Exercises

Review Questions

1. What is thermochemistry? Why is it important?
2. What is energy? What is work? List some examples of each.
3. What is kinetic energy? What is potential energy? List some examples of each.
4. What is the law of conservation of energy? How does it relate to energy exchanges between a thermodynamic system and its surroundings?
5. A friend claims to have constructed a machine that creates electricity but requires no energy input. Explain why you should be suspicious of your friend's claim.
6. What is a state function? List some examples of state functions.
7. What is internal energy? Is internal energy a state function?
8. If energy flows out of a chemical system and into the surroundings, what is the sign of ΔE_{system}?
9. If the internal energy of the products of a reaction is higher than the internal energy of the reactants, what is the sign of ΔE for the reaction? In which direction does energy flow?
10. What is heat? Explain the difference between heat and temperature.
11. How is the change in internal energy of a system related to heat and work?
12. Explain how the sum of heat and work can be a state function, even though heat and work are themselves not state functions.
13. What is heat capacity? Explain the difference between heat capacity and specific heat capacity.
14. Explain how the high specific heat capacity of water can affect the weather in coastal regions.
15. If two objects, A and B, of different temperature come into direct contact, what is the relationship between the heat lost by one object and the heat gained by the other? What is the relationship between the temperature changes of the two objects? (Assume that the two objects do not lose any heat to anything else.)
16. What is pressure–volume work? How is it calculated?
17. What is calorimetry? Explain the difference between a coffee-cup calorimeter and a bomb calorimeter. What is each designed to measure?
18. What is the change in enthalpy (ΔH) for a chemical reaction? How is ΔH different from ΔE?
19. Explain the difference between an exothermic and an endothermic reaction. Give the sign of ΔH for each type of reaction.
20. From a molecular viewpoint, where does the energy emitted in an exothermic chemical reaction come from? Why does the reaction mixture undergo an increase in temperature even though energy is emitted?
21. From a molecular viewpoint, where does the energy absorbed in an endothermic chemical reaction go? Why does the reaction mixture undergo a decrease in temperature even though energy is absorbed?
22. Is the change in enthalpy for a reaction an extensive property? Explain the relationship between ΔH for a reaction and the amounts of reactants and products that undergo reaction.
23. Explain how the value of ΔH for a reaction changes upon:
    a. multiplying the reaction by a factor
    b. reversing the reaction
    Why do these relationships hold?
24. What is Hess's law? Why is it useful?
25. What is a standard state? What is the standard enthalpy change for a reaction?
26. How can bond energies be used to estimate ΔH for a reaction?
27. Explain the difference between exothermic and endothermic reactions in terms of the relative strengths of the bonds that are broken and the bonds that are formed.
28. What is the standard enthalpy of formation for a compound? For a pure element in its standard state?
29. How do you calculate $\Delta H^{\circ}_{\text{rxn}}$ from tabulated standard enthalpies of formation?
30. What is lattice energy? How does lattice energy depend on ion size? On ion charge?

Problems by Topic

Note: Answers to all odd-numbered Problems can be found in Appendix III. Exercises in the Problems by Topic section are paired, with each odd-numbered problem followed by a similar even-numbered problem. Exercises in the Cumulative Problems section are also paired but more loosely. Because of their nature, Challenge Problems and Conceptual Problems are unpaired.

Internal Energy, Heat, and Work

31. Which statement is true of the internal energy of a system and its surroundings during an energy exchange with a negative ΔE_{sys}?

- **a.** The internal energy of the system increases, and the internal energy of the surroundings decreases.
- **b.** The internal energy of both the system and the surroundings increases.
- **c.** The internal energy of both the system and the surroundings decreases.
- **d.** The internal energy of the system decreases, and the internal energy of the surroundings increases.

32. During an energy exchange, a chemical system absorbs energy from its surroundings. What is the sign of ΔE_{sys} for this process? Explain.

33. Identify each energy exchange as primarily heat or work and determine the sign of ΔE (positive or negative) for the system.

- **a.** Sweat evaporates from skin, cooling the skin. (The evaporating sweat is the system.)
- **b.** A balloon expands against an external pressure. (The contents of the balloon are the system.)
- **c.** An aqueous chemical reaction mixture is warmed with an external flame. (The reaction mixture is the system.)

34. Identify each energy exchange as primarily heat or work and determine the sign of ΔE (positive or negative) for the system.

- **a.** A rolling billiard ball collides with another billiard ball. The first billiard ball (defined as the system) stops rolling after the collision.
- **b.** A book is dropped to the floor. (The book is the system.)
- **c.** A father pushes his daughter on a swing. (The daughter and the swing are the system.)

35. A system releases 622 kJ of heat and does 105 kJ of work on the surroundings. What is the change in internal energy of the system?

36. A system absorbs 196 kJ of heat, and the surroundings do 117 kJ of work on the system. What is the change in internal energy of the system?

37. The gas in a piston (defined as the system) warms and absorbs 655 J of heat. The expansion performs 344 J of work on the surroundings. What is the change in internal energy for the system?

38. The air in an inflated balloon (defined as the system) warms over a toaster and absorbs 115 J of heat. As it expands, it does 77 kJ of work. What is the change in internal energy for the system?

Heat, Heat Capacity, and Work

39. A person packs two identical coolers for a picnic, placing twenty-four 12-ounce soft drinks and 5 pounds of ice in each. However, the drinks put into cooler A were refrigerated for several hours before they were packed in the cooler, while the drinks put into cooler B were at room temperature. When the picnickers open the two coolers three hours later, most of the ice in cooler A is still present, while nearly all of the ice in cooler B has melted. Explain this difference.

40. A kilogram of aluminum metal and a kilogram of water are each warmed to 75 °C and placed in two identical insulated containers. One hour later, the two containers are opened, and the temperature of each substance is measured. The aluminum has cooled to 35 °C, while the water has cooled only to 66 °C. Explain this difference.

41. How much heat is required to warm 1.50 L of water from 25.0 °C to 100.0 °C? (Assume a density of 1.00 g/mL for the water.)

42. How much heat is required to warm 1.50 kg of sand from 25.0 °C to 100.0 °C?

43. Suppose that 25 g of each substance is initially at 27.0 °C. What is the final temperature of each substance upon absorbing 2.35 kJ of heat?

- **a.** gold
- **b.** silver

c. aluminum

d. water

44. An unknown mass of each substance, initially at 23.0 °C, absorbs 1.95×10^3 J of heat. The final temperature is recorded as indicated. Find the mass of each substance.

a. Pyrex glass $\left(T_f = 55.4\ ^\circ\text{C}\right)$

b. sand $\left(T_f = 66.1\ ^\circ\text{C}\right)$

c. ethanol $\left(T_f = 44.2\ ^\circ\text{C}\right)$

d. water $\left(T_f = 32.4\ ^\circ\text{C}\right)$

45. How much work (in J) is required to expand the volume of a pump from 0.0 L to 2.5 L against an external pressure of 1.1 atm?

46. The average human lung expands by about 0.50 L during each breath. If this expansion occurs against an external pressure of 1.0 atm, how much work (in J) is done during the expansion?

47. The air within a piston equipped with a cylinder absorbs 565 J of heat and expands from an initial volume of 0.10 L to a final volume of 0.85 L against an external pressure of 1.0 atm. What is the change in internal energy of the air within the piston?

48. A gas is compressed from an initial volume of 5.55 L to a final volume of 1.22 L by an external pressure of 1.00 atm. During the compression the gas releases 124 J of heat. What is the change in internal energy of the gas?

Enthalpy and Thermochemical Stoichiometry

49. When 1 mol of a fuel burns at constant pressure, it produces 3452 kJ of heat and does 11 kJ of work. What are ΔE and ΔH for the combustion of the fuel?

50. The change in internal energy for the combustion of 1.0 mol of octane at a pressure of 1.0 atm is 5084.3 kJ. If the change in enthalpy is 5074.1 kJ, how much work is done during the combustion?

51. Is each process exothermic or endothermic? Indicate the sign of ΔH.

a. natural gas burning on a stove

b. isopropyl alcohol evaporating from skin

c. water condensing from steam

52. Is each process exothermic or endothermic? Indicate the sign of ΔH.

a. dry ice evaporating

b. a sparkler burning

c. the reaction that occurs in a chemical cold pack used to ice athletic injuries

53. Consider the thermochemical equation for the combustion of acetone $\left(C_3H_6O\right)$, the main ingredient in nail polish remover:

$$C_3H_6O(l) + 4\ O_2(g) \rightarrow 3\ CO_2(g) + 3\ H_2O(g) \quad \Delta H^\circ_{rxn} = -1790\ \text{kJ}$$

If a bottle of nail polish remover contains 177 mL of acetone, how much heat is released by its complete combustion? The density of acetone is 0.788 g/mL.

54. What mass of natural gas $\left(CH_4\right)$ must burn to emit 267 kJ of heat?

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g) \quad \Delta H^\circ_{rxn} = -802.3\ \text{kJ}$$

55. Nitromethane (CH_3NO_2) burns in air to produce significant amounts of heat:

$$2\ CH_3NO_2(l) + \frac{3}{2}O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l) + N_2(g) \quad \Delta H^\circ_{rxn} = -1418\ \text{kJ}$$

How much heat is produced by the complete reaction of 5.56 kg of nitromethane?

56. Titanium reacts with iodine to form titanium(III) iodide, emitting heat:

$$2\ Ti(s) + 3\ I_2(g) \rightarrow 2\ TiI_3(s) \quad \Delta H^\circ_{rxn} = -839\ \text{kJ}$$

Determine the masses of titanium and iodine that react if 1.55×10^3 kJ of heat is emitted by the reaction.

57. The propane fuel $\left(C_3H_8\right)$ used in gas barbeques burns according to a thermochemical equation:

$$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(g) \quad \Delta H_{rxn} = -2217\ \text{kJ}$$

If a pork roast must absorb 1.6×10^3 kJ to fully cook, and if only 10% of the heat produced by the barbeque is actually absorbed by the roast, what mass of CO_2 is emitted into the atmosphere during the grilling of the pork roast?

58. Charcoal is primarily carbon. Determine the mass of CO_2 produced by burning enough carbon (in the form of charcoal) to produce 5.00×10^2 kJ of heat.

$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^{\circ}_{rxn} = -393.5\ \text{kJ}$$

Thermal Energy Transfer

59. We submerge a silver block, initially at 58.5 °C, into 100.0 g of water at 24.8 °C, in an insulated container. The final temperature of the mixture upon reaching thermal equilibrium is 26.2 °C. What is the mass of the silver block?

60. We submerge a 32.5-g iron rod, initially at 22.7 °C, into an unknown mass of water at 63.2 °C, in an insulated container. The final temperature of the mixture upon reaching thermal equilibrium is 59.5 °C. What is the mass of the water?

61. We submerge a 31.1-g wafer of pure gold initially at 69.3 °C into 64.2 g of water at 27.8 °C in an insulated container. What is the final temperature of both substances at thermal equilibrium?

62. We submerge a 2.85-g lead weight, initially at 10.3 °C, in 7.55 g of water at 52.3 °C in an insulated container. What is the final temperature of both substances at thermal equilibrium?

63. Two substances, A and B, initially at different temperatures, come into contact and reach thermal equilibrium. The mass of substance A is 6.15 g, and its initial temperature is 20.5 °C. The mass of substance B is 25.2 g, and its initial temperature is 52.7 °C. The final temperature of both substances at thermal equilibrium is 46.7 °C. If the specific heat capacity of substance B is 1.17 J/g · °C, what is the specific heat capacity of substance A?

64. A 2.74-g sample of a substance suspected of being pure gold is warmed to 72.1 °C and submerged into 15.2 g of water initially at 24.7 °C. The final temperature of the mixture is 26.3 °C. What is the heat capacity of the unknown substance? Could the substance be pure gold?

Calorimetry

65. Exactly 1.5 g of a fuel burns under conditions of constant pressure and then again under conditions of constant volume. In measurement A the reaction produces 25.9 kJ of heat, and in measurement B the reaction produces 23.3 kJ of heat. Which measurement (A or B) corresponds to conditions of constant pressure? Which one corresponds to conditions of constant volume? Explain.

66. In order to obtain the largest possible amount of heat from a chemical reaction in which there is a large increase in the number of moles of gas, should you carry out the reaction under conditions of constant volume or constant pressure? Explain.

67. When 0.514 g of biphenyl $\left(C_{12}H_{10}\right)$ undergoes combustion in a bomb calorimeter, the temperature rises from 25.8 °C to 29.4 °C. Find ΔE_{rxn} for the combustion of biphenyl in kJ/mol biphenyl. The heat capacity of the bomb calorimeter, determined in a separate experiment, is 5.86 kJ/°C.

68. Mothballs are composed primarily of the hydrocarbon naphthalene $\left(C_{10}H_8\right)$. When 1.025 g of naphthalene burns in a bomb calorimeter, the temperature rises from 24.25 °C to 32.33 °C. Find ΔE_{rxn} for the combustion of naphthalene. The heat capacity of the calorimeter, determined in a separate experiment, is 5.11 kJ/°C

69. Zinc metal reacts with hydrochloric acid according to the balanced equation:

$$Zn(s) + 2\ HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

When 0.103 g of Zn(s) is combined with enough HCl to make 50.0 mL of solution in a coffee-cup calorimeter, all of the zinc reacts, raising the temperature of the solution from 22.5 °C to 23.7 °C. Find ΔH_{rxn} for this reaction as written. (Use 1.0 g/mL for the density of the solution and 4.18 J/g · °C as the specific heat capacity.)

70. Instant cold packs used to ice athletic injuries on the field contain ammonium nitrate and water separated by a thin plastic divider. When the divider is broken, the ammonium nitrate dissolves according to the endothermic reaction:

$$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$$

$$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$$

In order to measure the enthalpy change for this reaction, 1.25 g of NH_4NO_3 is dissolved in enough water to make 25.0 mL of solution. The initial temperature is 25.8 °C, and the final temperature (after the solid dissolves) is 21.9 °C. Calculate the change in enthalpy for the reaction in kJ. (Use 1.0 g/mL as the density of the solution and 4.18 J/g · °C as the specific heat capacity.)

Quantitative Relationships Involving Δ*H* and Hess's Law

71. For each generic reaction, determine the value of ΔH_2 in terms of ΔH_1.

a.

$$\mathrm{A+B \rightarrow 2\,C} \quad \Delta H_1$$
$$\mathrm{2\,C \rightarrow A + B} \quad \Delta H_2 = ?$$

b.

$$\mathrm{A+\tfrac{1}{2}B \rightarrow C} \quad \Delta H_1$$
$$\mathrm{2\,A + B \rightarrow 2\,C} \quad \Delta H_2 = ?$$

c.

$$\mathrm{A \rightarrow B + 2\,C} \quad \Delta H_1$$
$$\mathrm{\tfrac{1}{2}B + C \rightarrow \tfrac{1}{2}A} \quad \Delta H_2 = ?$$

72. Consider the generic reaction:

$$\mathrm{A+2\,B \rightarrow C + 3\,D} \quad \Delta H = 155\ \mathrm{kJ}$$

Determine the value of Δ*H* for each related reaction:

a. $\mathrm{3\,A + 6\,B \rightarrow 3\,C + 9\,D}$

b. $\mathrm{C+3\,D \rightarrow A + 2\,B}$

c. $\mathrm{\tfrac{1}{2}\,C + \tfrac{3}{2}D \rightarrow \tfrac{1}{2}A + B}$

73. Calculate ΔH_{rxn} for the reaction:

$$Fe_2O_3(s) + 3\,CO(g) \rightarrow 2\,Fe(s) + 3\,CO_2(g)$$

Use the following reactions and given Δ*H* values:

$$2\,Fe(s) + \tfrac{3}{2}O_2(g) \rightarrow Fe_2O_3(s) \quad \Delta H = -824.2\ \mathrm{kJ}$$
$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta H = -282.7\ \mathrm{kJ}$$

74. Calculate ΔH_{rxn} for the reaction:

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$$

Use the following reactions and given Δ*H* values:

$$Ca(s) + CO_2(g) + \tfrac{1}{2}O_2(g) \rightarrow CaCO_3(s) \quad \Delta H = -812.8\ \mathrm{kJ}$$
$$2\,Ca(s) + O_2(g) \rightarrow 2\,CaO(s) \quad \Delta H = -1269.8\ \mathrm{kJ}$$

75. Calculate ΔH_{rxn} for the reaction:

$$5\,C(s) + 6\,H_2(g) \rightarrow C_5H_{12}(l)$$

Use the following reactions and given Δ*H* values:

$$C_5H_{12}(l) + 8\,O_2(g) \rightarrow 5\,CO_2(g) + 6\,H_2O(g) \quad \Delta H = -3244.8\ \mathrm{kJ}$$
$$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5\ \mathrm{kJ}$$
$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g) \quad \Delta H = -483.5\ \mathrm{kJ}$$

76. Calculate ΔH_{rxn} for the reaction:

$$CH_4(g) + 4\,Cl_2(g) \rightarrow CCl_4(g) + 4\,HCl(g)$$

Use the following reactions and given Δ*H* values:

$$C(s) + 2\,H_2(g) \rightarrow CH_4(g) \quad \Delta H = -74.6\ \mathrm{kJ}$$
$$C(s) + 2\,Cl_2(g) \rightarrow CCl_4(g) \quad \Delta H = -95.7\ \mathrm{kJ}$$
$$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g) \quad \Delta H = -92.3\ \mathrm{kJ}$$

$H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g) \quad \Delta H = -92.3\ kJ$

Using Bond Energies to Calculate ΔH_{rxn}

77. Hydrogenation reactions are used to add hydrogen across double bonds in hydrocarbons and other organic compounds. Use average bond energies to calculate ΔH_{rxn} for the hydrogenation reaction.

$$H_2C = CH_2(g) + H_2(g) \rightarrow H_3C\text{—}CH_3(g)$$

78. Ethanol is a possible fuel. Use average bond energies to calculate ΔH_{rxn} for the combustion of ethanol:

$$CH_3CH_2OH(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(g)$$

79. Hydrogen, a potential future fuel, can be produced from carbon (from coal) and steam by this reaction:

$$C(s) + 2\ H_2O(g) \rightarrow 2\ H_2(g) + CO_2(g)$$

Use average bond energies to calculate ΔH_{rxn} for the reaction, and then use standard enthalpies to calculate ΔH_{rxn}. Why are the two values different and which value is more accurate?

80. Hydroxyl radicals react with and eliminate many atmospheric pollutants. However, the hydroxyl radical does not clean up everything. For example, chlorofluorocarbons—which destroy stratospheric ozone—are not attacked by the hydroxyl radical. Consider the hypothetical reaction by which the hydroxyl radical might react with a chlorofluorocarbon:

$$OH(g) + CF_2Cl_2(g) \rightarrow HOF(g) + CFCl_2(g)$$

Use bond energies to explain why this reaction is improbable.

Enthalpies of Formation and ΔH

81. Write an equation for the formation of each compound from its elements in their standard states, and find ΔH_f° for each from Appendix IIB.

a. $NH_3(g)$
b. $CO_2(g)$
c. $Fe_2O_3(s)$
d. $CH_4(g)$

82. Write an equation for the formation of each compound from its elements in their standard states, and find ΔH_{rxn}° for each from Appendix IIB.

a. $NO_2(g)$
b. $MgCO_3(s)$
c. $C_2H_4(g)$
d. $CH_3OH(l)$

83. Hydrazine (N_2H_4) is a fuel used by some spacecraft. It is normally oxidized by N_2O_4 according to the equation:

$$N_2H_4(l) + N_2O_4(g) \rightarrow 2\ N_2O(g) + 2\ H_2O(g)$$

Calculate ΔH_{rxn}° for this reaction using standard enthalpies of formation.

84. Pentane (C_5H_{12}) is a component of gasoline that burns according to the following balanced equation:

$$C_5H_{12}(l) + 8\ O_2(g) \rightarrow 5\ CO_2(g) + 6\ H_2O(g)$$

Calculate ΔH_{rxn}° for this reaction using standard enthalpies of formation. (The standard enthalpy of formation of liquid pentane is -146.8 kJ/mol.)

85. Use standard enthalpies of formation to calculate ΔH_{rxn}° for each reaction.

a. $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$
b. $CO(g) + H_2O(g) \rightarrow H_2(g) + CO_2(g)$
c. $3\ NO_2(g) + H_2O(l) \rightarrow 2\ HNO_3(aq) + NO(g)$
d. $Cr_2O_3(s) + 3\ CO(g) \rightarrow 2\ Cr(s) + 3\ CO_2(g)$

86. Use standard enthalpies of formation to calculate ΔH_{rxn}° for each reaction.

86. Use standard enthalpies of formation to calculate ΔH°_{rxn} for each reaction.

a. $2\ H_2S(g) + 3\ O_2(g) \rightarrow 2\ H_2O(l) + 2\ SO_2(g)$

b. $SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$

c. $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

d. $N_2O_4(g) + 4\ H_2(g) \rightarrow N_2(g) + 4\ H_2O(g)$

87. During photosynthesis, plants use energy from sunlight to form glucose $\left(C_6H_{12}O_6\right)$ and oxygen from carbon dioxide and water. Write a balanced equation for photosynthesis and calculate ΔH°_{rxn}.

88. Ethanol can be made from the fermentation of crops and has been used as a fuel additive to gasoline. Write a balanced equation for the combustion of ethanol and calculate ΔH°_{rxn}.

89. Top fuel dragsters and funny cars burn nitromethane as fuel according to the balanced combustion equation:

$$2\ CH_3NO_2(l) + \frac{3}{2}O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l) + N_2(g) \quad \Delta H^\circ_{rxn} = -1418\ kJ$$

The enthalpy of combustion for nitromethane is −709.2 kJ/mol. Calculate the standard enthalpy of formation $\left(\Delta H^\circ_f\right)$ for nitromethane.

90. The explosive nitroglycerin $\left(C_3H_5N_3O_9\right)$ decomposes rapidly upon ignition or sudden impact according to the balanced equation:

$$4\ C_3H_5N_3O_9(l) \rightarrow 12\ CO_2(g) + 10\ H_2O(g) + 6\ N_2(g) + O_2(g) \quad \Delta H^\circ_{rxn} = -5678\ kJ$$

Calculate the standard enthalpy of formation $\left(\Delta H^\circ_f\right)$ for nitroglycerin.

Lattice Energies

91. Explain the trend in the lattice energies (shown here) of the alkaline earth metal oxides.

Metal Oxide	Lattice Energy (kJ/mol)
MgO	−3795
CaO	−3414
SrO	−3217
BaO	−3029

92. Rubidium iodide has a lattice energy of −617 kJ/mol, while potassium bromide has a lattice energy of −671 kJ/mol. Why is the lattice energy of potassium bromide more exothermic than the lattice energy of rubidium iodide?

93. The lattice energy of CsF is −744 kJ/mol whereas that of BaO is −3029 kJ/mol. Explain this large difference in lattice energy.

94. Arrange these compounds in order of increasing magnitude of lattice energy: KCl, SrO, RbBr, CaO.

95. Use the Born–Haber cycle and data from Appendix IIB and Chapters 3 and 9 to calculate the lattice energy of KCl. (ΔH_{sub} for potassium is 89.0 kJ/mol.)

96. Use the Born–Haber cycle and data from Appendix IIB and Table 9.3 to calculate the lattice energy of CaO. (ΔH_{sub} for calcium is 178 kJ/mol; IE_1 and IE_2 for calcium are 590 kJ/mol and 1145 kJ/mol, respectively; EA_1 and EA_2 for O are −141 kJ/mol and 744 kJ/mol, respectively.)

Cumulative Problems

97. The kinetic energy of a rolling billiard ball is given by $KE = \frac{1}{2}mv^2$. Suppose a 0.17-kg billiard ball is rolling down a pool table with an initial speed of 4.5 m/s. As it travels, it loses some of its energy as heat. The ball slows down to 3.8 m/s and then collides head-on with a second billiard ball of equal mass. The first billiard ball completely stops, and the second one rolls away with a velocity of 3.8 m/s. Assume the first billiard ball is the system and calculate w, q, and ΔE for the process.

98. A 100-W light bulb is placed in a cylinder equipped with a moveable piston. The light bulb is turned on for 0.015 hour, and the assembly expands from an initial volume of 0.85 L to a final volume of 5.88 L against an external pressure of 1.0 atm. Use the wattage of the light bulb and the time it is on to calculate ΔE in joules (assume that the cylinder and light bulb assembly is the system and assume two significant figures). Calculate w and q.

99. Evaporating sweat cools the body because evaporation is an endothermic process:

$$H_2O(l) \rightarrow H_2O(g) \quad \Delta H^\circ_{rxn} = +44.01 \text{ kJ}$$

Estimate the mass of water that must evaporate from the skin to cool the body by 0.50 °C. Assume a body mass of 95 kg and assume that the specific heat capacity of the body is 4.0 J/g · °C.

100. LP gas burns according to the exothermic reaction:

$$C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(g) \quad \Delta H^\circ_{rxn} = -2044 \text{ kJ}$$

What mass of LP gas is necessary to heat 1.5 L of water from room temperature (25.0 °C) to boiling (100.0 °C)? Assume that during heating, 15% of the heat emitted by the LP gas combustion goes to heat the water. The rest is lost as heat to the surroundings.

101. Use standard enthalpies of formation to calculate the standard change in enthalpy for the melting of ice. (The ΔH°_f for $H_2O(s)$ is −291.8 kJ/mol.) Use this value to calculate the mass of ice required to cool 355 mL of a beverage from room temperature (25.0 °C) to 0.0 °C. Assume that the specific heat capacity and density of the beverage are the same as those of water.

102. Dry ice is solid carbon dioxide. Instead of melting, solid carbon dioxide sublimes according to the equation:

$$CO_2(s) \rightarrow CO_2(g)$$

When dry ice is added to warm water, heat from the water causes the dry ice to sublime more quickly. The evaporating carbon dioxide produces a dense fog often used to create special effects. In a simple dry ice fog machine, dry ice is added to warm water in a Styrofoam cooler. The dry ice produces fog until it evaporates away, or until the water gets too cold to sublime the dry ice quickly enough. A small Styrofoam cooler holds 15.0 L of water heated to 85 °C. Use standard enthalpies of formation to calculate the change in enthalpy for dry ice sublimation, and calculate the mass of dry ice that should be added to the water so that the dry ice completely sublimes away when the water reaches 25 °C. Assume no heat loss to the surroundings. (The ΔH°_f for $CO_2(s)$ is −427.4 kJ/mol.)

When carbon dioxide sublimes, the gaseous CO_2 is cold enough to cause water vapor in the air to condense, forming fog.

103. A 25.5-g aluminum block is warmed to 65.4 °C and plunged into an insulated beaker containing 55.2 g water initially at 22.2 °C. The aluminum and the water are allowed to come to thermal equilibrium. Assuming that no heat is lost, what is the final temperature of the water and aluminum?

104. We mix 50.0 mL of ethanol (density = 0.789 g/mL) initially at 7.0 °C with 50.0 mL of water (density = 1.0 g/mL) initially at 28.4 °C in an insulated beaker. Assuming that no heat is lost, what is the final temperature of the mixture?

105. Palmitic acid $\left(C_{16}H_{32}O_2\right)$ is a dietary fat found in beef and butter. The caloric content of palmitic acid is typical of fats in general. Write a balanced equation for the complete combustion of palmitic acid and calculate the standard enthalpy of combustion. What is the caloric content of palmitic acid in Cal/g? Do the same calculation for table sugar (sucrose, $C_{12}H_{22}O_{11}$). Which dietary substance (sugar or fat) contains more Calories per gram? The standard enthalpy of formation of palmitic acid is −208 kJ/mol, and that of sucrose is −2226.1 kJ/mol. (Use $H_2O(l)$ in the balanced chemical equations because the metabolism of these compounds produces liquid water.)

106. Hydrogen and methanol have both been proposed as alternatives to hydrocarbon fuels. Write balanced reactions for the complete combustion of hydrogen and methanol and use standard enthalpies of formation to calculate the amount of heat released per kilogram of the fuel. Which fuel contains the most energy in the least mass? How does the energy of these fuels compare to that of octane $\left(C_8H_{18}\right)$?

107. One tablespoon of peanut butter has a mass of 16 g. It is combusted in a calorimeter whose heat capacity is 120.0 kJ/°C. The temperature of the calorimeter rises from 22.2 °C to 25.4 °C. Find the food caloric content of peanut butter.

108. A mixture of 2.0 mol of $H_2O(g)$ and 1.0 mol of $O_2(g)$ is placed in a sealed evacuated container made of a perfect insulating material at 25 °C. The mixture is ignited with a spark, and it reacts to form liquid water. Determine the temperature of the water.

109. A 20.0-L volume of an ideal gas in a cylinder with a piston is at a pressure of 3.0 atm. Enough weight is suddenly removed from the piston to lower the external pressure to 1.5 atm. The gas then expands at constant temperature until its pressure is 1.5 atm. Find ΔE, ΔH, q, and w for this change in state.

110. When we burn 10.00 g of phosphorus in $O_2(g)$ to form $P_4O_{10}(s)$, we generate enough heat to raise the temperature of 2950 g of water from 18.0 °C to 38.0 °C. Calculate the enthalpy of formation of $P_4O_{10}(s)$ under these conditions.

111. The ΔH for the oxidation of S in the gas phase to $SO_3(g)$ is −204 kJ/mol, and for the oxidation of $SO_2(g)$ to $SO_3(g)$ it is 89.5 kJ/mol. Find the enthalpy of formation of $SO_2(g)$ under these conditions.

112. The ΔH_f° of $TiI_3(s)$ is −328 kJ/mol, and the $\Delta H°$ for the reaction $2\ Ti(s) + 3\ I_2(g) \rightarrow 2\ TiI_3(s)$ is −839 kJ. Calculate the ΔH of sublimation (the state transition from solid to gas) of $I_2(s)$, which is a solid at 25 °C.

113. A copper cube measuring 1.55 cm on edge and an aluminum cube measuring 1.62 cm on edge are both heated to 55.0 °C and submerged in 100.0 mL of water at 22.2 °C. What is the final temperature of the water when equilibrium is reached? (Assume a density of 0.998 g/mL for water.)

114. A pure gold ring and pure silver ring have a total mass of 14.9 g. We heat the two rings to 62.0 °C and drop them into 15.0 mL of water at 23.5 °C. When equilibrium is reached, the temperature of the water is 25.0 °C. What is the mass of each ring? (Assume a density of 0.998 g/mL for water.)

115. The reaction of $Fe_2O_3(s)$ with Al(s) to form $Al_2O_3(s)$ and Fe(s) is called the thermite reaction and is highly exothermic. What role does lattice energy play in the exothermicity of the reaction?

116. NaCl has a lattice energy −787 kJ/mol. Consider a hypothetical salt XY. X^{3+} has the same radius as Na^+, and Y^{3-} has the same radius as Cl^-. Estimate the lattice energy of XY.

117. If hydrogen were used as a fuel, it could be burned according to this reaction:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$$

Use average bond energies to calculate ΔH_{rxn} for this reaction and also for the combustion of methane $\left(CH_4\right)$. Which fuel yields more energy per mole? Per gram?

118. Calculate ΔH_{rxn} for the combustion of octane $\left(C_8H_{18}\right)$, a component of gasoline, by using average bond energies, and then calculate it using enthalpies of formation from Appendix IIB. What is the percent difference between your results? Which result would you expect to be more accurate?

119. The heat of atomization is the heat required to convert a molecule in the gas phase into its constituent atoms in the gas phase. The heat of atomization is used to calculate average bond energies. Without using any tabulated bond energies, calculate the average C—Cl bond energy from the following data: The heat of atomization of CH_4 is 1660 kJ/mol, and that of CH_2Cl_2 is 1495 kJ/mol.

120. Calculate the heat of atomization (see previous problem) of C_2H_3Cl, using the average bond energies in Table 9.3.

Challenge Problems

121. A typical frostless refrigerator uses 655 kWh of energy per year in the form of electricity. Suppose that all of this electricity is generated at a power plant that burns coal containing 3.2% sulfur by mass and that all of the sulfur is emitted as SO_2 when the coal is burned. If all of the SO_2 goes on to react with rainwater to form H_2SO_4, what mass of H_2SO_4 does the annual operation of the refrigerator produce? (*Hint:* Assume that the remaining percentage of the coal is carbon and begin by calculating ΔH°_{rxn} for the combustion of carbon.)

122. A large sport utility vehicle has a mass of 2.5×10^3 kg. Calculate the mass of CO_2 emitted into the atmosphere upon accelerating the SUV from 0.0 mph to 65.0 mph. Assume that the required energy comes from the combustion of octane with 30% efficiency. (*Hint:* Use $KE = \frac{1}{2}mv^2$ to calculate the kinetic energy required for the acceleration.)

123. Combustion of natural gas (primarily methane) occurs in most household heaters. The heat given off in this reaction is used to raise the temperature of the air in the house. Assuming that all the energy given off in the reaction goes to heating up only the air in the house, determine the mass of methane required to heat the air in a house by 10.0 °C. Assume that the house dimensions are $30.0\ m \times 30.0\ m \times 3.0\ m$; specific heat capacity of air is 30 J/K · mol; and 1.00 mol of air occupies 22.4 L for all temperatures concerned.

124. When backpacking in the wilderness, hikers often boil water to sterilize it for drinking. Suppose that you are planning a backpacking trip and will need to boil 35 L of water for your group. What volume of fuel should you bring? Assume that the fuel has an average formula of C_7H_{16}; 15% of the heat generated from combustion goes to heat the water (the rest is lost to the surroundings); the density of the fuel is 0.78 g/mL; the initial temperature of the water is 25.0 °C; and the standard enthalpy of formation of C_7H_{16} is −224.4 kJ/mol.

125. An ice cube of mass 9.0 g is added to a cup of coffee. The coffee's initial temperature is 90.0 °C and the cup contains 120.0 g of liquid. Assume the specific heat capacity of the coffee is the same as that of water. The heat of fusion of ice (the heat associated with ice melting) is 6.0 kJ/mol. Find the temperature of the coffee after the ice melts.

126. Find ΔH, ΔE, q, and w for the freezing of water at −10.0 °C. The specific heat capacity of ice is 2.04 J/g · °C and its heat of fusion (the quantity of heat associated with melting) is −332 J/g.

127. The heat of vaporization of water at 373 K is 40.7 kJ/mol. Find q, w, ΔE, and ΔH for the evaporation of 454 g of water at this temperature at 1 atm.

128. Find ΔH for the combustion of ethanol $\left(C_2H_6O\right)$ to carbon dioxide and liquid water from the following data. The heat capacity of the bomb calorimeter is 34.65 kJ/K, and the combustion of 1.765 g of ethanol raises the temperature of the calorimeter from 294.33 K to 295.84 K.

129. The main component of acid rain $\left(H_2SO_4\right)$ forms from SO_2, a pollutant in the atmosphere, via these steps:

$$\begin{aligned} SO_2 + OH\cdot &\rightarrow HSO_3\cdot \\ HSO_3\cdot + O_2 &\rightarrow SO_3 + HOO\cdot \\ SO_3 + H_2O &\rightarrow H_2SO_4 \end{aligned}$$

Draw the Lewis structure for each of the species in these steps and use bond energies and Hess's law to estimate ΔH_{rxn} for the overall process. (Use 265 kJ/mol for the S—O single-bond energy.)

130. Use average bond energies together with the standard enthalpy of formation of C(g) (718.4 kJ/mol) to estimate the standard enthalpy of formation of gaseous benzene, $C_6H_6(g)$. (Remember that average bond energies apply to the gas phase only.) Compare the value you obtain using average bond energies to the actual standard enthalpy of formation of gaseous benzene, 82.9 kJ/mol. What does the difference between these two values tell you about the stability of benzene?

131. The standard heat of formation of $CaBr_2$ is −675 kJ/mol. The first ionization energy of Ca is 590 kJ/mol, and its second ionization energy is 1145 kJ/mol. The heat of sublimation of Ca $[Ca(s) \rightarrow Ca(g)]$ is 178 kJ/mol. The bond energy of Br_2 is 193 kJ/mol, the heat of vaporization of $Br_2(l)$ is 31 kJ/mol, and the electron affinity of Br is −325 kJ/mol. Calculate the lattice energy of $CaBr_2$.

132. The standard heat of formation of $PI_3(s)$ is −24.7 kJ/mol, and the PI bond energy in this molecule is 184 kJ/mol. The standard heat of formation of PI is 334 kJ/mol, and that of $I_2(g)$ is 62 kJ/mol. The I_2 bond energy is 151 kJ/mol. Calculate the heat of sublimation of $PI_3\left[PI_3(s) \rightarrow PI_3(g)\right]$.

Conceptual Problems

133. Which statement is true of the internal energy of the system and its surroundings following a process in which $\Delta E_{sys} = +65$ kJ? Explain.

a. The system and the surroundings both lose 65 kJ of energy.

b. The system and the surroundings both gain 65 kJ of energy.

c. The system loses 65 kJ of energy, and the surroundings gain 65 kJ of energy.

d. The system gains 65 kJ of energy, and the surroundings lose 65 kJ of energy.

134. Which expression describes the heat emitted in a chemical reaction when the reaction is carried out at constant pressure? Explain.

a. $\Delta E - w$

b. ΔE

c. $\Delta E - q$

135. Two identical refrigerators are plugged in for the first time. Refrigerator A is empty (except for air), and refrigerator B is filled with jugs of water. The compressors of both refrigerators immediately turn on and begin cooling the interiors of the refrigerators. After two hours, the compressor of refrigerator A turns off while the compressor of refrigerator B continues to run. The next day, the compressor of refrigerator A can be heard turning on and off every few minutes, while the compressor of refrigerator B turns off and on every hour or so (and stays on longer each time). Explain these observations.

136. A 1-kg cylinder of aluminum and a 1-kg jug of water, both at room temperature, are put into a refrigerator. After one hour, the temperature of each object is measured. One of the objects is much cooler than the other. Which one is cooler and why?

137. Two substances A and B, initially at different temperatures, are thermally isolated from their surroundings and allowed to come into thermal contact. The mass of substance A is twice the mass of substance B, but the specific heat capacity of substance B is four times the specific heat capacity of substance A. Which substance will undergo a larger change in temperature?

138. When 1 mol of a gas burns at constant pressure, it produces 2418 J of heat and does 5 J of work. Determine ΔE, ΔH, q, and w for the process.

139. In an exothermic reaction, the reactants lose energy and the reaction feels hot to the touch. Explain why the reaction feels hot even though the reactants are losing energy. Where does the energy come from?

140. Which statement is true of a reaction in which ΔV is positive? Explain.

a. $\Delta H = \Delta E$

b. $\Delta H > \Delta E$

c. $\Delta H < \Delta E$

141. Which statement is true of an endothermic reaction?

a. Strong bonds break and weak bonds form.

b. Weak bonds break and strong bonds form.

c. The bonds that break and those that form are of approximately the same strength.

142. When a firecracker explodes, energy is obviously released. The compounds in the firecracker can be viewed as being "energy rich." What does this mean? Explain the source of the energy in terms of chemical bonds.

Questions for Group Work

Active Classroom Learning

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

143. Have each group member write a problem involving the transfer of heat from one material in Table 9.2 to another material in the table. Working as a group, solve each problem. The group member who wrote the problem in question may act as the group facilitator when the group is working on that problem. What do all of your problems have in common? How do they differ?

144. Classify each process as endothermic or exothermic. What is the sign of ΔH for each process? Explain your answers.

a. gasoline burning in an engine

b. steam condensing on a mirror

c. water boiling in a pot

Have each member of your group provide an additional example. Provide at least two examples of exothermic processes and two additional examples of endothermic processes.

145. A propane tank on a home barbeque contains 10.4×10^3 g of propane.

a. Write the balanced chemical reaction for the combustion of gaseous propane (C_3H_8) to form water vapor and gaseous carbon dioxide.

b. Use the value for ΔH_{rxn} provided in the text to calculate the total amount of heat produced when the entire contents of the tank of propane is burned.

c. What mass of water could be warmed from 25 °C to 100 °C with this much heat?

146. Solid carbon–C(*s*, graphite), gaseous hydrogen–$H_2(g)$, and the sugar glucose–$C_6H_{12}O_6(s)$ are all burned with oxygen in a bomb calorimeter, and the amount of heat given off is determined for each process. How can these data obtained be used to determine the heat of formation of glucose? Your answer should include both chemical reactions and complete sentences.

147. Consider the decomposition of liquid hydrogen peroxide $\left(H_2O_2\right)$ to form water and oxygen.

a. What is the heat of formation for hydrogen peroxide?

b. What is the heat of formation for liquid water?

c. What is the heat of formation for gaseous oxygen? Why?

d. Write the balanced chemical equations that correspond to the ΔH values you looked up for parts a, b, and c.

e. Write the balanced chemical equation for the decomposition of hydrogen peroxide to form water and oxygen. (Write the equation such that the coefficient on oxygen is 1.)

f. What is the heat of reaction for the process in part e?

g. Draw a scale diagram of this reaction in which $1\ \text{cm} = 100\ \text{kJ}$ showing the relative energies of reactants (on the left), products (on the right), and the elements in their most stable states (in the middle). Label all the energies you know.

Data Interpretation and Analysis

148. The heating value of combustible fuels is evaluated based on the quantities known as the higher heating value (HHV) and the lower heating value (LHV). The HHV has a higher absolute value and assumes that the water formed in the combustion reaction is formed in the liquid state. The LHV has a lower absolute value and assumes that the water formed in the combustion reaction is formed in the gaseous state. The LHV is therefore the sum of the HHV (which is negative) and the heat of vaporization of water for the number of moles of water formed in the reaction (which is positive). The table on the right lists the enthalpy of combustion—which is equivalent to the HHV—for several closely related hydrocarbons.

Alkane Combustion Values

Alkane	ΔH_{comb} (kJ/mol)
$CH_4(g)$	−890
$C_2H_6(g)$	−1560
$C_3H_8(g)$	−2219
$C_4H_{10}(g)$	−2877
$C_5H_{12}(l)$	−3509
$C_6H_{14}(l)$	−4163
$C_7H_{16}(l)$	−4817
$C_8H_{18}(l)$	−5470

Use the information in the table at right to answer the following questions:

a. Write two balanced equations for the combustion of C_3H_8; one equation assuming the formation of liquid water and the other equation assuming the formation of gaseous water.

b. Given that the heat of vaporization of water is 44.0 kJ/mol, what is ΔH_{rxn} for each of the reactions in part a? Which quantity is the HHV? The LLV?

c. When propane is used to cook in an outdoor grill, is the amount of heat released the HHV or the LLV? What amount of heat is released upon combustion of 1.00 kg of propane in an outdoor grill?

d. For each CH_2 unit added to a linear alkane, what is the average increase in the absolute value of ΔH_{comb}?

Answers to Conceptual Connections

Cc 9.1 The correct answer is (**a**). When ΔE_{sys} is negative, energy flows out of the system and into the surroundings. The energy increase in the surroundings must exactly match the decrease in the system.

Cc 9.2 (**a**) heat, sign is positive (**b**) work, sign is positive (**c**) heat, sign is negative.

Cc 9.3 Bring the water; it has the higher heat capacity and will therefore release more heat as it cools (because it absorbed more heat when it was heated to 38 °C).

Cc 9.4 (**c**) The specific heat capacity of substance B is twice that of A, but because the mass of B is half that of A, the quantity $m \times C_s$ is identical for both substances so that the final temperature is exactly midway between the two initial temperatures.

Cc 9.5 ΔH represents only the heat exchanged; therefore $\Delta H = -2658$ kJ. ΔE represents the heat *and work* exchanged; therefore $\Delta E = -2661$ kJ. The signs of both ΔH and ΔE are negative because heat and work are flowing out of the system and into the surroundings. Notice that the values of ΔH and ΔE are similar in magnitude, as is the case in many chemical reactions.

Cc 9.6 An endothermic reaction feels cold to the touch because the reaction (acting here as the system) absorbs heat from the surroundings. When you touch the vessel in which the reaction occurs, you, being part of the surroundings, lose heat to the system (the reaction), which makes you feel cold. The heat absorbed by the reaction (from your body, in this case) does not contribute to increasing its temperature, but rather becomes potential energy.

Cc 9.7 The value of q_{rxn} with the greater magnitude (−12.5 kJ) must have come from the bomb calorimeter. Recall that $\Delta E_{\text{rxn}} = q_{\text{rxn}} + w_{\text{rxn}}$. In a bomb calorimeter, the energy change that occurs in the course of the reaction all takes the form of heat (q). In a coffee-cup calorimeter, the amount of energy released as heat may be smaller because some of the energy may be used to do work (w).

Cc 9.8 (**b**) In a highly exothermic reaction, the energy required to break bonds is less than the energy released when the new bonds form, resulting in a net release of energy.