times 10^6 \). The rate constant for the reverse reaction at this temperature is \( 0.54 \text{ M}^{-1} \text{s}^{-1} \). What is the value of the rate constant for the forward reaction at 700 K?

Writing Equilibrium Constant Expressions; Relationships between \( K_c \) and \( K_p \) Values

CONCEPT REVIEW

14.17. Under what conditions are the numerical values of \( K_c \) and \( K_p \) equal?

14.18. At what temperature are the \( K_c \) and \( K_p \) values of the following reaction equal?

\[
\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g)
\]

14.19. Nitrogen oxides play important roles in air pollution. Write expressions for \( K_c \) and \( K_p \) for the following reactions involving nitrogen oxides.

   a. \( \text{N}_2(g) + 2 \text{O}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \)
   b. \( 3 \text{ NO}(g) \rightleftharpoons \text{NO}_2(g) + \text{N}_2\text{O}(g) \)
   c. \( 2 \text{N}_2\text{O}(g) \rightleftharpoons 2 \text{N}_2(g) + \text{O}_2(g) \)

14.20. Write expressions for \( K_c \) and \( K_p \) for the following reactions, which contribute to the destruction of stratospheric ozone.

   a. \( \text{Cl}(g) + \text{O}_3(g) \rightleftharpoons \text{ClO}(g) + \text{O}_2(g) \)
   b. \( 2 \text{ClO}(g) \rightleftharpoons 2 \text{Cl}(g) + \text{O}_2(g) \)
   c. \( 2 \text{ O}_3(g) \rightleftharpoons 3 \text{ O}_2(g) \)

PROBLEMS

14.21. Use the graph in Figure P14.21 to estimate the value of the equilibrium constant \( K_c \) for the reaction

\[
\text{N}_2\text{O}(g) \rightleftharpoons \text{N}_2(g) + 1/2 \text{O}_2(g)
\]

![Figure P14.21](image)

14.22. Estimate the value of the equilibrium constant \( K_c \) for the reaction

\[
\text{N}_2\text{O}(g) \rightleftharpoons \text{N}_2(g) + 1/2 \text{O}_2(g)
\]
2 NO(g) + O_2(g) ⇌ 2 NO_2(g)

from the data in Figure P14.22.

**FIGURE P14.22**

14.23. At 1200 K the partial pressures of an equilibrium mixture of H_2S, H_2, and S are 0.020, 0.045, and 0.030 atm, respectively. Calculate the value of the equilibrium constant $K_p$ at 1200 K.

\[ H_2S(g) \rightleftharpoons H_2(g) + S(g) \]

14.24. At 1045 K the partial pressures of an equilibrium mixture of H_2O, H_2, and O_2 are 0.040, 0.0045, and 0.0030 atm, respectively. Calculate the value of the equilibrium constant $K_p$ at 1045 K.

\[ 2 H_2O(g) \rightleftharpoons 2 H_2(g) + O_2(g) \]

14.25. At equilibrium, the concentrations of gaseous N_2, O_2, and NO in a sealed reaction vessel are 

[\text{[N}_2\text{]} = 3.3 \times 10^{-3} \text{ M}, \text{[O}_2\text{]} = 5.8 \times 10^{-3} \text{ M}, \text{ and } \text{[NO]} = 3.1 \times 10^{-3} \text{ M}].

What is the value of the equilibrium constant $K_c$ for the following reaction at the temperature of the mixture?

\[ N_2(g) + O_2(g) \rightleftharpoons 2 NO(g) \]

14.26. Analyses of an equilibrium mixture of gaseous N_2O_4 and NO_2 gave the following results: 

[\text{[NO}_2\text{]} = 4.2 \times 10^{-3} \text{ M} and [\text{N}_2\text{O}_4] = 2.9 \times 10^{-3} \text{ M}].

What is the value of the equilibrium constant $K_c$ for the following reaction at the temperature of the mixture?

\[ 2 NO_2(g) \rightleftharpoons N_2O_4(g) \]

14.27. A sealed reaction vessel initially contains 1.50 \times 10^{-2} \text{ mol water vapor and 1.50 \times 10^{-2} mol CO. After the reaction } H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g) \text{ has come to equilibrium, the vessel contains 8.3 \times 10^{-3} mol CO}_2. \text{ What is the value of the equilibrium constant } K_c \text{ of the reaction at the temperature of the vessel?}

14.28. A 100 mL reaction vessel initially contains 2.60 \times 10^{-2} \text{ mol NO and 1.30 \times 10^{-2} mol H}_2. \text{ At equilibrium, the concentration of NO in the vessel is 0.161 M. At equilibrium the vessel also contains N}_2, H_2O, and H_2. \text{ What is the value of the equilibrium constant } K_c \text{ for the following reaction?}

\[ 2 H_2(g) + 2 NO(g) \rightleftharpoons 2 H_2O(g) + N_2(g) \]

14.29. The equilibrium constant $K_p$ for the following equilibrium is 32 at 298 K. What is the value of $K_c$ for this same equilibrium at 298 K?

\[ A(g) + B(g) \rightleftharpoons AB(g) \]

14.30. The equilibrium constant $K_c$ for the following equilibrium is 6.0 \times 10^4 at 500 K. What is the value of $K_p$ for this same equilibrium at 500 K?

\[ CD(g) \rightleftharpoons C(g) + D(g) \]

14.31. At 500°C, the equilibrium constant $K_p$ for the synthesis of ammonia,

\[ N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g) \]

is 1.45 \times 10^{-5}. \text{ What is the value of } K_c \text{ at 500°C?}

14.32. If the value of the equilibrium constant, $K_c$, for the following reaction is 5 \times 10^7 at 298 K, what is the value of $K_p$ at 298 K?

\[ 2 CO(g) + O_2(g) \rightleftharpoons 2 CO_2(g) \]

14.33. For which of the following reactions are the values of $K_c$ and $K_p$ equal?
14.34. For which of the following reactions are the values of $K_c$ and $K_p$ different?
   a. $\text{SO}_2(g) + \text{Cl}_2(g) \rightleftharpoons \text{SO}_2(g) + \text{Cl}_2(g)$
   b. $2 \text{NO}_2(g) \rightleftharpoons 2 \text{NO}_2(g)$
   c. $2 \text{O}_2(g) \rightleftharpoons 3 \text{O}_2(g)$

14.35. Bulletproof Glass Phosgene (COCl$_2$) is used in the manufacture of foam rubber and bulletproof glass. It is formed from carbon monoxide and chlorine in the following reaction:

   $$\text{Cl}_2(g) + \text{CO}(g) \rightleftharpoons \text{COCl}_2(g)$$

   The value of $K_c$ for the reaction is 5.0 at 327°C. What is the value of $K_p$ at 327°C?

14.36. If the value of $K_p$ for the following reaction

   $$\text{SO}_2(g) + \text{NO}_2(g) \rightleftharpoons \text{NO}(g) + \text{SO}_3(g)$$

   is 3.45 at 298 K, what is the value of $K_c$ for the reverse reaction?

**Manipulating Equilibrium Constant Expressions**

**CONCEPT REVIEW**

14.37. How is the value of the equilibrium constant affected by scaling up or down the coefficients of the reactants and products in the chemical equation describing the reaction?

14.38. Why must a written form of a reaction and the temperature be given when reporting the value of an equilibrium constant?

**PROBLEMS**

14.39. The equilibrium constant for the reaction

   $$\text{I}_2(g) + \text{Br}_2(g) \rightleftharpoons 2 \text{IBr}(g)$$

   is 120 at 425 K. What is the value of $K_p$ for the equilibrium

   $$\frac{1}{2} \text{I}_2(g) + \frac{1}{2} \text{Br}_2(g) \rightleftharpoons \text{IBr}(g)$$

   at 425 K?

14.40. The equilibrium constant $K_p$ for the synthesis of ammonia,

   $$\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$$

   is $4.3 \times 10^{-3}$ at 300°C. What is the value of $K_p$ for the equilibrium

   $$\frac{1}{2} \text{N}_2(g) + \frac{3}{2} \text{H}_2(g) \rightleftharpoons \text{NH}_3(g)$$

   at 300°C?

14.41. The following reaction is one of the elementary steps in the oxidation of NO:

   $$\text{NO}(g) + \text{NO}_3(g) \rightleftharpoons 2 \text{NO}_2(g)$$

   Write an expression for the equilibrium constant $K_c$ for this reaction and for the reverse reaction:

   $$2 \text{NO}_2(g) \rightleftharpoons \text{NO}(g) + \text{NO}_3(g)$$

   How are the two $K_c$ expressions related?

14.42. Making Ammonia The value of the equilibrium constant $K_p$ for the formation of ammonia,

   $$\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$$

   is $4.5 \times 10^{-5}$ at 450°C. What is the value of $K_p$ for the following reaction at 450°C?

   $$2 \text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3 \text{H}_2(g)$$

14.43. Air Pollutants Sulfur oxides are major air pollutants. The reaction between sulfur dioxide and oxygen can be written in two ways:

   $$\text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{SO}_3(g)$$

   and

   $$2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)$$

   Write expressions for the equilibrium constants for both reactions. How are they related?

14.44. At a given temperature, the equilibrium constant $K_c$ for the reaction

   $$2 \text{NO}(g) + 2 \text{H}_2(g) \rightleftharpoons \text{N}_2(g) + 2 \text{H}_2\text{O}(g)$$

   is 0.11. What is the equilibrium constant for the following reaction?
14.45. At a given temperature, the equilibrium constant \( K_c \) for the reaction
\[
2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)
\]
is \(2.4 \times 10^{-3}\). What is the value of the equilibrium constant for each of the following reactions at that temperature?

a. \( \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{SO}_3(g) \)
b. \( 2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g) \)
c. \( \text{SO}_3(g) \rightleftharpoons \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \)

14.46. If the equilibrium constant \( K_c \) for the reaction
\[
2 \text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}_2(g)
\]
is \(5 \times 10^{12}\), what is the value of the equilibrium constant for each of the following reactions at the same temperature?

a. \( \text{NO}(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{NO}_2(g) \)
b. \( 2 \text{NO}_2(g) \rightleftharpoons 2 \text{NO}(g) + \text{O}_2(g) \)
c. \( \text{NO}_2(g) \rightleftharpoons \text{NO}(g) + \frac{1}{2} \text{O}_2(g) \)

14.47. Calculate the value of the equilibrium constant \( K \) for the hypothetical reaction
\[
2 \text{D} \rightleftharpoons \text{A} + 2 \text{B}
\]
from the following information:
\[
\begin{align*}
\text{A} + 2 \text{B} & \rightleftharpoons \text{C} \quad K_c = 3.3 \\
\text{C} & \rightleftharpoons 2 \text{D} \quad K_c = 0.041
\end{align*}
\]

14.48. Calculate the value of the equilibrium constant \( K \) for the hypothetical reaction
\[
\text{E} + \text{F} \rightleftharpoons \text{G}
\]
from the following information:
\[
\begin{align*}
2 \text{G} & \rightleftharpoons \text{H} \quad K_c = 3.1 \times 10^{-4} \\
\text{H} & \rightleftharpoons 2 \text{E} + 2 \text{F} \quad K_c = 2.8 \times 10^{22}
\end{align*}
\]

**Equilibrium Constants and Reaction Quotients**

**CONCEPT REVIEW**

14.49. What is a reaction quotient?  
14.50. How is an equilibrium constant different from a reaction quotient?  
14.51. What does it mean when the reaction quotient \( Q \) is numerically equal to the equilibrium constant \( K \)?  
14.52. Explain how knowing \( Q \) and \( K \) for an equilibrium system enables you to say whether it is at equilibrium or whether it will shift in one direction or another.

**PROBLEMS**

14.53. If the equilibrium constant \( K_c \) for the hypothetical reaction \( \text{A}(g) \rightleftharpoons \text{B}(g) \) is 22 at a given temperature, and if \([\text{A}] = 0.10 \text{ M} \) and \([\text{B}] = 2.0 \text{ M} \) in a reaction mixture at that temperature, is the reaction at chemical equilibrium? If not, in which direction will the reaction proceed to reach equilibrium?

14.54. The equilibrium constant \( K_c \) for the hypothetical reaction \( 2 \text{C} \rightleftharpoons \text{D} + \text{E} \) is \(3 \times 10^{-3}\). At a particular time, the composition of the reaction mixture is \([\text{C}] = [\text{D}] = [\text{E}] = 5 \times 10^{-4} \text{ M} \). In which direction will the reaction proceed to reach equilibrium?

14.55. Suppose the value of the equilibrium constant \( K_p \) of the following hypothetical reaction
\[
\text{A}(g) + \text{B}(g) \rightleftharpoons \text{C}(g)
\]
is 1.00 at 300 K. Are either of the following reaction mixtures at chemical equilibrium at 300 K?

a. \( P_A = P_B = P_C = 1.0 \text{ atm} \)
b. \( [\text{A}] = [\text{B}] = [\text{C}] = 1.0 \text{ M} \)

14.56. In which direction will the following hypothetical reaction proceed to reach equilibrium under the conditions given?
\[
\text{A}(g) + \text{B}(g) \rightleftharpoons \text{C}(g) \quad K_p = 1.00 \text{ at } 300 \text{ K}
\]

a. \( P_A = P_C = 1.0 \text{ atm}, P_B = 0.50 \text{ atm} \)
b. \( [\text{A}] = [\text{B}] = [\text{C}] = 1.0 \text{ M} \)

14.57. If the equilibrium constant \( K_c \) for the reaction
\[
\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g)
\]
14.58. At 650 K, the value of the equilibrium constant \( K_p \) for the ammonia synthesis reaction

\[
\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)
\]

is \( 4.3 \times 10^{-4} \). If a vessel contains a reaction mixture in which \([\text{N}_2]\) = 0.010 \text{ M}, \([\text{H}_2]\) = 0.030 \text{ M}, and \([\text{NH}_3]\) = 0.00020 \text{ M}, will more ammonia form?

14.59. The hypothetical equilibrium \( X + Y \rightleftharpoons Z \) has \( K_c = 1.00 \) at 350 K. If the initial molar concentrations of \( X \), \( Y \), and \( Z \) in a solution are all 0.2 \text{ M}, in which direction will the reaction shift to reach equilibrium?

a. To the left, making more \( X \) and \( Y \)

b. To the right, making more \( Z \)

c. The system is at equilibrium and the concentrations will not change

14.60. In Problem 14.59, when the equilibrium shifts, does the concentration of \( X \) increase or decrease?

**Heterogeneous Equilibria**

**CONCEPT REVIEW**

14.61. Write the \( K_c \) expression for the following reaction:

\[
\text{CuS}(s) \rightleftharpoons \text{Cu}^{2+}(aq) + \text{S}^2-(aq)
\]

14.62. Write the \( K_c \) expression for the following reaction:

\[
\text{Al}_2\text{O}_3(s) + 3 \text{H}_2\text{O}(l) \rightleftharpoons 2 \text{Al}^{3+}(aq) + 6 \text{OH}^-(aq)
\]

14.63. Why does the \( K_c \) expression for the reaction

\[
\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)
\]

not contain terms for the concentrations of \( \text{CaCO}_3 \) and \( \text{CaO} \)?

14.64. How many partial pressure terms are there in the \( K_p \) expression for the thermal decomposition of sodium bicarbonate?

\[
2 \text{NaHCO}_3(s) \rightleftharpoons \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g)
\]

**Le Châtelier’s Principle**

**CONCEPT REVIEW**

14.65. Does adding reactants to a system at equilibrium increase the value of the equilibrium constant?

14.66. Increasing the concentration of a reactant shifts the position of chemical equilibrium toward formation of more products. What effect does adding a reactant have on the rates of the forward and reverse reactions?

14.67. Carbon Monoxide Poisoning Patients suffering from carbon monoxide poisoning are treated with pure oxygen to remove CO from the hemoglobin (Hb) in their blood. The two relevant equilibria are

\[
\text{Hb} + 4 \text{CO}(g) \rightleftharpoons \text{Hb(CO)}_4 \\
\text{Hb} + 4 \text{O}_2(g) \rightleftharpoons \text{Hb(O}_2)_4
\]

The value of the equilibrium constant for CO binding to Hb is greater than that for \( \text{O}_2 \). How, then, does this treatment work?

14.68. Is the equilibrium constant \( K_a \) for the reaction

\[
2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)
\]

in air the same in Los Angeles as in Denver if the atmospheric pressure in Denver is lower but the temperature is the same?

14.69. Henry’s law (Chapter 10) predicts that the solubility of a gas in a liquid increases with its partial pressure. Explain Henry’s law in relation to Le Châtelier’s principle.

*14.70. For the reaction

\[
2 \text{CO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{CO}_2(g)
\]

why does adding an inert gas such as argon to an equilibrium mixture of CO, \( \text{O}_2 \), and \( \text{CO}_2 \) in a sealed vessel increase the total pressure of the system but not affect the position of the equilibrium?

**PROBLEMS**

14.71. Which of the following equilibria will shift toward formation of more products if an equilibrium mixture is compressed into half its volume?

- a. \( 2 \text{N}_2\text{O}(g) \rightleftharpoons 2 \text{N}_2(g) + \text{O}_2(g) \)
- b. \( 2 \text{CO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{CO}_2(g) \)
- c. \( \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g) \)
- d. \( 2 \text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}_2(g) \)

14.72. Which of the following equilibria will shift toward formation of more products if the volume of a reaction mixture at equilibrium increases by a factor of 2?

- a. \( 2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g) \)
- b. \( \text{NO}(g) + \text{O}_3(g) \rightleftharpoons \text{NO}_2(g) + \text{O}_2(g) \)
c. 2 N₂O₅(g) ⇌ 4 NO₂(g) + O₂(g)  
d. N₂O₄(g) ⇌ 2 NO₂(g)

14.73. What would be the effect of the changes listed on the equilibrium concentrations of reactants and products in the following reaction?

\[ 2 \text{O}_2(g) \rightleftharpoons 3 \text{O}_3(g) \]

a. O₃ is added to the system.  
b. O₂ is added to the system.  
c. The mixture is compressed to one-tenth its initial volume.

14.74. How will the changes listed affect the position of the following equilibrium?

\[ 2 \text{NO}_2(g) \rightleftharpoons \text{NO}(g) + \text{NO}_3(g) \]

a. The concentration of NO is increased.  
b. The concentration of NO₂ is increased.  
c. The volume of the system is allowed to expand to 5 times its initial value.

14.75. How would reducing the partial pressure of O₂(g) affect the position of the equilibrium in the following reaction?

\[ 2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g) \]

*14.76. Ammonia is added to a gaseous reaction mixture containing H₂, Cl₂, and HCl that is at chemical equilibrium. How will the addition of ammonia affect the relative concentrations of H₂, Cl₂, and HCl if the equilibrium constant of reaction 2 is much greater than the equilibrium constant of reaction 1?

\[
\begin{align*}
(1) & \quad \text{H}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{HCl}(g) \\
(2) & \quad \text{HCl}(g) + \text{NH}_3(g) \rightleftharpoons \text{NH}_4\text{Cl}(s)
\end{align*}
\]

14.77. In which of the following hypothetical equilibria does the product yield increase with increasing temperature?

a. A + 2 B ⇌ C \quad \Delta H > 0  
b. A + 2 B ⇌ C \quad \Delta H = 0  
c. A + 2 B ⇌ C \quad \Delta H < 0

14.78. In which of the following hypothetical equilibria does the product yield decrease with increasing temperature?

a. 2 X + Y ⇌ Z \quad \Delta H > 0  
b. 2 X + Y ⇌ Z \quad \Delta H = 0  
c. 2 X + Y ⇌ Z \quad \Delta H < 0

Calculations Based on \( K \)

CONCEPT REVIEW

14.79. Why are calculations of how much product is formed in the reaction

\[ X + Y \rightleftharpoons Z \]

often simpler when there is no Z initially present and the value of \( K \) is very small (<10⁻⁶)?

14.80. Could the quadratic equation be used to solve for the equilibrium concentration of NO₂ in the following reaction?

\[ 2 \text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}_2(g) \]

PROBLEMS

14.81. Consider this reaction:

\[ \text{PCl}_3(g) \rightleftharpoons \text{PCl}_5(g) + \text{Cl}_2(g) \quad K_p = 23.6 \text{ at 500 K} \]

a. Calculate the equilibrium partial pressures of the reactants and products if the initial pressures are \( P_{\text{PCl}_3} = 0.560 \text{ atm} \) and \( P_{\text{PCl}_5} = 0.500 \text{ atm} \).  
b. If more chlorine is added after equilibrium is reached, how will the concentrations of PCl₅ and PCl₃ change?

14.82. Enough NO₂ gas is injected into a cylindrical vessel to produce a partial pressure, \( P_{\text{NO}_2} \) of 0.900 atm at 298 K. Calculate the equilibrium partial pressures of NO₂ and N₂O₄, given

\[ 2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \quad K_p = 4 \text{ at 298 K} \]

14.83. The value of \( K_c \) for the reaction between water vapor and dichlorine monoxide

\[ \text{H}_2\text{O}(g) + \text{Cl}_2\text{O}(g) \rightleftharpoons 2 \text{HOCl}(g) \]

is 0.0900 at 25°C. Determine the equilibrium concentrations of all three compounds if the starting concentrations of both reactants are 0.00432 M and no HOCl is present.

14.84. The value of \( K_p \) for the reaction

\[ \text{H}_2\text{O}(g) + \text{Cl}_2\text{O}(g) \rightleftharpoons 2 \text{HOCl}(g) \]
\[3 \text{H}_2(g) + \text{N}_2(g) \rightleftharpoons 2 \text{NH}_3(g)\]
is \(4.3 \times 10^{-4}\) at 648 K. Determine the equilibrium partial pressure of \(\text{NH}_3\) in a reaction vessel that initially contained 0.900 atm \(\text{N}_2\) and 0.500 atm \(\text{H}_2\) at 648 K.

14.85. The value of \(K_p\) for the reaction

\[\text{NO}(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{NO}_2(g)\]
is \(2 \times 10^6\) at 25°C. At equilibrium, what is the ratio of \(P_{\text{NO}_2}\) to \(P_{\text{NO}}\) in air at 25°C? Assume that \(P_{\text{O}_2} = 0.21\) atm and does not change.

*14.86. Making Hydrogen Gas  Passing steam over hot carbon produces a mixture of carbon monoxide and hydrogen:

\[\text{H}_2\text{O}(g) + \text{C}(s) \rightleftharpoons \text{CO}(g) + \text{H}_2(g)\]
The value of \(K_p\) for the reaction at 1000°C is \(3.0 \times 10^{-2}\).

a. Calculate the equilibrium partial pressures of the products and reactants if \(P_{\text{H}_2\text{O}} = 0.442\) atm and \(P_{\text{CO}} = 5.0\) atm at the start of the reaction. Assume that the carbon is in excess.

b. Determine the equilibrium partial pressures of the reactants and products after sufficient \(\text{CO}\) and \(\text{H}_2\) are added to the equilibrium mixture in part a to initially increase the partial pressures of both gases by 0.075 atm.

14.87. The value of \(K_p\) for the reaction

\[\text{CO}_2(g) + \text{C}(s) \rightleftharpoons 2 \text{CO}(g)\]
is 1.5 at 700°C. Calculate the equilibrium partial pressures of \(\text{CO}\) and \(\text{CO}_2\) if initially \(P_{\text{CO}_2} = 5.0\) atm and \(P_{\text{CO}} = 0.0\). Pure graphite is present both initially and when equilibrium is achieved.

14.88. Jupiter’s Atmosphere  Ammonium hydrogen sulfide (\(\text{NH}_3\text{SH}\)) has been detected in the atmosphere of Jupiter, where it probably exists in equilibrium with ammonia and hydrogen sulfide:

\[\text{NH}_3\text{SH}(s) \rightleftharpoons \text{NH}_3(g) + \text{H}_2\text{S}(g)\]
The value of \(K_p\) for the reaction at 24°C is 0.126. Suppose a sealed flask contains an equilibrium mixture of \(\text{NH}_3\text{SH}, \text{NH}_3,\) and \(\text{H}_2\text{S}\). At equilibrium, the partial pressure of \(\text{H}_2\text{S}\) is 0.355 atm. What is the partial pressure of \(\text{NH}_3\)?

*14.89. A flask containing pure \(\text{NO}_2\) is heated to 1000 K, a temperature at which the value of \(K_p\) for the decomposition of \(\text{NO}_2\) is 158.

\[2 \text{NO}_2(g) \rightleftharpoons 2 \text{NO}(g) + \text{O}_2(g)\]
The partial pressure of \(\text{O}_2\) at equilibrium is 0.136 atm.

a. Calculate the partial pressures of \(\text{NO}\) and \(\text{NO}_2\).

b. Calculate the total pressure in the flask at equilibrium.

14.90. The equilibrium constant \(K_p\) of the reaction

\[2 \text{SO}_2(g) \rightleftharpoons 2 \text{SO}_3(g) + \text{O}_2(g)\]
is 7.69 at 830°C. If a vessel at this temperature initially contains pure \(\text{SO}_3\) and if the partial pressure of \(\text{SO}_3\) at equilibrium is 0.100 atm, what is the partial pressure of \(\text{O}_2\) in the flask at equilibrium?

*14.91. \(\text{NO}_2\) Pollution  In a study of the formation of \(\text{NO}_2\) air pollution, a chamber heated to 2200°C was filled with air (0.79 atm \(\text{N}_2\), 0.21 atm \(\text{O}_2\)). What are the equilibrium partial pressures of \(\text{N}_2, \text{O}_2,\) and \(\text{NO}\) if \(K_p = 0.050\) for the following reaction at 2200°C?

\[\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g)\]

*14.92. The equilibrium constant \(K_p\) for the thermal decomposition of \(\text{NO}_2\)

\[2 \text{NO}_2(g) \rightleftharpoons 2 \text{NO}(g) + \text{O}_2(g)\]
is \(6.5 \times 10^{-6}\) at 450°C. If a reaction vessel at this temperature initially contains 0.500 atm \(\text{NO}_2\), what will be the partial pressures of \(\text{NO}_2, \text{NO},\) and \(\text{O}_2\) in the vessel when equilibrium has been attained?

14.93. The value of \(K_p\) for the thermal decomposition of hydrogen sulfide

\[2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g)\]
is \(2.2 \times 10^{-4}\) at 1400 K. A sample of gas in which \(\text{[H}_2\text{S]} = 6.00 \text{ M}\) is heated to 1400 K in a sealed high-pressure vessel. After chemical equilibrium has been achieved, what is the value of \(\text{[H}_2\text{S]}?\) Assume that no \(\text{H}_2\) or \(\text{S}_2\) was present in the original sample.

14.94. Urban Air  On a very smoggy day, the equilibrium concentration of \(\text{NO}_2\) in the air over an urban area reaches \(2.2 \times 10^{-7}\text{ M}\). If the temperature of the air is 25°C, what is the concentration of the dimer \(\text{N}_2\text{O}_4\) in the air? Given:

\[\text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g) \quad K_c = 6.1 \times 10^{-3}\]
14.95. Chemical Weapon. Phosgene, COCl₂, gained notoriety as a chemical weapon in World War I. Phosgene is produced by the reaction of carbon monoxide with chlorine:

\[ \text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g) \]

The value of \( K_c \) for this reaction is 5.0 at 600 K. What are the equilibrium partial pressures of the three gases if a reaction vessel initially contains a mixture of the reactants in which \( P_{\text{CO}} = P_{\text{Cl}_2} = 0.265 \text{ atm} \) and \( P_{\text{COCl}_2} = 0.000 \text{ atm} \)?

14.96. At 2000°C, the value of \( K_c \) for the reaction

\[ 2 \text{CO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{CO}_2(g) \]

is 1.0. What is the ratio of \([\text{CO}]\) to \([\text{CO}_2]\) in an atmosphere in which \([\text{O}_2]\) = 0.0045 \text{ M}?

14.97. The water–gas shift reaction is an important source of hydrogen. The value of \( K_c \) for the reaction

\[ \text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \]

at 700 K is 5.1. Calculate the equilibrium concentrations of the four gases if the initial concentration of each of them is 0.050 \text{ M}.

14.98. Sulfur dioxide reacts with NO₂, forming SO₃ and NO:

\[ \text{SO}_2(g) + \text{NO}_2(g) \rightleftharpoons \text{SO}_3(g) + \text{NO}(g) \]

If the value of \( K_c \) for the reaction is 2.50, what are the equilibrium concentrations of the products if the reaction mixture was initially 0.50 \text{ M} \text{SO}_2, 0.50 \text{ M} \text{NO}_2, 0.0050 \text{ M} \text{SO}_3, \text{ and } 0.0050 \text{ M} \text{NO}?

14.99. Nitrogen dioxide and nitric oxide react to form dinitrogen trioxide. The \( K_p \) for this reaction is 0.535 at 25°C:

\[ \text{NO}(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \frac{1}{2} \text{N}_2\text{O}_3(g) \]

If a 4.0 L flask contains 15 g NO and 69 g NO₂, what are the concentrations of all species at equilibrium?

14.100. For the decomposition of HI(g) into H₂(g) and I₂(g) at 400°C, \( K_c = 0.0183 \):

\[ 2 \text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g) \]

If 80.0 g of HI(g) is placed in a 2.5 L chamber at 400°C, what are the concentrations of all species when the system comes to equilibrium?

### Equilibrium and Thermodynamics

**CONCEPT REVIEW**

**14.101.** Do all reactions with equilibrium constants < 1 have values of \( \Delta G^\circ > 0 \)?

**14.102.** The equation \( \Delta G^\circ = -RT \ln K \) relates the value of \( K_p \), not \( K_c \), to the change in standard free energy for a reaction in the gas phase. Explain why.

**14.103.** Starting with pure reactants, in which direction will an equilibrium shift if \( \Delta G^\circ < 0 \)?

**14.104.** Starting with pure products, in which direction will an equilibrium shift if \( \Delta G^\circ < 0 \)?

### PROBLEMS

**14.105.** Which of the following reactions has the largest equilibrium constant at 25°C?

a. \( \text{Cl}_2(g) + \text{F}_2(g) \rightleftharpoons 2 \text{ClF}(g) \quad \Delta G^\circ = 115.4 \text{ kJ} \)

b. \( \text{Cl}_2(g) + \text{Br}_2(g) \rightleftharpoons 2 \text{ClBr}(g) \quad \Delta G^\circ = -2.0 \text{ kJ} \)

c. \( \text{Cl}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{ICl}(g) \quad \Delta G^\circ = -27.9 \text{ kJ} \)

**14.106.** The value of \( \Delta G^\circ \) for the reaction

\[ \frac{1}{2} \text{N}_2\text{O}_3(g) + \text{I}_2(g) \rightleftharpoons \text{NO}(g) + \frac{1}{2} \text{I}_2(g) \]

is 68.9 kJ. What is the value of the equilibrium constant for this reaction at 298 K?

**14.107.** At a temperature of 1000 K, \( \text{SO}_2(g) \) combines with oxygen to make \( \text{SO}_3(g) \):

\[ 2 \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{SO}_3(g) \]

Under these conditions, \( K_p = 3.4 \).

a. Use the appropriate thermodynamic data in Appendix 4 to calculate the value of \( \Delta H^\circ_{\text{rxn}} \) for this reaction.

b. What is the value of \( K_p \) for this reaction at 298 K?

c. Use the answer from part b to calculate the value of \( \Delta G^\circ_{\text{rxn}} \) at 298 K, and compare it to the value you obtained using the \( \Delta G^\circ_{\text{f}} \) values in Appendix 4.

**14.108.** The value of the equilibrium constant \( K_p \) for the reaction

\[ \text{H}_2(g) + \text{CO}_2(g) \rightleftharpoons \text{H}_2\text{O}(g) + \text{CO}(g) \]

is 0.534 at 700°C.

a. What is the value of \( K_p \) for this reaction at 298 K? (Hint: To perform this \( K_p \) calculation, you will need to calculate the value of \( \Delta H^\circ_{\text{rxn}} \) using the appropriate data from Appendix 4.)

b. Calculate the value of \( \Delta G^\circ_{\text{rxn}} \) at 298 K using your answer from part a. Then compare it to the \( \Delta G^\circ_{\text{rxn}} \) value you obtained using the \( \Delta G^\circ_{\text{f}} \) values in Appendix 4.
14.109. Use the following data to calculate the value of $K_p$ at 298 K for the reaction:

$$N_2(g) + 2 O_2(g) \rightleftharpoons 2 NO_2(g)$$

Given:

$$N_2(g) + O_2(g) \rightleftharpoons 2 NO(g) \quad \Delta G^\circ = 173.2 \text{ kJ}$$

$$2 NO(g) + O_2(g) \rightleftharpoons 2 NO_2(g) \quad \Delta G^\circ = -69.7 \text{ kJ}$$

14.110. Under the appropriate conditions, NO forms $N_2O$ and $NO_2$:

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

Use the values for $\Delta G^\circ$ for the following reactions to calculate the value of $K_p$ for the above reaction at 500°C.

$$2 NO(g) + O_2(g) \rightleftharpoons 2 NO_2(g) \quad \Delta G^\circ = -69.7 \text{ kJ}$$

$$2 N_2O(g) \rightleftharpoons 2 NO(g) + N_2(g) \quad \Delta G^\circ = -33.8 \text{ kJ}$$

$$N_2(g) + O_2(g) \rightleftharpoons 2 NO(g) \quad \Delta G^\circ = 173.2 \text{ kJ}$$

### Changing K with Changing Temperature

**CONCEPT REVIEW**

14.111. The value of the equilibrium constant of a reaction decreases with increasing temperature. Is this reaction endothermic or exothermic?

14.112. The reaction

$$2 CO(g) + O_2(g) \rightleftharpoons 2 CO_2(g)$$

is exothermic. Does the value of $K_p$ increase or decrease with increasing temperature?

14.113. The value of $K_p$ for the water–gas shift reaction

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$$

increases as the temperature decreases. Is the reaction exothermic or endothermic?

14.114. Does the value of $K_p$ for the reaction

$$CH_4(g) + H_2O(g) \rightleftharpoons 3 H_2(g) + CO(g) \quad \Delta H^\circ = 206 \text{ kJ}$$

increase, decrease, or remain unchanged as temperature increases?

### PROBLEMS

14.115. Air Pollution  Automobiles and trucks pollute the air with NO. At 2000°C, $K_c$ for the reaction

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

is $4.10 \times 10^{-4}$, and $\Delta H^\circ = 180.6 \text{ kJ}$. What is the value of $K_c$ at 25°C?

14.116. At 400 K the value of $K_p$ for the reaction

$$N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$$

is 41, and $\Delta H^\circ = -92.2 \text{ kJ}$. What is the value of $K_p$ at 700 K?

14.117. The equilibrium constant for the reaction

$$2 NO(g) + O_2(g) \rightleftharpoons 2 NO_2(g)$$

decreases from $1.5 \times 10^3$ at 430°C to 23 at 1000°C. From these data, calculate the value of $\Delta H^\circ$ for the reaction.

14.118. The value of $K_c$ for the reaction A B is 0.455 at 50°C and 0.655 at 100°C. Calculate $\Delta H^\circ$ for the reaction.

### Additional Problems

*14.119. CO as a Fuel*  Is carbon dioxide a viable source of the fuel CO? Pure carbon dioxide ($P_{CO_2} = 1 \text{ atm}$) decomposes at high temperatures. For the system

$$2 CO_2(g) \rightleftharpoons 2 CO(g) + O_2(g)$$

the percentage of decomposition of $CO_2(g)$ changes with temperature as follows:

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Decomposition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>0.048</td>
</tr>
</tbody>
</table>
Is the reaction endothermic? Calculate the value of \( K_p \) at each temperature and discuss the results. Is the decomposition of CO\(_2\) an antidote for global warming?

14.120. Ammonia decomposes at high temperatures. In an experiment to explore this behavior, 2.000 mol of gaseous NH\(_3\) is sealed in a rigid 1-liter vessel. The vessel is heated to 800 K and some of the NH\(_3\) decomposes in the following reaction:

\[
2 \text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3 \text{H}_2(g)
\]

The system eventually reaches equilibrium and is found to contain 0.0040 mol of NH\(_3\). What are the values of \( K_p \) and \( K_c \) for the decomposition reaction at 800 K?

*14.121. Elements of group 16 form hydrides with the generic formula H\(_2\)X. When gaseous H\(_2\)X is bubbled through a solution containing 0.3 M hydrochloric acid, the solution becomes saturated and [H\(_2\)X] = 0.1 M. The following equilibria exist in this solution:

\[
\text{H}_2\text{X}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HX}^-(aq) + \text{H}_3\text{O}^+(aq) \quad K_1 = 8.3 \times 10^{-8}
\]

Calculate the composition of \( \text{X}^\text{2-} \) in the solution.

*14.122. Nitrogen dioxide reacts with SO\(_2\) to form SO\(_3\) and NO:

\[
\text{NO}_2(g) + \text{SO}_2(g) \rightleftharpoons \text{NO}(g) + \text{SO}_3(g)
\]

An equilibrium mixture is analyzed at a certain temperature and found to contain [NO\(_2\)] = 0.100 M, [SO\(_2\)] = 0.300 M, [NO] = 2.00 M, and [SO\(_3\)] = 0.600 M. At the same temperature, extra SO\(_2\) is added to make [SO\(_2\)] = 0.800 M. Calculate the composition of the mixture when equilibrium has been reestablished.

*14.123. Carbon disulfide is a foul-smelling solvent that dissolves sulfur and other nonpolar substances. It can be made by heating sulfur in an atmosphere of methane:

\[
4 \text{CH}_4(g) + \text{S(s)} \rightleftharpoons 4 \text{CS}_2(g) + 8 \text{H}_2(g)
\]

Starting with the appropriate data in Appendix 4, calculate the values of \( K_p \) for the reaction at 25°C and 500°C.

*14.124. Making Hydrogen Debate continues on the practicality of using H\(_2\) gas as a fuel for cars. The equilibrium constant \( K_c \) for the reaction

\[
\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)
\]

is \(1.0 \times 10^5\) at 25°C. Starting with this value, calculate the value of \( \Delta G^\circ_{\text{rxn}} \) at 25°C, and, without doing any calculations, guess the sign of \( \Delta H^\circ_{\text{rxn}} \).

*14.125. Air Pollution Control Calcium oxide is used to remove the pollutant SO\(_2\) from smokestack gases. The \( \Delta G^\circ \) of the overall reaction

\[
\text{CaO(s)} + \text{SO}_2(g) + 1/2 \text{O}_2(g) \rightleftharpoons \text{CaSO}_4(s)
\]

is \(-418.6\) kJ. What is \( P_{\text{SO}_2} \) in equilibrium with air \( (P_{\text{O}_2} = 0.21\text{ atm}) \) and solid CaO?

*14.126. Volcanic Eruptions During volcanic eruptions, gases as hot as 700°C and rich in SO\(_2\) are released into the atmosphere. As air mixes with these gases, the following reaction converts some of this SO\(_2\) into SO\(_3\):

\[
2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)
\]

Calculate the value of \( K_p \) for this reaction at 700°C. What is the ratio of \( P_{\text{SO}_2} \) to \( P_{\text{SO}_3} \) in equilibrium with \( P_{\text{O}_2} = 0.21\text{ atm}\)?

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( K_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2500</td>
<td>17.6</td>
</tr>
<tr>
<td>3000</td>
<td>54.8</td>
</tr>
</tbody>
</table>
VISUAL PROBLEMS

(Answers to boldface end-of-chapter questions and problems are in the back of the book.)

15.1. Which of the lines in Figure P15.1 best represents the dependence of the degree of ionization of acetic acid on its concentration in aqueous solution?

![Figure P15.1](image1)

15.2. The bar graph in Figure P15.2 shows the degree of ionization of $1 \times 10^{-3} M$ solutions of three hypohalous acids: HClO, HBrO, and HIO. Which bar is the one for HIO?

![Figure P15.2](image2)

15.3. The graph in Figure P15.3 shows the titration curves of a 1 $M$ solution of a weak acid with a strong base and a 1 $M$ solution of a strong acid with the same base. Which curve is which?

![Figure P15.3](image3)

15.4. Estimate to within one pH unit the pH of a 0.5 $M$ solution of the sodium salt of the weak acid in Problem 15.3.

15.5. Suppose you have four color indicators to choose from for detecting the equivalence point of the titration reaction represented by the red curve (upper curve on the left side of the plot) in Figure P15.3. The $pK_a$ values of the four indicators are 3.3, 5.0, 7.0, and 9.0. Which indicator would be the best one to choose?

15.6. What is the $pK_a$ value of the weak acid in Figure P15.3?

15.7. One of the titration curves in Figure P15.7 represents the titration of an aqueous sample of Na$_2$CO$_3$ with strong acid; the other represents the titration of an aqueous sample of NaHCO$_3$ with the same acid. Which curve is which?
15.8. Consider the three beakers in Figure P15.8. Each contains a few drops of the color indicator bromthymol blue, which is yellow in acidic solutions and blue in basic solutions. One beaker contains a solution of ammonium chloride, one contains ammonium acetate, and the third contains sodium acetate. Which beaker contains which salt?

![Figure P15.8](image)

**QUESTIONS AND PROBLEMS**

**Acids and Bases: The Brønsted–Lowry Model**

**CONCEPT REVIEW**

15.9. In an aqueous solution of HBr, which compound acts as a Brønsted–Lowry acid and which is the Brønsted–Lowry base?
15.10. In an aqueous solution of HNO₃, which compound acts as a Brønsted–Lowry acid and which is the Brønsted–Lowry base?
15.11. In an aqueous solution of NaOH, which species acts as a Brønsted–Lowry acid and which is the Brønsted–Lowry base?
15.12. Both NaOH and Ca(OH)₂ are strong bases. Does this mean that solutions of the two compounds with the same molarity have the same capacity to neutralize strong acids? Why or why not?
15.13. Identify the acids and bases in the following reactions:
   a. HNO₃(aq) + NaOH(aq) → NaNO₃(aq) + H₂O(l)
   b. CaCO₃(s) + 2 HCl(aq) → CaCl₂(aq) + CO₂(g) + H₂O(l)
   c. NH₃(aq) + HCN(aq) → NH₄CN(aq)
15.14. Identify the acids and bases in the following reactions:
   a. NH₃(aq) + H₂O(l) ⇌ NH₄⁺(aq) + OH⁻(aq)
   b. HClO₄(aq) + H₂O(l) ⇌ ClO₄⁻(aq) + H₃O⁺(aq)
   c. HSO₄⁻(aq) + CO₃²⁻(aq) ⇌ SO₄²⁻(aq) + HCO₃⁻(aq)
15.15. Identify the conjugate base of each of the following compounds: HNO₂, HClO, H₃PO₄, and NH₃.
15.16. Identify the conjugate acid of each of the following species: NH₃, ClO₂⁻, SO₄²⁻, and OH⁻.

**PROBLEMS**

15.17. What is the concentration of H⁺ ions in a 1.50 M solution of HNO₃?
15.18. What is the concentration of H⁺ ions in a solution of hydrochloric acid that was prepared by diluting 20.0 mL of concentrated (11.6 M) HCl to a final volume of 500 mL?
15.19. What is the value of [OH⁻] in a 0.0800 M solution of Sr(OH)₂?
15.20. A particular drain cleaner contains NaOH. What is the value of [OH⁻] in a solution produced when 5.0 g of NaOH dissolves in enough water to make 250 mL of solution?
15.21. Describe how you would prepare 2.50 L of a NaOH solution in which [OH⁻] = 0.70 M, starting with solid NaOH.
15.22. How many milliliters of a 1.00 M solution of NaOH do you need to prepare 250 mL of a solution in which [OH⁻] = 0.0200 M?

**Acid Strength and Molecular Structure**

**CONCEPT REVIEW**

15.23. Explain why the $K_a$ of $H_2SO_3$ is much greater than the $K_a$ of $H_2SeO_4$.

15.24. Explain why the $K_a$ of $H_2SO_3$ is much greater than the $K_a$ of $H_2SO_4$.

15.25. Predict which acid in the following pairs of acids is the stronger acid: (a) $H_2SO_3$ or $H_2SeO_3$; (b) $H_2SeO_4$ or $H_2SeO_3$.

15.26. Predict which acid in the following pairs of acids is the stronger acid: (a) $HBrO$ or $HBrO_2$; (b) $HClO$ or $HBrO$.

**pH and the Autoionization of Water**

**CONCEPT REVIEW**

15.27. Explain why pH values decrease as acidity increases.

15.28. Solution A is 100 times more acidic than solution B. What is the difference in the pH values of solution A and solution B?

15.29. Under what conditions is the pH of a solution negative?

*15.30. In principle, ethanol (CH₃CH₂OH) can undergo autoionization. Propose an explanation for why the value of the equilibrium constant for the autoionization of ethanol is much less than that of water.

**PROBLEMS**

15.31. Calculate the pH and pOH of the solutions with the following hydrogen ion or hydroxide ion concentrations. Indicate which solutions are acidic, basic, or neutral.

a. $[H^+] = 3.45 \times 10^{-8}$ M
b. $[H^+] = 2.0 \times 10^{-3}$ M
c. $[H^+] = 7.0 \times 10^{-8}$ M
d. $[OH^-] = 8.56 \times 10^{-4}$ M

15.32. Calculate the pH and pOH of the solutions with the following hydrogen ion or hydroxide ion concentrations. Indicate which solutions are acidic, basic, or neutral.

a. $[OH^-] = 7.69 \times 10^{-3}$ M
b. $[OH^-] = 2.18 \times 10^{-9}$ M
c. $[H^+] = 4.0 \times 10^{-8}$ M
d. $[H^+] = 3.56 \times 10^{-4}$ M

15.33. What is the pH of stomach acid in which $[HCl] = 0.155$ M?

15.34. What is the pH of 0.00500 M HNO₃?

15.35. What are the pH and pOH of 0.0450 M NaOH?

15.36. What are the pH and pOH of 0.160 M KOH?

15.37. What is the pH of 2.3 $\times 10^{-8}$ M HNO₃?

*15.38. What is the pH of 6.9 $\times 10^{-8}$ M LiOH?

15.39. Suppose the pH of a volume of dilute hydrochloric acid is 2.0. What is the pH after an equal volume of deionized water is mixed with the dilute acid?

15.40. pH of Blood The pH of venous blood, which carries CO₂ back to the lungs, is 7.35, while that of arterial blood is 7.45. How many times more concentrated in H⁺ is venous blood compared with arterial blood?

**Calculations Involving pH, $K_a$, and $K_b$**

**CONCEPT REVIEW**

15.41. One-molar solutions of the following acids are prepared: CH₃COOH, HNO₂, HClO, HCN. Rank them in order of decreasing $[H^+]$.

15.42. On the basis of the following degree-of-ionization data for 0.100 M solutions, select which acid has the smallest $K_e$.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Degree of Ionization (%)</th>
</tr>
</thead>
</table>

15.43. What is the pH of 2.3 $\times 10^{-8}$ M HNO₃?
<table>
<thead>
<tr>
<th>Compound</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₅COOH</td>
<td>2.5</td>
</tr>
<tr>
<td>HF</td>
<td>8.5</td>
</tr>
<tr>
<td>HN₃</td>
<td>1.4</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>1.3</td>
</tr>
</tbody>
</table>

15.43. A 1.0 M aqueous solution of NaNO₂ is a much better conductor of electricity than is a 1.0 M solution of HNO₂. Explain why.

15.44. Hydrogen chloride and water are molecular compounds, yet a solution of HCl dissolved in H₂O is an excellent conductor of electricity. Explain why.

15.45. Hydrofluoric acid is a weak acid. Write the mass action expression for its acid ionization reaction.

15.46. In the formula of formic acid, HCOOH, one H atom is ionizable. Write the mass action expression for the acid ionization equilibrium of formic acid.

*15.47. The $K_a$ values of weak acids depend on the solvent in which they dissolve. For example, the $K_a$ of alanine in aqueous ethanol is less than its $K_a$ in water.

  a. In which solvent does alanine ionize to the largest degree?
  b. Which is the stronger Brønsted–Lowry base: water or ethanol?

*15.48. The $K_a$ of proline is $2.5 \times 10^{-11}$ in water, $2.8 \times 10^{-11}$ in an aqueous solution that is 28% ethanol, and $1.66 \times 10^{-8}$ in 37% aqueous formaldehyde at 25°C.

  a. In which solvent is proline the strongest acid?
  b. Rank these compounds on the basis of their strengths as Brønsted–Lowry bases: water, ethanol, and formaldehyde.

15.49. When methylamine, CH₃NH₂, dissolves in water, the resulting solution is slightly basic. Which compound is the Brønsted–Lowry acid and which is the base?

*15.50. When 1,2-diaminoethane, H₂NCH₂CH₂NH₂, dissolves in water, the resulting solution is basic. Write the formula of the ionic compound that is formed when hydrochloric acid is added to a solution of 1,2-diaminoethane.

PROBLEMS

15.51. Sore Muscles Muscles burn during strenuous exercise because of the buildup of lactic acid and other metabolites in muscle tissues. In a 1.00 M aqueous solution, 2.94% of lactic acid is ionized. What is the value of its $K_a$?

15.52. Rancid Butter The odor of spoiled butter is due in part to butanoic acid, which results from the chemical breakdown of butter fat. A 0.100 M solution of butanoic acid is 1.23% ionized. Calculate the value of $K_a$ for butanoic acid.

15.53. At equilibrium, the value of $[H^+]$ in a 0.250 M solution of an unknown acid is $4.07 \times 10^{-3}$ M. Determine the degree of ionization and the $K_a$ of the acid.

15.54. Nitric acid (HNO₃) is a strong acid that is completely ionized in aqueous solutions of concentrations ranging from 1% to 10% (1.5 M). However, in more concentrated solutions, part of the nitric acid is present as un-ionized molecules of HNO₃. For example, in a 50% solution (7.5 M) at 25°C, only 33% of the molecules of HNO₃ dissociate into H⁺ and NO₃⁻. What is the value of $K_a$ of HNO₃?

15.55. Ant Bites The venom of biting ants contains formic acid, HCOOH, $K_a = 1.8 \times 10^{-4}$ at 25°C. Calculate the pH of a 0.060 M solution of formic acid.

15.56. Gout Uric acid can collect in joints, giving rise to a medical condition known as gout. If the $pK_a$ of uric acid is 3.89, what is the pH of a 0.0150 M solution of uric acid?

15.57. Acid Rain I A weather system moving through the American Midwest produced rain with an average pH of 5.02. By the time the system reached New England, the rain it produced had an average pH of 4.66. How much more acidic was the rain falling in New England?

15.58. Acid Rain II A newspaper reported that the “level of acidity” in a sample taken from an extensively studied watershed in New Hampshire in February 1998 was “an astounding 200 times lower than the worst measurement” taken in the preceding 23 years. What is this difference expressed in units of pH?

15.59. The $K_a$ of dimethylamine [(CH₃)₂NH] is $5.9 \times 10^{-4}$ at 25°C. Calculate the pH of a 1.20 × 10⁻³ M solution of dimethylamine.
15.60. Painkiller I Morphine is an effective painkiller but is also highly addictive. Calculate the pH of a 0.115 M solution of morphine if its pK_a = 5.79.

15.61. Painkiller II Codeine is a popular prescription painkiller because it is much less addictive than morphine. Codeine contains a basic nitrogen atom that can be protonated to give the conjugate acid of codeine. Calculate the pH of a 3.42 × 10^{-4} M solution of codeine if the pK_a of the conjugate acid is 8.21.

15.62. Pyridine (C_5H_5N) is a particularly foul-smelling substance used in manufacturing pesticides and plastic resins. Calculate the pH of a 0.125 M solution of pyridine.

*15.63. Aspirin* Aspirin (Figure P15.63) is an acid substance whose pK_a = 3.50 at body temperature (37°C). One standard adult aspirin contains 325 mg of the drug. If you take 1 aspirin on a full stomach (assume a volume of 1 L and a pH of 2.0), what percent of the aspirin in your stomach is present as the anion?

![FIGURE P15.63](image)

*15.64. Cough Syrup* A typical cough syrup contains 30.0 mg of pseudoephedrine hydrochloride (Figure P15.64) in 1 tsp (5 mL) of medicine. Calculate the pH of cough syrup based on the presence of this substance if the pK_b of pseudoephedrine hydrochloride is 9.22.

![FIGURE P15.64](image)

### Polyprotic Acids

**CONCEPT REVIEW**

15.65. Why is the K_a value of phosphoric acid less than its K_b value but greater than its K_a value?

15.66. In calculating the pH of a 1.0 M solution of sulfurous acid, we can ignore the H^+ ions produced by the ionization of the bisulfite ion; however, in calculating the pH of a 1.0 M solution of sulfuric acid, we cannot ignore the H^+ ions produced by the ionization of the bisulfate ion. Why?

**PROBLEMS**

15.67. What is the pH of a 0.300 M solution of H_2SO_4?

15.68. What is the pH of a 0.150 M solution of sulfurous acid?

15.69. Ascorbic acid (vitamin C) is a triprotic acid. What is the pH of a 0.250 M solution of ascorbic acid?

15.70. Rhubarb Pie The leaves of the rhubarb plant contain high concentrations of diprotic oxalic acid (HOOC-COOH) and must be removed before the stems are used to make rhubarb pie. What is the pH of a 0.0288 M solution of oxalic acid?

15.71. Addiction to Tobacco Nicotine is responsible for the addictive properties of tobacco. What is the pH of a 1.00 × 10^{-3} M solution of nicotine?

15.72. 1,2-Diaminoethane, H_2NCH_2CH_2NH_2, is used extensively in the synthesis of compounds containing transition metals in water. If pK_b_1 = 3.29 and pK_b_2 = 6.44, what is the pH of a 2.50 × 10^{-4} M solution of 1,2-diaminoethane?

15.73. Malaria Treatment Quinine occurs naturally in the bark of the cinchona tree. For centuries it was the
only treatment for malaria. Calculate the pH of a 0.01050 M solution of quinine in water.

15.74. Dozens of pharmaceuticals ranging from Cyclizine for motion sickness to Viagra for impotence are derived from the organic compound piperazine, whose structure is shown in Figure P15.74.

![Piperazine Structure](image)

**FIGURE P15.74**

- a. Solutions of piperazine are basic ($K_b_1 = 5.38 \times 10^{-5}$; $K_b_2 = 2.15 \times 10^{-9}$). What is the pH of a 0.0133 M solution of piperazine?
- b. Draw the structure of the ionic form of piperazine that would be present in stomach acid (about 0.15 M HCl).

**pH of Salt Solutions**

CONCEPT REVIEW

*15.75. The $pK_a$ values of the ions shown in Figure P15.75 increase as more methyl (–CH$_3$) groups are added. Do more methyl groups increase or decrease the strength of the neutral conjugate bases of these ions?

![Methyl Groups](image)

**FIGURE P15.75**

- 15.76. Why is it unnecessary to publish tables of $K_b$ values of the conjugate bases of weak acids whose $K_a$ values are known?
- 15.77. Which of the following salts produces an acidic solution in water: ammonium acetate, ammonium nitrate, or sodium formate?
- 15.78. Which of the following salts produces a basic solution in water: NaF, KCl, or NH$_4$Cl?
- 15.79. Neutralizing the Smell of Fish Trimethylamine, (CH$_3$)$_3$N, $K_b = 6.5 \times 10^{-5}$ at 25°C, is a contributor to the “fishy” odor of not-so-fresh seafood. Some people squeeze fresh lemon juice (which contains a high concentration of citric acid) on cooked fish to reduce the fishy odor. Why is this practice effective?
- 15.80. Nutritional Value of Beets Beets contain high concentrations of the calcium salt of a dicarboxylic acid with the common name malonic acid and the formula HOOCCH$_2$COOH. Could the presence of the calcium salt of malonic acid affect the pH balance of beets? If so, in which direction? Explain why.

**PROBLEMS**

15.81. If the $K_a$ of the conjugate acid of the artificial sweetener saccharin is $2.1 \times 10^{-11}$, what is the $pK_a$ for saccharin?

15.82. If the $K_a$ value of chromic acid ($H_2CrO_4$) is 0.16 and its $K_a$ value is $3.2 \times 10^{-7}$, what are the values of $K_b$ and $K_{b_2}$ of the CrO$_4^{2-}$ anion?

15.83. Dental Health Sodium fluoride is added to many municipal water supplies to reduce tooth decay. Calculate the pH of a 0.00339 M solution of NaF at 25°C.

15.84. Calculate the pH of a 1.25 $\times 10^{-2}$ M solution of the decongestant ephedrine hydrochloride if the $pK_b$ of ephedrine (its conjugate base) is 3.86.

**The Common-Ion Effect and pH Buffers**

CONCEPT REVIEW

15.85. Why is a solution of sodium acetate and acetic acid a much better pH buffer than is a solution of sodium chloride and hydrochloric acid?

15.86. Why does a solution of a weak base and its conjugate acid act as a better buffer than does a solution of the weak base alone?

**PROBLEMS**

15.87. A buffer contains 0.244 M acetic acid and 0.122 M sodium acetate.
15.89. Calculate the pH and pOH of 500.0 mL of a phosphate buffer that is 0.225 M HPO$_4^{2-}$ and 0.225 M PO$_4^{3-}$ at 25°C.

15.90. Determine the pH and pOH of 0.250 L of a buffer that is 0.0200 M boric acid and 0.0250 M sodium borate at 25°C.

15.91. What is the ratio of acetate ion to acetic acid in a buffer containing these compounds at pH = 3.56?

15.92. What is the ratio of lactic acid to lactate in a solution with pH = 4.00?

15.93. What is the pH at 25°C of a solution that results from mixing together equal volumes of a 0.05 M solution of ammonia and a 0.025 M solution of hydrochloric acid?

15.94. What is the pH at 25°C of a solution that results from mixing together equal volumes of a 0.05 M solution of acetic acid and a 0.025 M solution of sodium hydroxide?

*15.95. How much 10.0 M HNO$_3$ must be added to 1.00 L of a buffer that is 0.010 M acetic acid and 0.10 M sodium acetate to reduce the pH to 5.00 at 25°C?

*15.96. How much 6.0 M NaOH must be added to 0.500 L of a buffer that is 0.0200 M acetic acid and 0.0250 M sodium acetate to raise the pH to 5.75 at 25°C?

*15.97. Calculate the pH at 25°C of 1.00 L of a buffer that is 0.120 M HNO$_2$ and 0.150 M NaNO$_2$ before and after the addition of 1.00 mL of 12.0 M HCl.

*15.98. Calculate the pH at 25°C of 100.0 mL of a buffer that is 0.100 M NH$_4$Cl and 0.100 M NH$_3$ before and after the addition of 1.0 mL of 6 M HNO$_3$.

**pH Indicators and Acid—Base Titrations**

**CONCEPT REVIEW**

15.99. What are the differences between the titration curve of a strong acid titrated with a strong base and that of a weak acid titrated with a strong base?

15.100. Do all titrations of a strong base with a strong acid have the same pH at the equivalence point?

15.101. Do all titrations of a weak acid with a strong base have the same pH at the equivalence point?

15.102. What properties must a compound have to serve as an acid–base indicator?

**PROBLEMS**

15.103. A 25.0 mL sample of 0.100 M acetic acid is titrated with 0.125 M NaOH. Calculate the pH at 25°C of the titration mixture after 10.0, 20.0, and 30.0 mL of the base have been added.

15.104. A 25.0 mL sample of a 0.100 M solution of aqueous trimethylamine is titrated with a 0.125 M solution of HCl. Calculate the pH of the solution after 10.0, 20.0, and 30.0 mL of acid have been added; pK$_b$ of (CH$_3$)$_3$N = 4.19 at 25°C.

15.105. What is the concentration of ammonia in a solution if 22.35 mL of 0.1145 M HCl is needed to titrate a 100.0 mL sample of the solution?

15.106. Alkaline Hot Springs In an alkalinity titration of a 100.0 mL sample of water from a hot spring, 2.56 mL of a 0.0355 M solution of HCl is needed to reach the first equivalence point (pH = 8.3) and another 10.42 mL is needed to reach the second equivalence point (pH = 4.0). If the alkalinity of the spring water is due only to the presence of carbonate and bicarbonate, what are the concentrations of each?

15.107. What volume of 0.100 M HCl is required to titrate 250 mL of 0.0100 M Na$_2$CO$_3$ to the first equivalence point? How much more 0.100 M HCl is needed to reach the second equivalence point?

15.108. What volumes of 0.0100 M HCl are required to titrate 250 mL of 0.0100 M Na$_2$CO$_3$ and to titrate 250 mL of 0.0100 M HCO$_3$?$^-$?

15.109. In the titration of a solution of a weak monoprotic acid with a 0.1025 M solution of NaOH, the pH halfway to the equivalence point was 4.44. In the titration of a second solution of the same acid, exactly twice as much of a 0.1025 M solution of NaOH was needed to reach the equivalence point. What was the pH halfway to the equivalence point in this titration?
15.110. A 125.0 mg sample of an unknown monoprotic acid was dissolved in 100.0 mL of distilled water and titrated with a 0.050 M solution of NaOH. The pH of the solution was monitored throughout the titration, and the following data were collected. Determine the $K_a$ of the acid.

<table>
<thead>
<tr>
<th>Volume of OH⁻ Added (mL)</th>
<th>pH</th>
<th>Volume of OH⁻ Added (mL)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.09</td>
<td>22.0</td>
<td>5.93</td>
</tr>
<tr>
<td>5</td>
<td>3.65</td>
<td>22.2</td>
<td>6.24</td>
</tr>
<tr>
<td>10</td>
<td>4.10</td>
<td>22.6</td>
<td>9.91</td>
</tr>
<tr>
<td>15</td>
<td>4.50</td>
<td>22.8</td>
<td>10.21</td>
</tr>
<tr>
<td>17</td>
<td>4.55</td>
<td>23.0</td>
<td>10.38</td>
</tr>
<tr>
<td>18</td>
<td>4.71</td>
<td>24.0</td>
<td>10.81</td>
</tr>
<tr>
<td>19</td>
<td>4.94</td>
<td>25.0</td>
<td>11.02</td>
</tr>
<tr>
<td>20</td>
<td>5.11</td>
<td>30.0</td>
<td>11.49</td>
</tr>
<tr>
<td>21</td>
<td>5.37</td>
<td>40.0</td>
<td>11.85</td>
</tr>
</tbody>
</table>

15.111. Sketch a titration curve for the titration of 50.0 mL of 0.250 M HNO₂ with 1.00 M NaOH. What is the pH at the equivalence point?

15.112. Indicators from Red Cabbage Red cabbage juice is a sensitive acid–base indicator; its colors range from red at acidic pH to yellow in alkaline solutions. What color would red cabbage juice have when 25 mL of a 0.10 M solution of acetic acid is titrated with 0.10 M NaOH to its equivalence point?

15.113. Sketch a titration curve for the titration of the malaria drug quinine if 40.0 mL of a 0.100 M solution of quinine is titrated with a 0.100 M solution of HCl.

15.114. Sketch a titration curve for the titration of 100 mL of $1.25 \times 10^{-2}$ M ascorbic acid with $1.00 \times 10^{-2}$ M NaOH. How many equivalence points should the curve have, and what color indicator(s) could be used?

**Solubility Equilibria**

**CONCEPT REVIEW**

15.115. What is the difference between molar solubility and solubility product?

15.116. Give an example of how the common-ion effect limits the dissolution of a sparingly soluble ionic compound.

15.117. Which of the following cations will precipitate first as a carbonate mineral from an equimolar solution of Mg²⁺, Ca²⁺, and Sr²⁺?

15.118. If the solubility of a compound increases with increasing temperature, does $K_{sp}$ increase or decrease?

15.119. The $K_{sp}$ of strontium sulfate increases from $2.8 \times 10^{-7}$ at 37°C to $3.8 \times 10^{-7}$ at 77°C. Is the dissolution of strontium sulfate endothermic or exothermic?

15.120. How will adding concentrated NaOH(aq) affect the solubility of an Al(III) salt?

15.121. The chemistry of tooth decay Tooth enamel is composed of a mineral known as hydroxyapatite with the formula Ca₅(PO₄)₃(OH). Explain why tooth enamel can be eroded by acidic substances released by bacteria growing in the mouth.

15.122. Fluoride and Dental Hygiene Fluoride ions in drinking water and toothpaste convert hydroxyapatite in tooth enamel into fluorapatite:

$$\text{Ca}_5\text{(PO}_4)_3\text{(OH)}(s) + F^-(aq) \rightleftharpoons \text{Ca}_5\text{(PO}_4)_3\text{F} (s) + \text{OH}^- (aq)$$

Why is fluorapatite less susceptible than hydroxyapatite to erosion by acids?

**PROBLEMS**

15.123. At a particular temperature the value of $[\text{Ba}^{2+}]$ in a saturated solution of barium sulfate is $1.04 \times 10^{-5}$ M. Starting with this information, calculate the $K_{sp}$ value of barium sulfate at this temperature.
15.124. Suppose a saturated solution of barium fluoride contains $1.5 \times 10^{-2} \text{ M } F^-$. What is the $K_{sp}$ value of BaF$_2$?

15.125. What are the equilibrium concentrations of Cu$^{2+}$ and Cl$^-$ in a saturated solution of copper(I) chloride if $K_{sp} = 1.02 \times 10^{-6}$?

15.126. What are the equilibrium concentrations of Pb$^{2+}$ and F$^-$ in a saturated solution of lead fluoride if the $K_{sp}$ value of PbF$_2$ is $3.2 \times 10^{-8}$?

15.127. What is the solubility of calcite (CaCO$_3$) in grams per milliliter at a temperature at which its $K_{sp} = 9.9 \times 10^{-9}$?

15.128. What is the solubility of silver iodide in grams per milliliter at a temperature at which its $K_{sp} = 1.50 \times 10^{-10}$?

15.129. What is the pH at 25°C of a saturated solution of silver hydroxide?

15.130. pH of Milk of Magnesia What is the pH at 25°C of a saturated solution of magnesium hydroxide (the active ingredient in the antacid milk of magnesia)?

15.131. Suppose you have 100 mL of each of the following solutions. In which will the most CaCO$_3$ dissolve? (a) 0.1 M NaCl; (b) 0.1 M Na$_2$CO$_3$; (c) 0.1 M NaOH; (d) 0.1 M HCl

15.132. In which of the following solutions will CaF$_2$ be most soluble? (a) 0.010 M Ca(NO$_3$)$_2$; (b) 0.01 M NaF; (c) 0.001 M NaF; (d) 0.10 M Ca(NO$_3$)$_2$

15.133. Composition of Seawater The average concentration of sulfate in surface seawater is about 0.028 M. The average concentration of Sr$^{2+}$ is $9 \times 10^{-5} \text{ M }$. If the $K_{sp}$ value of strontium sulfate is $3.4 \times 10^{-7}$, is the concentration of strontium in the sea probably controlled by the insolubility of its sulfate salt?

15.134. Fertilizing the Sea to Combat Global Warming Some scientists have proposed adding Fe(III) compounds to large expanses of the open ocean to promote the growth of phytoplankton that would in turn remove CO$_2$ from the atmosphere through photosynthesis. The average pH of open ocean water is 8.1. What is the maximum value of [Fe$^{3+}$] in seawater if the $K_{sp}$ value of Fe(OH)$_3$ is $1.1 \times 10^{-30}$?

15.135. Will calcium fluoride precipitate when 125 mL of 0.375 M Ca(NO$_3$)$_2$ is added to 245 mL of 0.255 M NaCl at 25°C?

15.136. Will strontium sulfate precipitate at 25°C when 345 mL of a solution that is 0.0100 M in Sr$^{2+}$(aq) is added to 75 mL of 0.175 M K$_2$SO$_4$?

15.137. A solution is 0.010 M in both Br$^-$ and SO$_4^{2-}$. A 0.250 M solution of lead(II) nitrate is slowly added to it.

a. Which anion will precipitate first?

b. What is the concentration in the solution of the first ion when the second one starts to precipitate at 25°C?

*15.138. Solution A is 0.0250 M in Ag$^+$ ion and Pb$^{2+}$ ion. You have access to two other solutions: (B) 0.500 M NaCl and (C) 0.500 M NaBr.

a. Which would be the better solution to add to solution A to separate lead from silver by precipitation? (The better solution is the one that has less silver remaining in solution when the lead begins to precipitate.)

b. Using the solution you selected in part a, is the separation of the two ions complete? ("Complete" is defined as the point when less than 0.10% of the silver ion is left in the solution when the lead ion begins to precipitate.)

Additional Problems

15.139. Describe the intermolecular forces and changes in bonding that lead to the formation of a basic solution when methylamine (CH$_3$NH$_2$) dissolves in water.

15.140. Describe the chemical reactions of sulfur that begin with the burning of high-sulfur fossil fuel and that end with the reaction between acid rain and building exteriors made of marble (CaCO$_3$).

15.141. Suggest acid/conjugate base pairs that could be used to prepare buffers at each of these pH values: 3.00, 5.00, 7.00, and 12.00.

15.142. The value of $K_w$ of phosphorous acid, H$_3$PO$_3$, is nearly the same as the $K_w$ of phosphoric acid,
Identify the ionizable hydrogen atoms in Figure P15.142.

\[ \text{H}_3\text{PO}_4 \]

**FIGURE P15.142**

*15.143. pH of Baking Soda A cook dissolves a teaspoon of baking soda (\(\text{NaHCO}_3\)) in a cup of water, then discovers that the recipe calls for a tablespoon, not a teaspoon. So, the cook adds two more teaspoons of baking soda to make up the difference. Does the additional baking soda change the pH of the solution? Explain why or why not.

*15.144. Antacid Tablets Antacids contain a variety of bases such as \(\text{NaHCO}_3\), \(\text{MgCO}_3\), \(\text{CaCO}_3\), and \(\text{Mg(OH)}_2\). Only \(\text{NaHCO}_3\) has appreciable solubility in water.

a. Write a net ionic equation for the reaction of each base with aqueous HCl.

b. Explain how insoluble substances can act as effective antacids.

*15.145. pH of Natural Waters I In a 1985 study of Little Rock Lake in Wisconsin, 400 gallons of 18 M sulfuric acid were added to the lake over 6 years. The initial pH of the lake was 6.1 and the final pH was 4.7. If none of the acid was consumed in chemical reactions, estimate the volume of the lake.

15.146. pH of Natural Waters II Between 1993 and 1995, sodium phosphate was added to Seathwaite Tarn in the English Lake District to increase its pH. Explain why addition of this compound increased pH.

15.147. Acid–Base Properties of Pharmaceuticals I Zoloft is a common prescription drug for the treatment of depression. It is sold as a salt of HCl.

\[ \text{HN} \quad \text{CH}_3 \]

\[ \text{HC} \quad \text{CH} \quad \text{CH}_2 \]

\[ \text{HC} \quad \text{CH} \quad \text{CH}_2 \quad \text{Cl}^– \]

\[ \text{Zoloft} \]

**FIGURE P15.147**

a. In the reaction shown in Figure P15.147, which structure is that of the acid salt?

b. When Zoloft dissolves in water, will the resulting solution be acidic or basic?

15.148. Acid–Base Properties of Pharmaceuticals II Prozac is another popular antidepressant drug. Its structure is given in Figure P15.148.

\[ \text{F} \quad \text{C} \quad \text{HC} \quad \text{CH} \quad \text{O} \quad \text{CH}_2 \quad \text{NH} \quad \text{CH}_3 \]

\[ \text{HC} \quad \text{CH} \quad \text{CH} \quad \text{CH}_3 \]

\[ \text{Prozac} \]

**FIGURE P15.148**

a. Is a solution of Prozac in water likely to be slightly basic or slightly acidic? Explain your answer.

b. Prozac is also sold as a salt of HCl. Which atom, N or O, is more likely to react with HCl?

c. Prozac is sold as a salt of HCl because the solubility of the salt in water is higher than Prozac itself. Why is the salt more soluble?

15.149. Hydrogen fluoride (HF) behaves as a weak acid in aqueous solution. Two equilibria influence which fluorine-containing species are present in solution:

\[ \text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^–(aq) \quad K_a = 1.1 \times 10^{-3} \]
\[ \text{F}^-(aq) + \text{HF}(aq) \rightleftharpoons \text{HF}_2^-(aq) \quad K = 2.6 \times 10^{-3} \]

a. What is the equilibrium constant for this equilibrium?

\[ 2 \text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HF}_2^-(aq) \]

b. What is the equilibrium concentration of \( \text{HF}_2^- \) in a 0.150 \( M \) solution of HF?

*15.150. Pentafluorocyclopentadiene, which has the structure shown in Figure P15.150, is a strong acid.

[Chemical structure image]

**FIGURE P15.150**

a. Draw the conjugate base of \( \text{C}_5\text{F}_5\text{H} \).

b. Why is the compound so acidic when most organic acids are weak?

15.151. Anti-inflammatories Naproxen (also known as Aleve) is an anti-inflammatory drug used to reduce pain, fever, inflammation, and stiffness caused by conditions such as osteoarthritis and rheumatoid arthritis. Naproxen is an organic acid; its structure is shown in Figure P15.151. Naproxen has limited solubility in water, so it is sold as its sodium salt.

[Chemical structure image]

**FIGURE P15.151**

a. Draw the molecular structure of the sodium salt.

b. Should a solution of the salt be acidic or basic? Explain why.

c. Explain why the salt is more soluble than naproxen itself.

*15.152. Greenhouse Gases and Ocean pH Some climate models predict a decrease in the pH of the oceans of 0.77 pH units because of increases in atmospheric carbon dioxide.

a. Explain, by using the appropriate chemical reactions and equilibria, how an increase in atmospheric \( \text{CO}_2 \) could produce a decrease in oceanic pH.

b. How much more acidic (in terms of [H\(^+\)]) would the oceans be if their pH dropped this much?

c. Oceanographers are concerned about the impact of a drop in oceanic pH on the survival of coral reefs. Why?
VISUAL PROBLEMS

(Answers to boldface end-of-chapter questions and problems are in the back of the book.)

17.1. In the voltaic cell shown in Figure P17.1, the greater density of a concentrated solution of CuSO$_4$ allows a less concentrated solution of ZnSO$_4$ solution to be (carefully) layered on top of it. Why is a porous separator not needed in this cell?

![Figure P17.1](image)

17.2. In the voltaic cell shown in Figure P17.2, the concentrations of Cu$^{2+}$ and Cd$^{2+}$ are 1.00 M. On the basis of the standard potentials in Appendix 6, identify which electrode is the anode and which is the cathode. Indicate the direction of electron flow.

![Figure P17.2](image)

17.3. In the voltaic cell shown in Figure P17.3, [Ag$^+$] = [H$^+$] = 1.00 M. On the basis of the standard potentials in Appendix 6, identify which electrode is the anode and which is the cathode. Indicate the direction of electron flow.

![Figure P17.3](image)

*17.4. In many electrochemical cells the electrodes are metals that carry electrons to and from the cell but are not chemically changed by the cell reaction. Each of the highlighted clusters in the periodic table in Figure P17.4 consists of three metals. Which of the highlighted clusters is best suited to form inert electrodes?
17.5. Which of the four curves in Figure P17.5 best represents the dependence of the potential of a lead–acid battery on the concentration of sulfuric acid? Note that the scale of the $x$-axis is logarithmic.

![Figure P17.5](image)

**FIGURE P17.5**

17.6. Consider the four types of batteries in Figure P17.6. From top to bottom the sizes are AAA, AA, C, and D. The performance of batteries like these is often expressed in units such as (a) volts, (b) watt-hours, or (c) milliampere-hours. Which of the values differ significantly between the four batteries?

![Figure P17.6](image)

**FIGURE P17.6**

17.7. The apparatus in Figure P17.7 is used for the electrolysis of water. Hydrogen and oxygen gas are collected in the two inverted burets. An inert electrode at the bottom of the left buret is connected to the negative terminal of a 6-volt battery; the electrode in the buret on the right is connected to the positive terminal. A small quantity of sulfuric acid is added to speed up the electrolytic reaction.

a. What are the half-reactions at the left and right electrodes and their standard potentials?

b. Why does sulfuric acid make the electrolysis reaction go more rapidly?

17.8. An electrolytic apparatus identical to the one shown in Figure P17.7 is used to electrolyze water, but the reaction is speeded up by the addition of sodium carbonate instead of sulfuric acid.

a. What are the half-reactions and the standard potentials for the electrodes on the left and right?

b. Why does sodium carbonate make the electrolysis reaction go more rapidly?
QUESTIONS AND PROBLEMS

Redox Chemistry Revisited and Electrochemical Cells

CONCEPT REVIEW

17.9. What is meant by a half-reaction?

17.10. The Zn/Cu reactions in Figures 17.1 and 17.2 are the same. However, the reaction in the cell in Figure 17.2 generates electricity; the reaction in the beaker in Figure 17.1 does not. Why?

17.11. Why can’t a wire perform the same function as a porous separator in an electrochemical cell?

17.12. In a voltaic cell, why is the cathode labeled the positive terminal and the anode the negative terminal?

PROBLEMS

17.13. Balance the following half-reactions by adding the appropriate number of electrons. Identify the oxidation half-reactions and the reduction half-reactions.
   a. $\text{Br}_2(\ell) \rightarrow 2 \text{Br}^{-}(aq)$
   b. $\text{Pb}(s) + 2 \text{Cl}^{-}(aq) \rightarrow \text{PbCl}_2(s)$
   c. $\text{O}_3(g) + 2 \text{H}^{+}(aq) \rightarrow \text{O}_2(g) + \text{H}_2\text{O}(l)$
   d. $\text{H}_2\text{S}(g) \rightarrow \text{S}(s) + 2 \text{H}^{+}(aq)$

17.14. Balance the following half-reactions by adding the appropriate number of electrons. Which are oxidation half-reactions and which are reduction half-reactions?
   a. $\text{Fe}^{2+}(aq) \rightarrow \text{Fe}^{3+}(aq)$
   b. $\text{Ag}(s) \rightarrow \text{Ag}^{+}(aq) + \text{I}^{-}(aq)$
   c. $\text{VO}_2^{+}(aq) + 2 \text{H}^{+}(aq) \rightarrow \text{VO}^{2+}(aq) + \text{H}_2\text{O}(l)$
   d. $\text{I}_2(s) + 6 \text{H}_2\text{O}(l) \rightarrow 2 \text{IO}_3^{-}(aq) + 12 \text{H}^{+}(aq)$

*17.15. Groundwater Chemistry Write a half-reaction for the oxidation of magnetite ($\text{Fe}_3\text{O}_4$) to hematite ($\text{Fe}_2\text{O}_3$) in acidic groundwater. Add $\text{H}_2\text{O}$, $\text{H}^+$, and electrons as needed to balance the half-reaction.

*17.16. Write a half-reaction for the oxidation of the manganese in MnCO$_3$ to MnO$_2$ in neutral groundwater where the principal carbonate species is HCO$_3^-$. Add $\text{H}_2\text{O}$, $\text{H}^+$, and electrons as needed to balance the half-reaction.

17.17. A voltaic cell with an aqueous electrolyte is based on the reaction between Pb$^{2+}(aq)$ and Zn(s), producing Pb(s) and Zn$^{2+}(aq)$.
   a. Write half-reactions for the anode and cathode.
   b. Write a balanced cell reaction.
   c. Diagram the cell.

17.18. A voltaic cell is based on the reaction between Ag$^+(aq)$ and Ni(s), producing Ag(s) and Ni$^{2+}(aq)$.
   a. Write the anode and cathode half-reactions.
   b. Write a balanced cell reaction.
17.19. A voltaic cell with a basic aqueous background electrolyte is based on the oxidation of Cd\((s)\) to Cd(OH)\(_2\)(aq) and the reduction of MnO\(_4^-\) (aq) to MnO\(_2\)(s).
   a. Write half-reactions for the cell’s anode and cathode.
   b. Write a balanced cell reaction.
   c. Diagram the cell.

17.20. A voltaic cell is based on the reduction of Ag\(^+\) (aq) to Ag(s) and the oxidation of Sn(s) to Sn\(^2+\) (aq).
   a. Write half-reactions for the cell’s anode and cathode.
   b. Write a balanced cell reaction.
   c. Diagram the cell.

17.21. Super Iron Batteries. In 1999, scientists in Israel developed a battery based on the following cell reaction with iron(VI), nicknamed “super iron”:

   \[ 2 \text{K}_2\text{FeO}_4(aq) + 3 \text{Zn}(s) \rightarrow \text{Fe}_2\text{O}_3(s) + \text{ZnO}(s) + 2 \text{K}_2\text{ZnO}_2(aq) \]

   a. Determine the number of electrons transferred in the cell reaction.
   b. What are the oxidation states of the transition metals in the reaction?
   c. Diagram the cell.

17.22. Aluminum–Air Batteries In recent years engineers have been working on an aluminum–air battery as an alternative energy source for electric vehicles. The battery consists of an aluminum anode, which is oxidized to solid aluminum hydroxide, immersed in an electrolyte of aqueous KOH. At the cathode, oxygen from the air is reduced to hydroxide ions on an inert metal surface. Write the two half-reactions for the battery and diagram the cell. Use the generic M\((s)\) symbol for the metallic cathode material.

### Standard Potentials

**CONCEPT REVIEW**

17.23. In some textbooks the formula used to calculate standard cell potentials from the standard reduction potentials of the half-reactions occurring at the cathode and anode is given as

   \[ E^{\circ}_{\text{cell}} = E^{\circ}_{\text{reduction (cathode)}} + E^{\circ}_{\text{oxidation (anode)}} \]

   Show how this equation is equivalent to Equation 17.1.

*17.24. Why is O\(_2\) a stronger oxidizing agent in acid than in base? Use standard reduction potentials from Appendix 6 to support your answer.*

### PROBLEMS

17.25. Using standard reduction potentials from Appendix 6, and the following equations for half-reactions:

   \[ \text{Cu}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Cu}(s) \]
   \[ \text{Co}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Co}(s) \]
   \[ \text{Hg}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Hg}(s) \]

   a. Identify the combination of half-reactions that would lead to the largest value of \(E^{\circ}_{\text{cell}}\).
   b. Identify the combination of half-reactions that would lead to the smallest positive value of \(E^{\circ}_{\text{cell}}\).

17.26. From the table of standard reduction potentials in Appendix 6,

   a. Select an oxidizing agent that will oxidize Cr\((s)\) to Cr\(^{3+}\) (aq) but not Cd\((s)\) to Cd\(^{2+}\) (aq).
   b. Select a reducing agent that will reduce Br\(_2\) (aq) to Br\(^-\) (aq) but not I\(_2\) (aq) to I\(^-\) (aq).

17.27. If a piece of silver is placed in a solution in which \([\text{Ag}^{+}] = [\text{Cu}^{2+}] = 1.00 \text{ M}\), will the following reaction proceed spontaneously?

   \[ 2 \text{Ag}(s) + \text{Cu}^{2+}(aq) \rightarrow 2 \text{Ag}^+(aq) + \text{Cu}(s) \]

17.28. A piece of cadmium is placed in a solution in which \([\text{Cd}^{2+}] = [\text{Sn}^{2+}] = 1.00 \text{ M}\). Will the following reaction proceed spontaneously?

   \[ \text{Cd}(s) + \text{Sn}^{2+}(aq) \rightarrow \text{Cd}^{2+}(aq) + \text{Sn}(s) \]

17.29. In a voltaic cell similar to the Zn/Cu\(^{2+}\) cell in Figure 17.2, the Cu electrode is replaced with one made
of Ni immersed in a solution of NiSO₄. Will the standard potential of this cell be greater than, the same as, or less than 1.10 V?

17.30. Suppose the copper half of the Zn/Cu²⁺ cell in Figure 17.2 was replaced with a silver wire in contact with 1 M Ag⁺(aq).
   a. What would be the value of $E^\circ_{\text{cell}}$?
   b. Which electrode would be the anode?

17.31. Voltaic cells based on the following pairs of half-reactions are prepared so that all reactants and products are in their standard states. For each pair, write a balanced equation for the cell reaction, and identify which half-reaction takes place at the anode and which at the cathode.
   a. Hg²⁺(aq) + 2 e⁻ → Hg(l)
      Zn²⁺(aq) + 2 e⁻ → Zn(s)
   b. ZnO(s) + H₂O(l) + 2 e⁻ → Zn(s) + 2 OH⁻(aq)
      Ag₂O(s) + H₂O(l) + 2 e⁻ → 2 Ag(s) + 2 OH⁻(aq)
   c. Ni(OH)₂(s) + 2 e⁻ → Ni(s) + 2 OH⁻(aq)
      O₂(g) + 2 H₂O(l) + 4 e⁻ → 4 OH⁻(aq)

17.32. Voltaic cells based on the following pairs of half-reactions are constructed. For each pair, write a balanced equation for the cell reaction, and identify which half-reaction takes place at each anode and cathode.
   a. Cd²⁺(aq) + 2 e⁻ → Cd(s)
      Ag⁺(aq) + e⁻ → Ag(s)
   b. AgBr(s) + e⁻ → Ag(s) + Br⁻(aq)
      MnO₂(s) + 4 H⁺(aq) + 2 e⁻ → Mn²⁺(aq) + 2 H₂O(l)
   c. PtCl₂⁺(aq) + 2 e⁻ → Pt(s) + 4 Cl⁻(aq)
      AgCl(s) + e⁻ → Ag(s) + Cl⁻(aq)

**Chemical Energy and Electrical Work**

**CONCEPT REVIEW**

17.33. The negative sign in Equation 17.3 (w_elec = $-\Delta G$) seems to indicate that a voltaic cell with a positive cell potential does negative electrical work. How is this possible?

*17.34. Mechanical work (w) is done by exerting a force (F) to move an object through a distance (d) according to the equation $w = F \cdot d$. Explain how this definition of work relates to electrical work.

**PROBLEMS**

17.35. Starting with the appropriate standard free energies of formation from Appendix 4, calculate the value of $\Delta G^\circ$ and $E^\circ_{\text{cell}}$ of the following reactions:
   a. 2 Cu⁺(aq) → Cu²⁺(aq) + Cu(s)
   b. Ag(s) + Fe³⁺(aq) → Ag⁺(aq) + Fe²⁺(aq)

17.36. Starting with the appropriate standard free energies of formation from Appendix 4, calculate the values of $\Delta G^\circ$ and $E^\circ_{\text{cell}}$ of the following reactions:
   a. FeO(s) + H₂(g) → Fe(s) + H₂O(l)
   b. 2 Pb(s) + O₂(g) + 2 H₂SO₄(aq) → 2 PbSO₄(s) + 2 H₂O(l)

17.37. Flashlights For many years the 1.50 V batteries used to power flashlights were based on the following cell reaction:
   Zn(s) + 2 NH₄Cl(s) + 2 MnO₂(s) → Zn(NH₄)₂Cl₂(s) + Mn₂O₃(s) + H₂O(l)

   What is the value of $\Delta G^\circ_{\text{cell}}$?

17.38. Laptops The first generation of laptop computers was powered by nickel–cadmium (nicad) batteries, which generated 1.20 V based on the following cell reaction:
   Cd(s) + 2 NiO(OH)(s) + 2 H₂O(l) → Cd(OH)₂(s) + 2 Ni(OH)₂(s)

   What is the value of $\Delta G^\circ_{\text{cell}}$?

17.39. The cells in the nickel–metal hydride battery packs used in many hybrid vehicles produce 1.20 V based on the following cell reaction:
   MH(s) + NiO(OH)(s) → M(s) + Ni(OH)₂(s)

   What is the value of $\Delta G^\circ_{\text{cell}}$?
17.40. A cell in a lead–acid battery delivers exactly 2.00 V of cell potential based on the following cell reaction:

\[
Pb(s) + PbO_2(s) + 2 H_2SO_4(aq) \rightarrow 2 PbSO_4(s) + 2 H_2O(l)
\]

What is the value of \( \Delta G_{\text{cell}} \)?

17.41. Starting with standard potentials listed in Appendix 6, calculate the values of \( E^{\circ}_{\text{cell}} \) and \( \Delta^oG \) of the following reactions.

a. \( \text{Cu}(s) + \text{Sn}^{2+}(aq) \rightarrow \text{Cu}^{2+}(aq) + \text{Sn}(s) \)

b. \( \text{Zn}(s) + \text{Ni}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Ni}(s) \)

17.42. Starting with the standard potentials listed in Appendix 6, calculate the values of \( E^{\circ}_{\text{cell}} \) and \( \Delta^oG \) of the following reactions.

a. \( \text{Fe}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{Cu}(s) \)

b. \( \text{Ag}(s) + \text{Fe}^{3+}(aq) \rightarrow \text{Ag}^+(aq) + \text{Fe}^{2+}(aq) \)

A Reference Point: The Standard Hydrogen Electrode

CONCEPT REVIEW

17.43. What is the function of platinum in the standard hydrogen electrode?

17.44. Is it possible to build a battery in which the anode chemistry is based on a half-reaction in which none of the species is a solid conductor? For example,

\[
\text{Fe}^{3+}(aq) \rightarrow \text{Fe}^{2+}(aq) + e^-
\]

The Effect of Concentration on \( E^{\circ}_{\text{cell}} \)

CONCEPT REVIEW

17.45. Why does the operating cell potential of most batteries change little until the battery is nearly discharged?

17.46. The standard potential of the Zn/Cu\(^{2+} \) cell reaction

\[
\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)
\]

is 1.10 V. Would the potential of the cell differ from 1.10 V if the concentrations of both Cu\(^{2+} \) and Zn\(^{2+} \) were 0.25 M?

PROBLEMS

17.47. Calculate the \( E^{\circ}_{\text{cell}} \) value at 298 K for the cell based on the reaction

\[
\text{Fe}^{3+}(aq) + \text{Cr}^{3+}(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{Cr}^{3+}(aq)
\]

when \([\text{Fe}^{3+}] = [\text{Cr}^{3+}] = 1.50 \times 10^{-3} \text{ M} \) and \([\text{Fe}^{2+}] = [\text{Cr}^{3+}] = 2.5 \times 10^{-4} \text{ M} \).

17.48. Calculate the \( E^{\circ}_{\text{cell}} \) value at 298 K for the cell based on the reaction

\[
\text{Cu}(s) + 2 \text{Ag}^+(aq) \rightarrow \text{Cu}^{2+}(aq) + 2 \text{Ag}(s)
\]

when \([\text{Ag}^+] = 2.56 \times 10^{-3} \text{ M} \) and \([\text{Cu}^{2+}] = 8.25 \times 10^{-4} \text{ M} \).

17.49. Using the appropriate standard potentials from Appendix 6, determine the equilibrium constant for the following reaction at 298 K:

\[
\text{Fe}^{3+}(aq) + \text{Cr}^{3+}(aq) \rightarrow \text{Fe}^{2+}(aq) + \text{Cr}^{3+}(aq)
\]

17.50. Using the appropriate standard potentials from Appendix 6, determine the equilibrium constant at 298 K for the following reaction between MnO\(_2\) and Fe\(^{3+}\) in acid solution:

\[
4 \text{H}^+(aq) + \text{MnO}_2(s) + 2 \text{Fe}^{2+}(aq) \rightarrow \text{Mn}^{2+}(aq) + 2 \text{Fe}^{3+}(aq) + 2 \text{H}_2\text{O}(l)
\]

17.51. If the potential of a hydrogen electrode based on the half-reaction

\[
2 \text{H}^+(aq) + 2 e^- \rightarrow \text{H}_2(g)
\]

is 0.000 V at pH = 0.00, what is the potential of the same electrode at pH = 7.00?

17.52. Glucose Metabolism The standard potentials for the reduction of nicotinamide adenine dinucleotide (NAD\(^+\)) and oxaloacetate (reactants in the multistep metabolism of glucose) are as follows:

\[
\text{NAD}^+(aq) + 2 \text{H}^+(aq) + 2 e^- \rightarrow \text{NADH}(aq) + \text{H}^+(aq)
\]
Oxaloacetate(aq) + 2 H⁺(aq) + 2 e⁻ → malate(aq)  \[ E° = -0.320 \text{ V} \]

\[ E° = -0.166 \text{ V} \]

molate(aq) + NAD⁺(aq)

17.53. Permanganate ion can oxidize sulfite to sulfate in basic solution as follows:
\[
2 \text{MnO}_4^- (aq) + 3 \text{SO}_3^{2-} (aq) + \text{H}_2\text{O}(l) \rightarrow 2 \text{MnO}_2(s) + 3 \text{SO}_4^{2-} (aq) + 2 \text{OH}^- (aq)
\]

Determine the potential for the reaction \( E_{\text{rxn}} \) at 298 K when the concentrations of the reactants and products are as follows: \([\text{MnO}_4^-] = 0.150 \text{ M}, [\text{SO}_3^{2-}] = 0.256 \text{ M}, [\text{SO}_4^{2-}] = 0.178 \text{ M}, \) and \([\text{OH}^-] = 0.0100 \text{ M}\). Will the value of \( E_{\text{rxn}} \) increase or decrease as the reaction proceeds?

17.54. Manganese dioxide is reduced by iodide ion in acid solution as follows:
\[
\text{MnO}_2(s) + 2 \text{I}^- (aq) + 4 \text{H}^+(aq) \rightarrow \text{Mn}^{2+}(aq) + \text{I}_2(aq) + 2 \text{H}_2\text{O}(l)
\]

Determine the electrical potential of the reaction at 298 K when the initial concentrations of the components are as follows: \([\text{I}^-] = 0.225 \text{ M}, [\text{H}^+] = 0.900 \text{ M}, [\text{Mn}^{2+}] = 0.100 \text{ M}, \) and \([\text{I}_2] = 0.00114 \text{ M}\). If the solubility of iodine in water is approximately 0.114 M, will the value of \( E_{\text{rxn}} \) increase or decrease as the reaction proceeds?

17.55. A copper penny dropped into a solution of nitric acid produces a mixture of nitrogen oxides. The following reaction describes the formation of NO, one of the products:
\[
3 \text{Cu}(s) + 8 \text{H}^+(aq) + 2 \text{NO}_3^-(aq) \rightarrow 2 \text{NO}(g) + 3 \text{Cu}^{2+}(aq) + 4 \text{H}_2\text{O}(l)
\]

a. Starting with the appropriate standard potentials from Appendix 6, calculate \( E_{\text{rxn}} \) for this reaction.

b. Calculate \( E_{\text{rxn}} \) at 298 K when \([\text{H}^+] = 0.100 \text{ M}, [\text{NO}_3^-] = 0.0250 \text{ M}, [\text{Cu}^{2+}] = 0.0375 \text{ M}, \) and the partial pressure of NO = 0.00150 atm.

17.56. Chlorine dioxide (ClO₂) is produced by the following reaction of chlorate (ClO₃⁻) with Cl⁻ in acid solution:
\[
2 \text{ClO}_3^-(aq) + 2 \text{Cl}^-(aq) + 4 \text{H}^+(aq) \rightarrow 2 \text{ClO}_2(g) + \text{Cl}_2(g) + 2 \text{H}_2\text{O}(l)
\]

a. Determine \( E° \) for the reaction.

b. The reaction produces a mixture of gases in the reaction vessel in which \( P_{\text{ClO}_2} = 2.0 \text{ atm} \); \( P_{\text{Cl}_2} = 1.00 \text{ atm} \). Calculate \([\text{ClO}_2^-]\) if, at equilibrium \((T = 298 \text{ K})\), \([\text{H}^+] = [\text{Cl}^-] = 10.0 \text{ M}\).

*17.57. The oxidation of NH₄⁺ to NO₃⁻ in acid solution is described by the following equation:
\[
\text{NH}_4^+(aq) + 2 \text{O}_2(g) \rightarrow \text{NO}_3^-(aq) + 2 \text{H}^+(aq) + \text{H}_2\text{O}(l)
\]

a. Calculate \( E° \) for the overall reaction.

b. If the reaction is in equilibrium with air \((P_{\text{O}_2} = 0.21 \text{ atm})\) at pH 5.60, what is the ratio of \([\text{NO}_3^-]\) to \([\text{NH}_4^+]\) at 298 K?

17.58. What is the value of \( E° \) for the following reaction?
\[
2 \text{AgCl(s)} + \text{H}_2(g) \rightarrow 2 \text{Ag(s)} + 2 \text{HCl(aq)}
\]

Relating Battery Capacity to Quantities

**CONCEPT REVIEW**

17.59. One 12-volt lead–acid battery has a higher ampere-hour rating than another. Which of the following parameters are likely to be different for the two batteries?
a. Individual cell potentials
b. Anode half-reactions
c. Total masses of electrode materials
d. Number of cells
e. Electrolyte composition
f. Combined surface areas of their electrodes

17.60. In a voltaic cell based on the \( \text{Zn}/\text{Cu}^{2+} \) cell reaction,
\[
\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq)
\]
there is exactly 1 mole of each reactant and product. A second cell based on this cell reaction:
\[
\text{Cd}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Cu}(s) + \text{Cd}^{2+}(aq)
\]
also has exactly 1 mole of each reactant and product. Which of the following statements about these two cells is true?

a. Their cell potentials are the same.
b. The masses of their electrodes are the same.
c. The quantities of electric charge that they can produce are the same.
d. The quantities of electric energy that they can produce are the same.

PROBLEMS

17.61. Which of the following voltaic cells will produce the greater quantity of electric charge per gram of anode material?
\[
\text{Cd}(s) + 2 \text{NiO(OH)}(s) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{Ni(OH)}_2(s) + \text{Cd(OH)}_2(s)
\]
or
\[
4 \text{Al}(s) + 3 \text{O}_2(g) + 6 \text{H}_2\text{O}(l) + 4 \text{OH}^-(aq) \rightarrow 4 \text{Al(OH)}_4^-(aq)
\]

17.62. Which of the following voltaic cells will produce the greater quantity of electric charge per gram of anode material?
\[
\text{Zn}(s) + \text{MnO}_2(s) + \text{H}_2\text{O}(l) \rightarrow \text{ZnO}(s) + \text{Mn(OH)}_2(s)
\]
or
\[
\text{Li}(s) + \text{MnO}_2(s) \rightarrow \text{LiMnO}_2(s)
\]

17.63. Which of the following voltaic cell reactions delivers more electrical energy per gram of anode material at 298 K?
\[
\text{Zn}(s) + 2 \text{NiO(OH)}(s) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{Ni(OH)}_2(s) + \text{Zn(OH)}_2(s) \quad E^\circ_{\text{cell}} = 1.20 \text{ V}
\]
or
\[
\text{Li}(s) + \text{MnO}_2(s) \rightarrow \text{LiMnO}_2(s) \quad E^\circ_{\text{cell}} = 3.15 \text{ V}
\]

17.64. Which of the following voltaic cell reactions delivers more electrical energy per gram of anode material at 298 K?
\[
\text{Zn}(s) + \text{Ni(OH)}_2(s) \rightarrow \text{Zn(OH)}_2(s) + \text{Ni}(s) \quad E^\circ_{\text{cell}} = 1.50 \text{ V}
\]
or
\[
2 \text{Zn}(s) + 6 \text{H}_2\text{O}(l) + 6 \text{OH}^-(aq) \rightarrow 2 \text{Zn(OH)}_4^{2-}(aq) \quad E^\circ_{\text{cell}} = 2.08 \text{ V}
\]

Electrolytic Cells and Rechargeable Batteries

CONCEPT REVIEW

17.65. The positive terminal of a voltaic cell is the cathode. However, the cathode of an electrolytic cell is connected to the negative terminal of a power supply. Explain this difference in polarity.

17.66. The anode in an electrochemical cell is defined as the electrode where oxidation takes place. Why is the anode in an electrolytic cell connected to the positive (+) terminal of an external supply, whereas the anode in a voltaic cell battery is connected to the negative (−) terminal?

17.67. The salts obtained from the evaporation of seawater can act as a source of halogens, principally Cl\(_2\) and Br\(_2\), through the electrolysis of the molten alkali metal halides. As the potential of the anode in an electrolytic cell is increased, which of these two halogens forms first?
In the electrolysis described in Problem 17.67, why is it necessary to use molten salts rather than seawater itself?

Quantitative Analysis  Electrolysis can be used to determine the concentration of Cu\(^{2+}\) in a given volume of solution by electrolyzing the solution in a cell equipped with a platinum cathode. If all of the Cu\(^{2+}\) is reduced to Cu metal at the cathode, the increase in mass of the electrode provides a measure of the concentration of Cu\(^{2+}\) in the original solution. To ensure the complete (99.99\%) removal of the Cu\(^{2+}\) from a solution in which [Cu\(^{2+}\)] is initially about 1.0 \(\text{M}\), will the potential of the cathode (versus SHE) have to be more negative or less negative than 0.34 \(\text{V}\) (the standard potential for Cu\(^{2+}\) + 2 e\(^-\) → Cu)?

A high school chemistry student wishes to demonstrate how water can be separated into hydrogen and oxygen by electrolysis. She knows that the reaction will proceed more rapidly if an electrolyte is added to the water. She has access to 2.00 \(\text{M}\) solutions of these compounds: \(\text{H}_2\text{SO}_4\), \(\text{HBr}\), NaI, NaCl, \(\text{Na}_2\text{SO}_4\), and \(\text{Na}_2\text{CO}_3\) Which one(s) should she use? Explain your selection(s).

Suppose the current from a battery is used to electroplate an object with silver. Calculate the mass of silver that would be deposited by a battery that delivers 1.7 \(\text{A}\) a hr of charge.

A battery charger used to recharge the NiMH batteries in a digital camera can deliver as much as 0.50 \(\text{A}\) of current to each battery. If it takes 100 min to recharge one battery, how much Ni(OH)\(_2\) (in grams) is oxidized to NiO(OH)?

A quantity of electric charge deposits 0.732 g of Ag(s) from an aqueous solution of silver nitrate. When that same quantity of charge is passed through a solution of a gold salt, 0.446 g of Au(s) is formed. What is the oxidation state of the gold ion in the salt?

What amount of current is required to deposit 0.750 g of Pt(s) from a solution containing the [PtCl\(_4\)]\(^{-2}\) ion within a time of 2.5 hours?

A NiMH battery containing 4.10 g of NiO(OH) is 50% discharged when it is connected to a charger with an output of 2.00 \(\text{A}\) at 1.3 \(\text{V}\). How long does it take to recharge the battery?

How long does it take to deposit a coating of gold 1.00 \(\mu\text{m}\) thick on a disk-shaped medallion 4.0 cm in diameter and 2.0 mm thick at a constant current of 85 \(\text{A}\)? The density of the electroplating process is 19.3 \(\text{g/cm}^2\). The electroplating solution contains gold(III). Why are electrolytes needed? What are the other compounds that could be used?

Oxygen Supply in Submarines Nuclear submarines can stay under water nearly indefinitely because they can produce their own oxygen by the electrolysis of water. a. How many liters of \(\text{O}_2\) at 298 K and 1.00 \(\text{bar}\) are produced in 1 hr in an electrolytic cell operating at a current of 0.025 \(\text{A}\)? b. Could seawater be used as the source of oxygen in this electrolysis? Explain why or why not.

In the electrolysis of water, how long will it take to produce 125 liters of \(\text{H}_2\) at 20\(^\circ\)C and a pressure of 750 torr using an electrolytic cell through which the current is 52 \(\text{mA}\)?

Calculate the minimum (least negative) cathode potential (versus SHE) needed to begin electroplating nickel from 0.35 \(\text{M}\) Ni\(^{3+}\) onto a piece of iron.

What is the minimum (least negative) cathode potential (versus SHE) needed to electroplate silver onto cutlery in a solution of Ag\(^+\) and NH\(_3\) in which most of the silver ions are present as the complex Ag(NH\(_2\))\(_2\)\(^+\) and the concentration of Ag\(^+\)(aq) is only 3.50 \(\times\) \(10^{-5}\) M?

**Fuel Cells**

**CONCEPT REVIEW**

Describe two advantages of hybrid (gasoline engine–electric motor) power systems over all-electric systems based on fuel cells. Describe two disadvantages.

Describe three factors limiting the more widespread use of cars and other vehicles powered by fuel cells.

Methane can serve as the fuel for electric cars powered by fuel cells. Carbon dioxide is a product of the fuel cell reaction. All cars powered by internal combustion engines burning natural gas (mostly methane) produce CO\(_2\). Why are electric vehicles powered by fuel cells likely to produce less CO\(_2\) per mile?

To make the refueling of fuel cells easier, several manufacturers are developing converters that turn readily available fuels—such as natural gas, propane, and methanol—into \(\text{H}_2\) and CO\(_2\). Although vehicles with such power systems are not truly “zero emission,” they still offer significant environmental benefits over vehicles powered by internal combustion engines. Describe a few of
Fuel cells with molten alkali metal carbonates as electrolytes can use methane as a fuel. The methane is first converted into hydrogen in a two-step process:

\[
\begin{align*}
\text{CH}_4(g) + \text{H}_2\text{O}(g) & \rightarrow \text{CO}(g) + 3 \text{H}_2(g) \\
\text{CO}(g) + \text{H}_2\text{O}(g) & \rightarrow \text{H}_2(g) + \text{CO}_2(g)
\end{align*}
\]

a. Assign oxidation numbers to carbon and hydrogen in the reactants and products.
b. Using the standard free energy of formation values from Appendix 4, calculate the standard free energy changes in the two reactions and the overall \( \Delta G^\circ \) for the formation of \( \text{H}_2 + \text{CO}_2 \) from methane and steam.

Molten carbonate fuel cells fueled with \( \text{H}_2 \) convert as much as 60% of the free energy released by the formation of water from \( \text{H}_2 \) and \( \text{O}_2 \) into electrical energy. Determine the quantity of electrical energy obtained from converting 1 mole of \( \text{H}_2 \) into \( \text{H}_2\text{O}(l) \) in such a fuel cell.

Suppose there were a scale for expressing electrode potentials in which the standard potential for the reduction of water in base:

\[
2 \text{H}_2\text{O}(l) + 2 e^- \rightarrow \text{H}_2(g) + 2 \text{OH}^- (aq)
\]

was assigned an \( E^\circ \) value of 0.000 V. How would the standard potential values on this new scale differ from those in Appendix 6?

To inhibit corrosion of steel structures in contact with seawater, pieces of other metals (often zinc) are attached to the structures to serve as “sacrificial anodes.” Explain how these attached pieces of metal might protect the structures, and describe which properties of zinc make it a good selection.

Sometimes the anode half-reaction in the zinc–air battery (Figure 17.6) is written with zincate ion, \( \text{Zn(OH)}_4^{2-} \), as the product. Write a balanced equation for the cell reaction based on this product.

Solar-Powered Lamps Rechargeable nickel–cadmium (nicad) batteries are used to store energy in solar-powered landscape lamps (Figure P17.90). The batteries contain Cd anodes and cathodes made of NiO(OH). The products of the cell reaction include cadmium(II) and nickel(II) hydroxide. Write a net ionic equation describing the cell reaction.

The half-reactions and standard potentials for a nickel–metal hydride battery with a titanium–zirconium anode are as follows:

\[
\begin{align*}
\text{Cathode:} & \quad \text{NiO(OH)}(s) + \text{H}_2\text{O}(l) + e^- \rightarrow \text{Ni(OH)}_2(s) + \text{OH}^- (aq) \quad E^\circ = 1.32 \text{ V} \\
\text{Anode:} & \quad \text{TiZr}_2\text{H}(s) + \text{OH}^- (aq) \rightarrow \text{TiZr}_2(s) + \text{H}_2\text{O}(l) + e^- \quad E^\circ = 0.00 \text{ V}
\end{align*}
\]

a. Write the overall cell reaction for this battery.
b. Calculate the standard cell potential.

Scientists at the University of Texas, Austin, and at MIT developed a cathode material for lithium–ion batteries based on LiFePO₄, which is the composition of the cathode when
the battery is fully discharged. Batteries with this cathode are more powerful than those of the same mass with LiCoO₂ cathodes. They are also more stable at high temperatures.

a. What is the formula of the LiFePO₄ cathode when the battery is fully charged?
b. Is Fe oxidized or reduced as the battery discharges?
c. Is the cell potential of a lithium–ion battery with an iron phosphate cathode likely to differ from one with a cobalt oxide cathode? Explain your answer.

17.93. Describe in your own words the meaning of this cell diagram:

\[
\begin{array}{c|c}
\text{Sn(s)} & \text{Sn}^{2+}(aq) (0.025 M) \parallel \text{Ag}^+(aq) (0.010 M) \parallel \text{Ag(s)} \\
\end{array}
\]

Start your description with “The cell consists of a tin anode, which is...”

17.94. In a NiMH battery, what are the oxidation states of (a) Ni in NiO(OH), (b) H in MH, (c) M in MH, and (d) H in H₂O?

17.95. A magnesium battery can be constructed from an anode of magnesium metal and a cathode of molybdenum sulfide, Mo₃S₄. The half-reactions are:

Anode: \( \text{Mg(s)} \rightarrow \text{Mg}^{2+}(aq) + 2e^- \quad E_{\text{anode}} = 2.37 \text{ V} \)

Cathode: \( \text{Mg}^{2+}(aq) + \text{Mo}_3\text{S}_4(s) + 2e^- \rightarrow \text{MgMo}_3\text{S}_4(s) \)

\( E_{\text{cathode}} = ? \)

a. If the standard cell potential for the battery is 1.50 \text{ V}, what is the value of \( E^0 \) for the reduction of \( \text{Mg}_2\text{S}_3? \)
b. What are the apparent oxidation states and electron configurations of Mo in \( \text{Mo}_3\text{S}_4 \) and in \( \text{MgMo}_3\text{S}_4? \)
c. The electrolyte in the battery contains a complex magnesium salt, \( \text{Mg(AlCl}_3\text{CH}_3)_2 \). Why is it necessary to include \( \text{Mg}^{2+} \) ions in the electrolyte?

17.96. Clinical Chemistry The concentration of Na⁺ ions in red blood cells (11 m\text{M}) and in the surrounding plasma (140 m\text{M}) are quite different. Calculate the electrochemical potential (emf) across the cell membrane at 37°C as a result of this concentration gradient.

*17.97. The element fluorine, F₂, was first produced in 1886 by electrolysis of HF. Chemical syntheses of F₂ did not happen until 1986 when Karl O. Christe successfully prepared F₂ by this reaction:

\[ \text{K}_2\text{MnF}_6(s) + 2 \text{SbF}_5(l) \rightarrow 2 \text{KSbF}_6(s) + \text{MnF}_3(s) + 1/2 \text{F}_2(g) \]

a. Assign oxidation numbers to each compound and determine the number of electrons involved in the process.
b. Using the following \( \Delta H_f^o \) values, calculate \( \Delta H_f^o \) for the reaction.

\[
\begin{align*}
\Delta H_f^o \text{KSbF}_6(l) &= -1324 \text{ kJ/mol} \\
\Delta H_f^o \text{MnF}_3(l) &= -2435 \text{ kJ/mol} \\
\Delta H_f^o \text{K}_2\text{MnF}_6(l) &= -1579 \text{ kJ/mol} \\
\Delta H_f^o \text{SbF}_5(l) &= -2080 \text{ kJ/mol}
\end{align*}
\]

c. If we assume that \( \Delta S \) is relatively small, such that \( \Delta G = \Delta H \), estimate \( E^o \) for this reaction.
d. If \( \Delta S \) for the reaction is greater than zero, is our value for \( E^o \) in part c too high or too low?
e. The electrochemical synthesis of F₂ is described by the electrolytic cell reaction:

\[ 2 \text{KF}_2(l) \rightarrow 2 \text{KF}(l) + \text{H}_2(g) + \text{F}_2(g) \]

Assign oxidation numbers and determine the number of electrons involved in this process.

17.98. Corrosion of Copper Pipes The copper pipes frequently used in household plumbing may corrode and eventually leak. The corrosion reaction is believed to involve the formation of copper(I) chloride:

\[ 2 \text{Cu(s)} + \text{Cl}_2(aq) \rightarrow 2 \text{CuCl}(s) \]

a. Write balanced equations for the half-reactions in this redox reaction.
b. Calculate \( E^o_{\text{red}} \) and \( \Delta G^o_{\text{red}} \) for the reaction.

17.99. Elemental uranium may be produced from uranium dioxide by the following two-step process:

\[ \text{UO}_2(s) + 4 \text{HF}(g) \rightarrow \text{UF}_4(s) + 2 \text{H}_2\text{O}(l) \]

\[ \text{UF}_4(s) + 2 \text{Mg}(s) \rightarrow \text{U}(s) + 2 \text{MgF}_2(aq) \]

a. Identify the reducing agent.
b. Identify the element that is reduced.
c. Using data from the table of standard reduction potentials in Appendix 6, find the maximum \( E^o \) value for the reduction of UF₄ for the second reaction.
d. Will 1.00 g of Mg(s) be sufficient to produce 1.00 g of uranium?

17.100. Which element is oxidized and which is reduced in the lithium–ion cell reaction described by Equation 17.13?

*17.101. Electrolysis of Seawater Magnesium metal is obtained by the electrolysis of molten Mg²⁺ salts obtained from evaporated seawater.

a. Does elemental Mg form at the cathode or anode?
b. Do you think the principal ingredient in sea salt (NaCl) needs to be separated from the Mg$^{2+}$ salts before electrolysis? Explain your answer.

c. Would electrolysis of an aqueous solution of MgCl$_2$ also produce elemental Mg?

d. If your answer to part c was no, what would the products of electrolysis be?

17.102. Silverware Tarnish  Low concentrations of hydrogen sulfide in air react with silver to form Ag$_2$S, more familiar to us as tarnish. Silver polish contains aluminum metal powder in a basic suspension.

a. Write a balanced net ionic equation for the redox reaction between Ag$_2$S and Al metal that produces Ag metal and Al(OH)$_3$.

b. Calculate $E^\circ$ for the reaction. Hint: Derive $E^\circ$ values for the half-reactions in which Ag$_2$S is reduced to Ag metal and Al(OH)$_3$ is reduced to Al metal. Then, replace the [Ag$^+$] and [Al$^{3+}$] terms in the Nernst equations for these two half-reactions with terms based on the $K_{sp}$ values of Ag$_2$S and Al(OH)$_3$ and the concentrations of sulfide and hydroxide ions (both of which are equal to one molar under standard conditions).
VISUAL PROBLEMS

(Answers to boldface end-of-chapter questions and problems are in the back of the book.)

21.1. Which of the highlighted elements in Figure P21.1 currently plays a key role in the controlled fusion of hydrogen?

21.2. Exposure to which of the highlighted elements in Figure P21.1 could cause anemia and bone disease?

21.3. Which of the highlighted elements in Figure P21.1 are products of the decay of uranium-238?

21.4. Which of the graphs in Figure P21.4 illustrates $\alpha$ decay? Which decay pathway does the other graph illustrate?

21.5. Which of the graphs in Figure P21.5 illustrates $\beta$ decay?

21.6. Which of the graphs in Figure P21.6 illustrates the overall effect of neutron capture followed by $\beta$ decay?

21.7. Which of the curves in Figure P21.7 represents the decay of an isotope that has a half-life of 2.0 days?
21.8. Which of the curves in Figure P21.7 do not represent a radioactive decay curve?

21.9. Which of the models in Figure P21.9 represents fission and which represents fusion?

21.10. Isotopes in a nuclear decay series emit particles with a positive charge and particles with a negative charge. The two kinds of particles penetrate a column of water as shown in Figure P21.10. Is the “X” particle the positive or the negative one?

**QUESTIONS AND PROBLEMS**

**Fusion and the Quest for Clean Energy**

**CONCEPT REVIEW**

21.11. Arrange the following particles in order of increasing mass: electron, ß particle, positron, proton, neutron, α particle, deuteron.

21.12. Electromagnetic radiation is emitted when a neutron and proton fuse to make a deuteron. In which region of the electromagnetic spectrum is the radiation?

21.13. Scientists at the Fermi National Accelerator Laboratory in Illinois announced in the fall of 1996 that they had created “antihydrogen.” How does antihydrogen differ from hydrogen?


21.15. In what ways are the fusion reactions that formed alpha particles during primordial nucleosynthesis different from those that fuel our sun today?

21.16. How are the fusion reactions that are the basis for power production in the tokamak described in Section 21.2 different from those that power our sun?

**PROBLEMS**

21.17. Calculate the energy and wavelength of the two gamma rays released by the annihilation of a proton and an antiproton.

21.18. Calculate the energy released and the wavelength of the two photons emitted in the annihilation of an electron and a positron.

21.19. All of the following fusion reactions produce ²⁸Si. Calculate the energy released in each reaction from the masses of the isotopes: ⁷H (2.0146 amu), ⁴He (4.00260 amu), ¹⁰B (10.0129 amu), ¹²C (12.00 amu), ¹⁴N (14.00307 amu), ¹⁶O (15.99491 amu), ²⁴Mg (23.98504 amu), ²⁸Si (27.97693 amu).

a. ¹⁴N + ¹⁴N → ²⁸Si
b. $^{10}\text{B} + ^{16}\text{O} + {^2}\text{H} \rightarrow ^{28}\text{Si}$

21.20. All of the following fusion reactions produce $^{32}\text{S}$. Calculate the energy released in each reaction from the masses of the isotopes: $^{4}\text{He}$ (4.00260 amu), $^{4}\text{Li}$ (6.01512 amu), $^{12}\text{C}$ (12.000 amu), $^{14}\text{N}$ (14.00307 amu), $^{16}\text{O}$ (15.99491 amu), $^{24}\text{Mg}$ (23.98504 amu), $^{28}\text{Si}$ (27.97693 amu), $^{32}\text{S}$ (31.97207 amu).

a. $^{16}\text{O} + ^{16}\text{O} \rightarrow ^{32}\text{S}$
b. $^{28}\text{Si} + ^{4}\text{He} \rightarrow ^{32}\text{S}$
c. $^{14}\text{N} + ^{12}\text{C} + ^{4}\text{He} \rightarrow ^{32}\text{S}$
d. $^{24}\text{Mg} + 2^4\text{He} \rightarrow ^{32}\text{S}$

21.21. Tokamak Radiochemistry How much energy is released per nucleus of tritium produced during the following reactions? The mass of $^3\text{H}$ is 5.00827 × 10^{-27} kg.

a. $^1\alpha + ^3\text{Li} \rightarrow ^2\text{He} + ^3\text{H}$
b. $^1\alpha + ^3\text{Li} \rightarrow ^2\text{He} + ^3\text{H} + ^0\text{neutron}$

21.22. Tokamak Radiochemistry It has been proposed that electrical power production in the future might be based on the fusion of deuterium to helium-4.

a. Write a radiochemical equation describing the reaction (assume that $^4\text{He}$ is the only product).
b. Calculate how much energy is released during the formation of one mole of $^4\text{He}$. The masses of the two nuclides are $^3\text{D} = 2.014102$ amu and $^4\text{He} = 4.002603$ amu.

The Belt of Stability

CONCEPT REVIEW

21.23. How can the belt of stability be used to predict the probable decay mode of an unstable nuclide?


21.25. The ratio of neutrons to protons in stable nuclei increases with increasing atomic number. Use this trend to explain why multiple $\alpha$ decay steps in the $^{238}\text{U}$ decay series are often followed by $\beta$ decay.

21.26. If a $^{10}\text{B}$ nucleus absorbs a proton, the radionuclide that is produced may undergo $\alpha$ decay. What nuclide is produced in the decay process? Is it stable or radioactive?

PROBLEMS

21.27. Iodine-137 decays to give xenon-137, which decays to give cesium-137. What are the modes of decay in these two reactions?

21.28. Write a balanced nuclear equation for:

a. Beta emission by $^{28}\text{Mg}$

b. Alpha emission by $^{255}\text{W}$

c. Electron capture by $^{129}\text{Cs}$

d. Positron emission by $^{25}\text{Al}$

21.29. If the mass number of an isotope is more than twice the atomic number, is the neutron-to-proton ratio less than, greater than, or equal to 1?

21.30. In each of the following pairs of isotopes, which isotope has more protons and which has more neutrons? (a) $^{127}\text{I}$ or $^{131}\text{I}$; (b) $^{186}\text{Re}$ or $^{188}\text{W}$; (c) $^{14}\text{N}$ or $^{15}\text{C}$

21.31. Aluminum atoms in Earth’s crust are all $^{27}\text{Al}$. However, $^{26}\text{Al}$ is formed in stars. It decays to $^{26}\text{Mg}$ with a half-life of 7.4 × 10^5 years. Write an equation describing the decay of $^{26}\text{Al}$ to $^{26}\text{Mg}$.

21.32. Which nuclide is produced by the $\beta$ decay of $^{131}\text{I}$?

21.33. Predict the modes of decay for the following radioactive isotopes: (a) $^{16}\text{C}$; (b) $^{39}\text{Ne}$; (c) $^{20}\text{Ti}$.

21.34. Predict the decay pathways of the following radioactive isotopes: (a) $^{36}\text{Ni}$; (b) $^{36}\text{Sr}$; (c) $^{116}\text{Sb}$.

21.35. Elements in a Supernova The isotopes $^{56}\text{Co}$ and $^{44}\text{Ti}$ were detected in supernova SN 1987A. Predict the decay pathway for these radioactive isotopes.

21.36. Nine isotopes of sulfur have mass numbers ranging from 30 to 38. Five of the nine are radioactive: $^{30}\text{S}$, $^{31}\text{S}$, $^{33}\text{S}$, $^{35}\text{S}$, and $^{38}\text{S}$. Which of these isotopes do you expect to decay by $\beta$ decay?

Rates of Radioactive Decay

PROBLEMS

21.37. What percentage of a sample’s original radioactivity remains after two half-lives?

21.38. What percentage of a sample’s original radioactivity remains after five half-lives?

21.39. What is the half-life of a radionuclide if 87.5% of it decays in 6.6 days?

21.40. What is the half-life of a radionuclide if only 6.25% of it remains after 8 hours and 20 minutes?

21.41. Explosions at a disabled nuclear power station in Fukushima, Japan, in 2011 may have released more cesium-137 ($t_{1/2} = 30.2$ years) into the
ocean than any other single event. How long will it take the radioactivity of this radionuclide to decay to 5.0% of the level released in 2011?

21.42. Spent fuel removed from nuclear power stations contains plutonium-239 ($t_{1/2} = 2.41 \times 10^4$ years). How long will it take a sample of this radionuclide to reach a level of radioactivity that is 2.5% of the level it had when it was removed from a reactor?

**Nuclear Fission**

**CONCEPT REVIEW**

21.43. How is the rate of energy release controlled in a nuclear reactor?

21.44. How does a breeder reactor create fuel and energy at the same time? *21.45. Why are neutrons always by-products of the fission of most massive nuclides? *(Hint: Look closely at the neutron-to-proton ratios shown in Figure 21.2.)*

21.46. Seaborgium (Sg, element 106) is prepared by the bombardment of curium-248 with neon-22, which produces two isotopes, $^{265}$Sg and $^{266}$Sg. Write balanced nuclear reactions for the formation of both isotopes. Are these reactions better described as fusion or fission processes?

**PROBLEMS**

21.47. The fission of uranium produces dozens of isotopes. For each of the following fission reactions, determine the identity of the unknown nuclide:

- a. $^{235}$U + n $\rightarrow ^{90}$Zr + ? + 2 n
- b. $^{235}$U + n $\rightarrow ^{99}$Nb + ? + 4 n
- c. $^{235}$U + n $\rightarrow ^{90}$Rh + ? + 3 n

21.48. For each of the following fission reactions, determine the identity of the unknown nuclide:

- a. $^{235}$U + n $\rightarrow ^{137}$I + ? + 2 n
- b. $^{235}$U + n $\rightarrow ^{137}$Cs + ? + 3 n
- c. $^{235}$U + n $\rightarrow ^{141}$Ce + ? + 2 n

21.49. For each of the following fission reactions, determine the identity of the unknown nuclide:

- a. $^{235}$U + n $\rightarrow ^{131}$I + ? + 2 n
- b. $^{235}$U + n $\rightarrow ^{96}$Ru + ? + 3 n
- c. $^{235}$U + n $\rightarrow ^{92}$Zr + ? + 3 n

21.50. For each of the following fission reactions, determine the identity of the unknown nuclide:

- a. $^{235}$U + n $\rightarrow ^{148}$Pm + ? + 2 n
- b. $^{235}$U + n $\rightarrow ^{97}$Kr + ? + 2 n
- c. $^{235}$U + n $\rightarrow ^{95}$Sr + ? + 3 n

**Measuring Radioactivity; Biological Effects of Radioactivity**

**CONCEPT REVIEW**

21.51. What is the difference between a level of radioactivity and a dose of radioactivity?

21.52. What are some of the molecular effects of exposure to radioactivity?

21.53. Describe the dangers of exposure to radon-222.

21.54. Food Safety Periodic outbreaks of food poisoning from E. coli–contaminated meat have renewed the debate about irradiation as an effective treatment of food. In one newspaper article on the subject, the following statement appeared: “Irradiating food destroys bacteria by breaking apart their molecular structure.” How would you improve or expand on this explanation?

**PROBLEMS**

21.55. Radiation Exposure from Dental X-rays Dental X-rays expose patients to about 5 $\mu$Sv of radiation. Given an RBE of 1 for X-rays, how many grays of radiation does 5 $\mu$Sv represent? For a 50 kg person, how much energy does 5 $\mu$Sv correspond to?

21.56. Radiation Exposure at Chernobyl Some workers responding to the explosion at the Chernobyl nuclear power plant were exposed to 5 Sv of radiation, resulting in death for many of them. If the exposure was primarily in the form of $\gamma$ rays with an energy of $3.3 \times 10^{-14}$ J and an RBE of 1, how many $\gamma$ rays did an 80 kg person absorb?

*21.57. Strontium-90 in Milk* In the years immediately following the explosion at the Chernobyl nuclear power plant, the concentration of $^{90}$Sr in cow’s milk in southern Europe was slightly elevated. Some samples contained as much as 1.25 Bq/L of $^{90}$Sr radioactivity. The half-life of strontium-90 is 28.8 years.

- a. Write a balanced nuclear equation describing the decay of $^{90}$Sr.
- b. How many atoms of $^{90}$Sr are in a 200 mL glass of milk with 1.25 Bq/L of $^{90}$Sr radioactivity?
- c. Why would strontium-90 be more concentrated in milk than other foods, such as grains, fruits, or vegetables?

*21.58. Radium Watch Dials* If exactly 1.00 $\mu$g of $^{226}$Ra was used to paint the glow-in-the-dark dial of a wristwatch made in 1914, how radioactive is the watch today? Express your answer in microcuries and becquerels. The half-life of $^{226}$Ra is $1.60 \times 10^3$ years.

21.59. In 1999, the U.S. Environmental Protection Agency set a maximum radon level for drinking water at 4.0 pCi per milliliter.

- a. How many decay events occur per second in a milliliter of water for this level of radon radioactivity?
- b. If the above radioactivity were due to decay of $^{222}$Rn ($t_{1/2}$ = 3.8 days), how many $^{222}$Rn atoms would there be in 1.0 mL of water?

The other people at his table did not suffer from radiation sickness, even though they were very near the radioactive food the victim ate. Why were they not affected?

Medical Applications of Radionuclides

CONCEPT REVIEW

21.61. How does the selection of an isotope for radiotherapy relate to (a) its half-life, (b) its mode of decay, and (c) the properties of the products of decay?
21.62. Are the same radioactive isotopes likely to be used for both imaging and cancer treatment? Why or why not?

PROBLEMS

21.63. Predict the most likely mode of decay for the following isotopes used as imaging agents in nuclear medicine:
(a) $^{197}$Hg (kidney); (b) $^{75}$Se (parathyroid gland); (c) $^{19}$F (bone).
21.64. Predict the most likely mode of decay for the following isotopes used as imaging agents in nuclear medicine: (a) $^{133}$Xe (cerebral blood flow); (b) $^{51}$Co (tumor detection); (c) $^{51}$Cr (red blood cell mass); (d) $^{67}$Ga (tumor detection).

21.65. A 1.00 mg sample of $^{192}$Ir was inserted into the artery of a heart patient. After 30 days, 0.756 mg remained. What is the half-life of $^{192}$Ir?

21.66. In a treatment that decreases pain and reduces inflammation of the lining of the knee joint, a sample of dysprosium-165 with an radioactivity of 1100 counts per second was injected into the knee of a patient suffering from rheumatoid arthritis. After 24 hr, the radioactivity had dropped to 1.14 counts per second. Calculate the half-life of $^{165}$Dy.

21.67. Treatment of Tourette’s Syndrome Tourette’s syndrome is a condition whose symptoms include sudden movements and vocalizations. Iodine isotopes are used in brain imaging of people suffering from Tourette’s syndrome. To study the uptake and distribution of iodine in cells, mammalian brain cells in culture were treated with a solution containing $^{131}$I with an initial radioactivity of 108 counts per minute. The cells were removed after 30 days, and the remaining solution was found to have a radioactivity of 4.1 counts per minute. Did the brain cells absorb any $^{131}$I ($t_{1/2} = 8.1$ days)?

21.68. A patient is administered mercury-197 to evaluate kidney function. Mercury-197 has a half-life of 65 hr. What fraction of an initial dose of mercury-197 remains after 6 days?

21.69. Carbon-11 is an isotope used in positron-emission tomography and has a half-life of 20.4 min. How long will it take for 99% of the $^{11}$C injected into a patient to decay?

21.70. Sodium-24 is used to treat leukemia and has a half-life of 15 hr. A patient was injected with a salt solution containing sodium-24. What percentage of the $^{24}$Na remained after 48 hr?

21.71. Boron Neutron-Capture Therapy In boron neutron-capture therapy (BNCT), a patient is given a compound containing $^{10}$B that accumulates inside cancer tumors. Then the tumors are irradiated with neutrons, which are absorbed by $^{10}$B nuclei. The product of neutron capture is an unstable form of $^{11}$B that undergoes $\alpha$ decay to $^7$Li.
   a. Write a balanced nuclear equation for the neutron absorption and $\alpha$ decay process.
   b. Calculate the energy released by each nucleus of boron-10 that captures a neutron and undergoes $\alpha$ decay, given the following masses of the particles in the process: $^{10}$B (10.0129 amu), $^7$Li (7.01600 amu), $^8$He (4.00260 amu), and $^1$n (1.00866 amu).
   c. Why is the formation of a nuclide that undergoes $\alpha$ decay a particularly effective cancer therapy?

21.72. Balloon Angioplasty and Arteriosclerosis Balloon angioplasty is a common procedure for unblocking arteries in patients suffering from arteriosclerosis. Iridium-192 therapy is being tested as a treatment to prevent reclogging of the arteries. In the procedure, a thin ribbon containing pellets of $^{192}$Ir is threaded into the artery. The half-life of $^{192}$Ir is 74 days. How long will it take for 99% of the radioactivity from 1.00 mg of $^{192}$Ir to disappear?

Radiometric Dating

CONCEPT REVIEW

21.73. Explain why radiocarbon dating is reliable only for artifacts and fossils younger than about 50,000 years.

21.74. Which of the following statements about $^{14}$C dating are true?
   a. The amount of $^{14}$C in all objects is the same.
   b. Carbon-14 is unstable and is readily lost from the atmosphere.
   c. The ratio of $^{14}$C to $^{12}$C in the atmosphere is a constant.
   d. Living tissue will absorb $^{13}$C but not $^{14}$C.

21.75. Why is $^{26}$K dating ($t_{1/2} = 1.28 \times 10^9$ years) useful only for rocks older than 300,000 years?

21.76. Where does the $^{12}$C found in plants come from?

PROBLEMS

21.77. First Humans in South America Archeologists continue to debate the origins and dates of arrival of the first humans in the Western Hemisphere. Radiocarbon dating of charcoal from a cave in Chile was used to establish the earliest date of human habitation in South America as 8700 years ago. What fraction of the $^{14}$C present initially remained in the charcoal after 8700 years?

21.78. For thousands of years native Americans living along the north coast of Peru used knotted cotton strands called quipu (Figure P21.78) to record financial transactions and governmental actions. A particular quipu sample is 4800 years old. Compared with the fibers of cotton
plants growing today, what is the ratio of carbon-14 to carbon-12 in the sample?

![Figure P21.78](image1)

*21.79. Figure P21.79 is a close-up of the center of a giant sequoia tree cut down in 1891 in what is now Kings Canyon National Park. It contained 1342 annual growth rings. If samples of the tree were removed for radiocarbon dating today, what would be the difference in $^{14}\text{C}/^{12}\text{C}$ ratio in the innermost (oldest) ring compared with that ratio in the youngest ring?

![Figure P21.79](image2)

*21.80. Geologists who study volcanoes can develop historical profiles of previous eruptions by determining the $^{14}\text{C}/^{12}\text{C}$ ratios of charred plant remains trapped in old magma and ash flows. If the uncertainty in determining these ratios is 0.1%, could radiocarbon dating distinguish between debris from the eruptions of Mt. Vesuvius that occurred in the years 472 and 512? *(Hint: Calculate the $^{14}\text{C}/^{12}\text{C}$ ratios for samples from the two dates.)*

21.81. Figure P21.81 shows a carved mammoth tusk that was uncovered at an ancient camp site in the Ural Mountains in 2001. The $^{14}\text{C}/^{12}\text{C}$ ratio in the tusk was only 1.19% of that in modern elephant tusks. How old is the mammoth tusk?

![Figure P21.81](image3)

21.82. The Destruction of Jericho  
The Bible describes the Exodus as a period of 40 years that began with plagues in Egypt and ended with the destruction of Jericho. Archeologists seeking to establish the exact dates of these events have proposed that the plagues coincided with a huge eruption of the volcano Thera in the Aegean Sea.

a. Radiocarbon dating suggests that the eruption occurred around 1360 BCE, though other records place the eruption of Thera in the year 1628 BCE. What is the percent difference in the $^{14}\text{C}$ decay rate in biological samples from these two dates?

b. Radiocarbon dating of blackened grains from the site of ancient Jericho provides a date of 1315 BCE ±13 years for the fall of the city. What is the $^{14}\text{C}/^{12}\text{C}$ ratio in the blackened grains compared with that of grain harvested last year?

Additional Problems

21.83. Thirty years before the creation of antihydrogen, television producer Gene Roddenberry (1921–1991) proposed to use this form of antimatter to fuel the powerful “warp” engines of the fictional starship *Enterprise.*

a. Why would antihydrogen have been a particularly suitable fuel?

b. Describe the challenges of storing such a fuel on a starship.

21.84. Tiny concentrations of radioactive tritium ($^{3}\text{H}$) occur naturally in rain and groundwater. The half-life of $^{3}\text{H}$ is 12 years. Assuming that tiny
concentrations of tritium can be determined accurately, could the isotope be used to determine whether a bottle of wine with the year 1969 on its label actually contained wine made from grapes that were grown in 1969? Explain your answer.

21.85. The energy released during the fission of $^{235}\text{U}$ is about $3.2 \times 10^{-11}$ J per atom of the isotope. Compare this quantity of energy with that released by the fusion of four hydrogen atoms to make an atom of helium-4:

$$4\,^1\text{H} \rightarrow ^1\text{He} + 2\,^0\alpha$$

Assume that the positrons are annihilated in collisions with electrons so that the masses of the positrons are converted into energy. In your comparison, express the energies released by the fission and fusion processes in joules per nucleon for $^{235}\text{U}$ and $^4\text{He}$, respectively.

21.86. How much energy is required to remove a neutron from the nucleus of an atom of carbon-13 (mass = 13.00335 amu)? (Hint: The mass of an atom of carbon-12 is exactly 12.00000 amu.)

21.87. Smoke Detectors Americium-241 ($t_{1/2} = 433$ yr) is used in smoke detectors. The $\alpha$ particles from this isotope ionize nitrogen and oxygen in the air, creating an electric current. When smoke is present, the current decreases, setting off the alarm.

a. Does a smoke detector bear a closer resemblance to a Geiger counter or to a scintillation counter?

b. How long will it take for the radioactivity of a sample of $^{241}\text{Am}$ to drop to 1% of its original radioactivity?

c. Why are smoke detectors containing $^{241}\text{Am}$ safe to handle without protective equipment?

*21.88. Colorectal Cancer Treatment Cancer therapy with radioactive rhenium-188 shows promise in patients suffering from colorectal cancer.

a. Write the symbol for rhenium-188 and determine the number of neutrons, protons, and electrons.

b. Are most rhenium isotopes likely to have fewer neutrons than rhenium-188?

c. The half-life of rhenium-188 is 17 hours. If it takes 30 minutes to bind the isotope to an antibody that delivers the rhenium to the tumor, what percentage of the rhenium remains after binding to the antibody?

d. The effectiveness of rhenium-188 is thought to result from penetration of $\beta$ particles as deep as 8 mm into the tumor. Why wouldn’t an $\alpha$ emitter be more effective?

e. Using an appropriate reference text, such as the CRC Handbook of Chemistry and Physics, pick out the two most abundant isotopes of rhenium. List their natural abundances and explain why the one that is radioactive decays by the pathway that it does.

21.89. In 2006 an international team of scientists confirmed the synthesis of a total of three atoms of $^{294}_{118}\text{Uuo}$ in experiments run in 2002 and 2005. They bombarded a $^{249}\text{Cf}$ target with $^{48}\text{Ca}$ nuclei.

a. Write a balanced nuclear equation describing the synthesis of $^{294}_{118}\text{Uuo}$.

b. The synthesized isotope of Uuo undergoes $\alpha$ decay ($t_{1/2} = 0.9$ ms). What nuclide is produced by the decay process?

c. The nuclide produced in part b also undergoes $\alpha$ decay ($t_{1/2} = 10$ ms). What nuclide is produced by this decay process?

d. The nuclide produced in part c also undergoes $\alpha$ decay ($t_{1/2} = 0.16$ s). What nuclide is produced by this decay process?

e. If you had to select an element that occurs in nature and that has physical and chemical properties similar to Uuo, which element would it be?

*21.90. Consider the following decay series:

$$\text{A} \quad (t_{1/2} = 4.5 \text{ s}) \rightarrow \text{B} \quad (t_{1/2} = 15.0 \text{ days}) \rightarrow \text{C}$$

If we start with $10^6$ atoms of A, how many atoms of A, B, and C are there after 30 days?

21.91. Which element in the following series will be present in the greatest amount after 1 year?

$$\begin{align*}
2^{12}_{40}\text{Bi} & \rightarrow 2^{12}_{41}\text{Tl} & \rightarrow 2^{20}_{82}\text{Pb} & \rightarrow 2^{12}_{42}\text{Bi} \\
t_{1/2} &= 20 \text{ min} & 1.3 \text{ min} & 20 \text{ yr} & 5 \text{ d}
\end{align*}$$

*21.92. Dating Cave Paintings Cave paintings in Gua Saleh Cave in Borneo have been dated by measuring the amount of $^{14}\text{C}$ in calcium carbonate that formed over the pigments used in the paint. The source of the carbonate ion was atmospheric CO$_2$.

a. What is the ratio of the $^{14}\text{C}$ radioactivity in calcium carbonate that formed 9900 years ago to that in calcium carbonate formed today?

b. The archaeologists also used a second method, uranium–thorium dating, to confirm the age of the paintings by measuring trace quantities of these elements present as contaminants in the calcium carbonate. Shown below are two candidates for the U–Th dating method.

Which isotope of uranium do you suppose was chosen? Explain your answer.

$$\begin{align*}
2^{23}_{92}\text{U} & \rightarrow 2^{235}_{92}\text{U} & \rightarrow 2^{235}_{92}\text{Th} & \rightarrow 2^{231}_{90}\text{Pa} & \rightarrow 2^{238}_{92}\text{U} & \rightarrow 2^{234}_{90}\text{Th} & \rightarrow 2^{228}_{88}\text{Pa} \\
t_{1/2} &= 7.04 \times 10^5 \text{ yr} & 25.6 \text{ hr} & 3.25 \times 10^4 \text{ yr} & 2.44 \times 10^5 \text{ yr} & 7.7 \times 10^4 \text{ hr} & 1600 \text{ yr}
\end{align*}$$

21.93. The synthesis of new elements and specific isotopes of known elements in linear accelerators involves the fusion of smaller nuclei.

a. An isotope of platinum can be prepared from nickel-64 and tin-124. Write a balanced equation for this nuclear reaction. (You may assume that no neutrons are ejected in the fusion reaction.)

b. Substitution of tin-132 for tin-124 increases the rate of the fusion reaction 10 times. Which isotope of Pt is formed in this reaction?

21.94. A sample of drinking water collected from a suburban Boston municipal water system in 2002 contained 0.5 pCi/L of radon. Assume that this level of radioactivity was due to the decay of $^{222}\text{Rn}$ ($t_{1/2} = 3.8$ days).

a. What was the level of radioactivity (Bq/L) of this nuclide in the sample?

b. How many decay events per hour would occur in 2.5 L of the water?

21.95. Stone Age Skeletons The discovery of six skeletons in an Italian cave at the beginning of the 20th century was considered a significant find in Stone Age archaeology. The age of these bones has been debated. The first attempt at radiocarbon dating indicated an age of 15,000 years. Redetermination of the age in 2004 indicated an older age for two bones, between 23,300 and 26,400 years. What is the ratio of $^{14}\text{C}$ in a sample 15,000 years old to one 25,000 years old?
21.96. There was once a plan to store radioactive waste that contained plutonium-239 in the reefs of the Marshall Islands. The planners claimed that the plutonium would be “reasonably safe” after 240,000 years. If the half-life is 24,400 years, what percentage of the $^{239}$Pu would remain after 240,000 years?

21.97. **Dating Prehistoric Bones** In 1997 anthropologists uncovered three partial skulls of prehistoric humans in the Ethiopian village of Herto. Based on the amount of $^{40}$Ar in the volcanic ash in which the remains were buried, their age was estimated at between 154,000 and 160,000 years old.
   a. $^{40}$Ar is produced by the decay of $^{40}$K ($t_{1/2} = 1.28 \times 10^9$ yr). Propose a decay mechanism for $^{40}$K to $^{40}$Ar.
   b. Why did the researchers choose $^{40}$Ar rather than $^{14}$C as the isotope for dating these remains?

*21.98. **Biblical Archaeology** The Old Testament describes the construction of the Siloam Tunnel, used to carry water into Jerusalem under the reign of King Hezekiah (727–698 BCE). An inscription on the tunnel has been interpreted as evidence that the tunnel was not built until 200–100 BCE. $^{14}$C dating (in 2003) indicated a date close to 700 BCE. What is the ratio of $^{14}$C in a wooden object made in 100 BCE to one made from the same kind of wood in 700 BCE?

21.99. Thorium-232 slowly decays to bismuth-212 ($t_{1/2} = 1.4 \times 10^{10}$ yr). Bismuth-212 decays to lead-208 by two pathways: first $\beta$ and then $\alpha$ decay, or $\alpha$ and then $\beta$ decay. The intermediate nuclide in the second pathway is thallium-208. The thallium-208 can be separated from a sample of thorium nitrate by passing a solution of the sample through a filter pad containing ammonium phosphomolybdate. The radioactivity of $^{208}$Tl trapped on the filter is measured as a function of time. In one such experiment, the following data were collected:

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Counts/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>62</td>
</tr>
<tr>
<td>120</td>
<td>40</td>
</tr>
<tr>
<td>180</td>
<td>35</td>
</tr>
<tr>
<td>240</td>
<td>22</td>
</tr>
<tr>
<td>300</td>
<td>16</td>
</tr>
<tr>
<td>360</td>
<td>10</td>
</tr>
</tbody>
</table>

Use the data in the table to determine the half-life of $^{208}$Tl.