5.27 Calculate ΔE and determine whether the process is endothermic or exothermic for the following cases: **(a)** $q = 0.763$ kJ and $w = -840$ J; **(b)** a system releases 66.1 kJ of heat to its surroundings while the surroundings do 44.0 kJ of work on the system; **(c)** the system absorbs 7.25 kJ of heat from the surroundings while its volume remains constant (assume that only *P-V* work can be done).

5.40 The decomposition of *slaked lime*, $Ca(OH)_2(s)$, into *lime*, $CaO(s)$, and $H_2O(g)$ at constant pressure requires the addition of 109 kJ of heat per mole of $Ca(OH)_2$. **(a)** Write a balanced thermochemical equation for the reaction. **(b)** Draw an enthalpy diagram for the reaction.

5.44 Consider the following reaction:

$$2\,CH_3OH(g) \longrightarrow 2\,CH_4(g) + O_2(g) \qquad \Delta H = +252.8\ kJ$$

(a) Is this reaction exothermic or endothermic? **(b)** Calculate the amount of heat transferred when 24.0 g of $CH_3OH(g)$ is decomposed by this reaction at constant pressure. **(c)** For a given sample of CH_3OH, the enthalpy change during the reaction is 82.1 kJ. How many grams of methane gas are produced? **(d)** How many kilojoules of heat are released when 38.5 g of $CH_4(g)$ reacts completely with $O_2(g)$ to form $CH_3OH(g)$ at constant pressure?

5.57 A 2.200-g sample of quinone ($C_6H_4O_2$) is burned in a bomb calorimeter whose total heat capacity is 7.854 kJ/°C. The temperature of the calorimeter increases from 23.44 °C to 30.57 °C. What is the heat of combustion per gram of quinone? Per mole of quinone?

5.60 Under constant-volume conditions, the heat of combustion of benzoic acid (C_6H_5COOH) is 26.38 kJ/g. A 2.760-g sample of benzoic acid is burned in a bomb calorimeter. The temperature of the calorimeter increases from 21.60 °C to 29.93 °C. **(a)** What is the total heat capacity of the calorimeter? **(b)** A 1.440-g sample of a new organic substance is combusted in the same calorimeter. The temperature of the calorimeter increases from 22.14 °C to 27.09 °C. What is the heat of combustion per gram of the new substance? **(c)** Suppose that in changing samples, a portion of the water in the calorimeter were lost. In what way, if any, would this change the heat capacity of the calorimeter?

A piece of unknown metal with a mass of 5.19 g is heated to 100.00 °C and dropped into 10.0 mL of water at 22.00 °C. The final temperature of the system is 23.83 °C. What is the specific heat capacity of the metal? Attempt to identify the metal using the attached data.

5.64 From the enthalpies of reaction

$$2\,C(s) + O_2(g) \longrightarrow 2\,CO(g) \qquad \Delta H = -221.0\ kJ$$

$$2\,C(s) + O_2(g) + 4\,H_2(g) \longrightarrow 2\,CH_3OH(g) \qquad \Delta H = -402.4\ kJ$$

calculate ΔH for the reaction

$$CO(g) + 2\,H_2(g) \longrightarrow CH_3OH(g)$$

5.70 Write balanced equations that describe the formation of the following compounds from elements in their standard states, and use Appendix C to obtain the values of their standard enthalpies of formation: **(a)** $H_2O_2(g)$, **(b)** $CaCO_3(s)$, **(c)** $POCl_3(l)$, **(d)** $C_2H_5OH(l)$.

5.72 Many portable gas heaters and grills use propane, $C_3H_8(g)$, as a fuel. Using standard enthalpies of formation, calculate the quantity of heat produced when 10.0 g of propane is completely combusted in air under standard conditions.

19.42 For each of the following pairs, indicate which substance possesses the larger standard entropy: **(a)** 1 mol of $P_4(g)$ at 300 °C, 0.01 atm, or 1 mol of $As_4(g)$ at 300 °C, 0.01 atm; **(b)** 1 mol of $H_2O(g)$ at 100 °C, 1 atm, or 1 mol of $H_2O(l)$ at 100 °C, 1 atm; **(c)** 0.5 mol of $N_2(g)$ at 298 K, 20-L volume, or 0.5 mol $CH_4(g)$ at 298 K, 20-L volume; **(d)** 100 g $Na_2SO_4(s)$ at 30 °C or 100 g $Na_2SO_4(aq)$ at 30 °C.

19.43 Predict the sign of the entropy change of the system for each of the following reactions:

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

(b) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

(c) $3\,C_2H_2(g) \longrightarrow C_6H_6(g)$

(d) $Al_2O_3(s) + 3\,H_2(g) \longrightarrow 2\,Al(s) + 3\,H_2O(g)$

19.57 For a certain chemical reaction, $\Delta H^\circ = -35.4\ \text{kJ}$ and $\Delta S^\circ = -85.5\ \text{J/K}$. **(a)** Is the reaction exothermic or endothermic? **(b)** Does the reaction lead to an increase or decrease in the randomness or disorder of the system? **(c)** Calculate ΔG° for the reaction at 298 K. **(d)** Is the reaction spontaneous at 298 K under standard conditions?

19.65 Classify each of the following reactions as one of the four possible types summarized in Table 19.3:

(a) $N_2(g) + 3F_2(g) \longrightarrow 2NF_3(g)$

$\Delta H^\circ = -249\ \text{kJ}; \Delta S^\circ = -278\ \text{J/K}$

(b) $N_2(g) + 3Cl_2(g) \longrightarrow 2NCl_3(g)$

$\Delta H^\circ = 460\ \text{kJ}; \Delta S^\circ = -275\ \text{J/K}$

(c) $N_2F_4(g) \longrightarrow 2NF_2(g)$

$\Delta H^\circ = 85\ \text{kJ}; \Delta S^\circ = 198\ \text{J/K}$

19.85 The value of K_a for nitrous acid (HNO_2) at 25 °C is given in Appendix D. **(a)** Write the chemical equation for the equilibrium that corresponds to K_a. **(b)** By using the value of K_a, calculate $\Delta G°$ for the dissociation of nitrous acid in aqueous solution. **(c)** What is the value of ΔG at equilibrium? **(d)** What is the value of ΔG when $[H^+] = 5.0 \times 10^{-2}\,M$, $[NO_2^-] = 6.0 \times 10^{-4}\,M$, and $[HNO_2] = 0.20\,M$?