5.19 (a) What is meant by the term *system* in thermodynamics? (b) What is a *closed system*? (c) What do we call the part of the universe that is not part of the system?

5.20 In a thermodynamic study a scientist focuses on the properties of a solution in an apparatus as illustrated. A solution is continuously flowing into the apparatus at the top and out at the bottom, such that the amount of solution in the apparatus is constant with time. (a) Is the solution in the apparatus a closed system, open system, or isolated system? Explain your choice. (b) If it is not a closed system, what could be done to make it a closed system?

5.21 (a) What is work? (b) How do we determine the amount of work done, given the force associated with the work?

5.22 (a) What is heat? (b) Under what conditions is heat transferred from one object to another?

5.23 Identify the force present and explain whether work is being performed in the following cases: (a) You lift a pencil off the top of a desk. (b) A spring is compressed to half its normal length.

5.24 Identify the force present and explain whether work is done when (a) a positively charged particle moves in a circle at a fixed distance from a negatively charged particle; (b) an iron nail is pulled off a magnet.

THE FIRST LAW OF THERMODYNAMICS (section 5.2)

5.25 (a) State the first law of thermodynamics. (b) What is meant by the *internal energy* of a system? (c) By what means can the internal energy of a closed system increase?

5.26 (a) Write an equation that expresses the first law of thermodynamics in terms of heat and work. (b) Under what conditions will the quantities q and w be negative numbers?

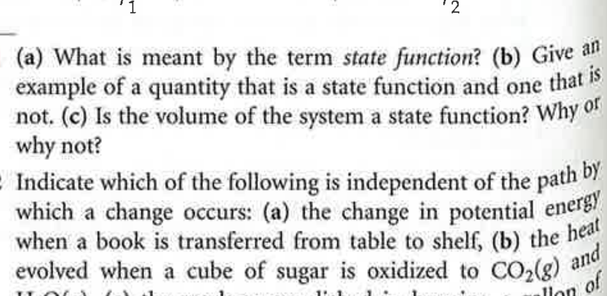
5.27 Calculate ΔE and determine whether the process is endothermic or exothermic for the following cases: (a) $q = 0.763$ kJ and $w = -840$ J; (b) a system releases 66.1 kJ of heat to its surroundings while the surroundings do 44.0 kJ of work on the system; (c) the system absorbs 7.25 kJ of heat from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

5.28 For the following processes, calculate the change in internal energy of the system and determine whether the process is endothermic or exothermic: (a) A balloon is cooled by removing 0.655 kJ of heat. It shrinks on cooling, and the atmosphere does 382 J of work on the balloon. (b) A 100.0-g bar of gold is heated from 25 °C to 50 °C during which it absorbs 322 J of heat. Assume the volume of the gold bar remains constant. (c) The surroundings do 1.44 kJ of work compressing gas in a perfectly insulated cylinder.

5.29 A gas is confined to a cylinder fitted with a piston and an electrical heater, as shown here:

Suppose that current is supplied to the heater so that 100 J of energy is added. Consider two different situations. In case (1) the piston is allowed to move as the energy is added. In case (2) the piston is fixed so that it cannot move. (a) In which case does the gas have the higher temperature after addition of the electrical energy? Explain. (b) What can you say about the values of q and w in each case? (c) What can you say about the relative values of ΔE for the system (the gas in the cylinder) in the two cases?

5.30 Consider a system consisting of two oppositely charged spheres hanging by strings and separated by a distance r_1, as shown in the accompanying illustration. Suppose they are separated to a larger distance r_2, by moving them apart along a track. (a) What change, if any, has occurred in the potential energy of the system? (b) What effect, if any, does this process have on the value of ΔE? (c) What can you say about q and w for this process?



5.31 (a) What is meant by the term *state function*? (b) Give an example of a quantity that is a state function and one that is not. (c) Is the volume of the system a state function? Why or why not?

5.32 Indicate which of the following is independent of the path by which a change occurs: (a) the change in potential energy when a book is transferred from table to shelf, (b) the heat evolved when a cube of sugar is oxidized to $CO_2(g)$ and $H_2O(g)$, (c) the work accomplished in burning a gallon of gasoline.

ENTHALPY (sections 5.3 and 5.4)

5.33 (a) Why is the change in enthalpy usually easier to measure than the change in internal energy? (b) H is a state function, but q is not a state function. Explain. (c) For a given process at constant pressure, ΔH is positive. Is the process endothermic or exothermic?

5.34 (a) Under what condition will the enthalpy change of a process equal the amount of heat transferred into or out of the system? (b) During a constant-pressure process, the system releases heat to the surroundings. Does the enthalpy of the system increase or decrease during the process? (c) In a constant-pressure process, $\Delta H = 0$. What can you conclude about ΔE, q, and w?

5.35 You are given ΔH for a process that occurs at constant pressure. What additional information do you need to determine ΔE for the process?

5.36 Suppose that the gas-phase reaction $2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$ were carried out in a constant-volume container at constant temperature. Would the measured heat change represent ΔH or ΔE? If there is a difference, which quantity is larger for this reaction? Explain.

5.37 A gas is confined to a cylinder under constant atmospheric pressure, as illustrated in Figure 5.4. When the gas undergoes a particular chemical reaction, it absorbs 824 J of heat from its surroundings and has 0.65 kJ of P-V work done on it by its surroundings. What are the values of ΔH and ΔE for this process?

5.38 A gas is confined to a cylinder under constant atmospheric pressure, as illustrated in Figure 5.4. When 0.49 kJ of heat is added to the gas, it expands and does 214 J of work on the surroundings. What are the values of ΔH and ΔE for this process?

5.39 The complete combustion of ethanol, $C_2H_5OH(l)$, to form $H_2O(g)$ and $CO_2(g)$ at constant pressure releases 1235 kJ of heat per mole of C_2H_5OH. (a) Write a balanced thermochemical equation for this reaction. (b) Draw an enthalpy diagram for the reaction.

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.

5.41 Ozone, $O_3(g)$, is a form of elemental oxygen that is important in the absorption of ultraviolet radiation in the stratosphere. It decomposes to $O_2(g)$ at room temperature and pressure according to the following reaction:

$$2\,O_3(g) \longrightarrow 3\,O_2(g) \qquad \Delta H = -284.6\text{ kJ}$$

(a) What is the enthalpy change for this reaction per mole of $O_3(g)$? (b) Which has the higher enthalpy under these conditions, $2\,O_3(g)$ or $3\,O_2(g)$?

5.42 Without referring to tables, predict which of the following has the higher enthalpy in each case: (a) 1 mol $CO_2(s)$ or 1 mol $CO_2(g)$ at the same temperature, (b) 2 mol of hydrogen atoms or 1 mol of H_2, (c) 1 mol $H_2(g)$ and 0.5 mol $O_2(g)$ at 25 °C or 1 mol $H_2O(g)$ at 25 °C, (d) 1 mol $N_2(g)$ at 100 °C or 1 mol $N_2(g)$ at 300 °C.

5.43 Consider the following reaction:

$$2\,Mg(s) + O_2(g) \longrightarrow 2\,MgO(s) \qquad \Delta H = -1204\text{ kJ}$$

(a) Is this reaction exothermic or endothermic? (b) Calculate the amount of heat transferred when 3.55 g of $Mg(s)$ reacts at constant pressure. (c) How many grams of MgO are produced during an enthalpy change of -234 kJ? (d) How many kilojoules of heat are absorbed when 40.3 g of $MgO(s)$ is decomposed into $Mg(s)$ and $O_2(g)$ at constant pressure?

5.44 Consider the following reaction:

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

(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?

5.45 When solutions containing silver ions and chloride ions are mixed, silver chloride precipitates:

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s) \qquad \Delta H = -65.5\text{ kJ}$$

(a) Calculate ΔH for production of 0.450 mol of AgCl by this reaction. (b) Calculate ΔH for the production of 9.00 g of AgCl. (c) Calculate ΔH when 9.25×10^{-4} mol of AgCl dissolves in water.

5.46 At one time, a common means of forming small quantities of oxygen gas in the laboratory was to heat $KClO_3$:

$$2\,KClO_3(s) \longrightarrow 2\,KCl(s) + 3\,O_2(g) \qquad \Delta H = -89.4\text{ kJ}$$

For this reaction, calculate ΔH for the formation of (a) 1.36 mol of O_2 and (b) 10.4 g of KCl. (c) The decomposition of $KClO_3$ proceeds spontaneously when it is heated. Do you think that the reverse reaction, the formation of $KClO_3$ from KCl and O_2, is likely to be feasible under ordinary conditions? Explain your answer.

5.47 Consider the combustion of liquid methanol, $CH_3OH(l)$:

$$CH_3OH(l) + \tfrac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H = -726.5\text{ kJ}$$

(a) What is the enthalpy change for the reverse reaction? (b) Balance the forward reaction with whole-number coefficients. What is ΔH for the reaction represented by this equation? (c) Which is more likely to be thermodynamically favored, the forward reaction or the reverse reaction? (d) If the reaction were written to produce $H_2O(g)$ instead of $H_2O(l)$, would you expect the magnitude of ΔH to increase, decrease, or stay the same? Explain.

5.48 Consider the decomposition of liquid benzene, $C_6H_6(l)$, to gaseous acetylene, $C_2H_2(g)$:

$$C_6H_6(l) \longrightarrow 3\,C_2H_2(g) \qquad \Delta H = +630\text{ kJ}$$

(a) What is the enthalpy change for the reverse reaction? (b) What is ΔH for the formation of 1 mol of acetylene? (c) Which is more likely to be thermodynamically favored, the forward reaction or the reverse reaction? (d) If $C_6H_6(g)$ were consumed instead of $C_6H_6(l)$, would you expect the magnitude of ΔH to increase, decrease, or stay the same? Explain.

CALORIMETRY (section 5.5)

5.49 (a) What are the units of molar heat capacity? (b) What are the units of specific heat? (c) If you know the specific heat of copper, what additional information do you need to calculate the heat capacity of a particular piece of copper pipe?

5.50 Two solid objects, A and B, are placed in boiling water and allowed to come to temperature there. Each is then lifted out and placed in separate beakers containing 1000 g water at 10.0 °C. Object A increases the water temperature by 3.50 °C; B increases the water temperature by 2.60 °C. (a) Which object has the larger heat capacity? (b) What can you say about the specific heats of A and B?

5.51 (a) What is the specific heat of liquid water? (b) What is the molar heat capacity of liquid water? (c) What is the heat capacity of 185 g of liquid water? (d) How many kJ of heat are needed to raise the temperature of 10.00 kg of liquid water from 24.6 °C to 46.2 °C?

5.52 (a) Which substance in Table 5.2 requires the smallest amount of energy to increase the temperature of 50.0 g of that substance by 10 K? (b) Calculate the energy needed for this temperature change.

5.53 The specific heat of *octane*, $C_8H_{18}(l)$, is 2.22 J/g-K. (a) How many J of heat are needed to raise the temperature of 80.0 g of octane from 10.0 °C to 25.0 °C? (b) Which will require more heat, increasing the temperature of 1 mol of $C_8H_{18}(l)$ by a certain amount or increasing the temperature of 1 mol of $H_2O(l)$ by the same amount?

5.54 Consider the data about gold metal in Exercise 5.28(b). (a) Based on the data, calculate the specific heat of Au(*s*). (b) Suppose that the same amount of heat is added to two 10.0-g blocks of metal, both initially at the same temperature. One block is gold metal and one is iron metal. Which block will have the greater rise in temperature after the addition of the heat? (c) What is the molar heat capacity of Au(*s*)?

5.55 When a 6.50-g sample of solid sodium hydroxide dissolves in 100.0 g of water in a coffee-cup calorimeter (Figure 5.18), the temperature rises from 21.6 °C to 37.8 °C. Calculate ΔH (in kJ/mol NaOH) for the solution process

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$

Assume that the specific heat of the solution is the same as that of pure water.

5.56 (a) When a 4.25-g sample of solid ammonium nitrate dissolves in 60.0 g of water in a coffee-cup calorimeter (Figure 5.18), the temperature drops from 22.0 °C to 16.9 °C. Calculate ΔH (in kJ/mol NH_4NO_3) for the solution process

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

Assume that the specific heat of the solution is the same as that of pure water. (b) Is this process endothermic or exothermic?

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?

5.58 A 1.800-g sample of phenol (C_6H_5OH) was burned in a bomb calorimeter whose total heat capacity is 11.66 kJ/°C. The temperature of the calorimeter plus contents increased from 21.36 °C to 26.37 °C. (a) Write a balanced chemical equation for the bomb calorimeter reaction. (b) What is the heat of combustion per gram of phenol? Per mole of phenol?

5.59 Under constant-volume conditions, the heat of combustion of glucose ($C_6H_{12}O_6$) is 15.57 kJ/g. A 3.500-g sample of glucose is burned in a bomb calorimeter. The temperature of the calorimeter increased from 20.94 °C to 24.72 °C. (a) What is the total heat capacity of the calorimeter? (b) If the size of the glucose sample had been exactly twice as large, what would the temperature change of the calorimeter have been?

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?

HESS'S LAW (section 5.6)

5.61 What is the connection between Hess's law and the fact that *H* is a state function?

5.62 Consider the following hypothetical reactions:

$$A \longrightarrow B \qquad \Delta H = +30 \text{ kJ}$$
$$B \longrightarrow C \qquad \Delta H = +60 \text{ kJ}$$

(a) Use Hess's law to calculate the enthalpy change for the reaction $A \longrightarrow C$. (b) Construct an enthalpy diagram for substances A, B, and C, and show how Hess's law applies.

5.63 Calculate the enthalpy change for the reaction

$$P_4O_6(s) + 2\,O_2(g) \longrightarrow P_4O_{10}(s)$$

given the following enthalpies of reaction:

$$P_4(s) + 3\,O_2(g) \longrightarrow P_4O_6(s) \qquad \Delta H = -1640.1 \text{ kJ}$$
$$P_4(s) + 5\,O_2(g) \longrightarrow P_4O_{10}(s) \qquad \Delta H = -2940.1 \text{ kJ}$$

5.64 From the enthalpies of reaction

$$2\,C(s) + O_2(g) \longrightarrow 2\,CO(g) \qquad \Delta H = -221.0 \text{ kJ}$$
$$2\,C(s) + O_2(g) + 4\,H_2(g) \longrightarrow 2\,CH_3OH(g) \qquad \Delta H = -402.4 \text{ kJ}$$

calculate ΔH for the reaction

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

5.65 From the enthalpies of reaction

$$H_2(g) + F_2(g) \longrightarrow 2\,HF(g) \qquad \Delta H = -537 \text{ kJ}$$
$$C(s) + 2\,F_2(g) \longrightarrow CF_4(g) \qquad \Delta H = -680 \text{ kJ}$$
$$2\,C(s) + 2\,H_2(g) \longrightarrow C_2H_4(g) \qquad \Delta H = +52.3 \text{ kJ}$$

calculate ΔH for the reaction of ethylene with F_2:

$$C_2H_4(g) + 6\,F_2(g) \longrightarrow 2\,CF_4(g) + 4\,HF(g)$$

5.66 Given the data

$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g) \qquad \Delta H = +180.7\ \text{kJ}$$
$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g) \qquad \Delta H = -113.1\ \text{kJ}$$
$$2\,N_2O(g) \longrightarrow 2\,N_2(g) + O_2(g) \qquad \Delta H = -163.2\ \text{kJ}$$

use Hess's law to calculate ΔH for the reaction

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

ENTHALPIES OF FORMATION (section 5.7)

5.67 **(a)** What is meant by the term *standard conditions* with reference to enthalpy changes? **(b)** What is meant by the term *enthalpy of formation*? **(c)** What is meant by the term *standard enthalpy of formation*?

5.68 **(a)** Why are tables of standard enthalpies of formation so useful? **(b)** What is the value of the standard enthalpy of formation of an element in its most stable form? **(c)** Write the chemical equation for the reaction whose enthalpy change is the standard enthalpy of formation of sucrose (table sugar), $C_{12}H_{22}O_{11}(s)$, $\Delta H_f^\circ[C_{12}H_{22}O_{11}]$.

5.69 For each of the following compounds, write a balanced thermochemical equation depicting the formation of one mole of the compound from its elements in their standard states and use Appendix C to obtain the value of ΔH_f°: **(a)** $NO_2(g)$, **(b)** $SO_3(g)$, **(c)** $NaBr(s)$, **(d)** $Pb(NO_3)_2(s)$.

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)** $C_2H_5OH(l)$.

5.71 The following is known as the thermite reaction [Figure 5.8(b)]:

$$2\,Al(s) + Fe_2O_3(s) \longrightarrow Al_2O_3(s) + 2\,Fe(s)$$

This highly exothermic reaction is used for welding massive units, such as propellers for large ships. Using standard enthalpies of formation in Appendix C, calculate ΔH° for this reaction.

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.

5.73 Using values from Appendix C, calculate the standard enthalpy change for each of the following reactions:

(a) $2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$

(b) $Mg(OH)_2(s) \longrightarrow MgO(s) + H_2O(l)$

(c) $N_2O_4(g) + 4\,H_2(g) \longrightarrow N_2(g) + 4\,H_2O(g)$

(d) $SiCl_4(l) + 2\,H_2O(l) \longrightarrow SiO_2(s) + 4\,HCl(g)$

5.74 Using values from Appendix C, calculate the value of ΔH° for each of the following reactions:

(a) $CaO(s) + 2\,HCl(g) \longrightarrow CaCl_2(s) + H_2O(g)$

(b) $4\,FeO(s) + O_2(g) \longrightarrow 2\,Fe_2O_3(s)$

(c) $2\,CuO(s) + NO(g) \longrightarrow Cu_2O(s) + NO_2(g)$

(d) $4\,NH_3(g) + O_2(g) \longrightarrow 2\,N_2H_4(g) + 2\,H_2O(l)$

5.75 Complete combustion of 1 mol of acetone (C_3H_6O) liberates 1790 kJ:

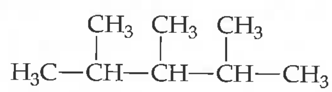
$$C_3H_6O(l) + 4\,O_2(g) \longrightarrow 3\,CO_2(g) + 3\,H_2O(l) \qquad \Delta H^\circ = -1790\ \text{kJ}$$

Using this information together with data from Appendix C, calculate the enthalpy of formation of acetone.

5.76 Calcium carbide (CaC_2) reacts with water to form acetylene (C_2H_2) and $Ca(OH)_2$. From the following enthalpy of reaction data and data in Appendix C, calculate ΔH_f° for $CaC_2(s)$:

$$CaC_2(s) + 2\,H_2O(l) \longrightarrow Ca(OH)_2(s) + C_2H_2(g) \qquad \Delta H^\circ = -127.2\ \text{kJ}$$

5.77 Gasoline is composed primarily of hydrocarbons, including many with eight carbon atoms, called *octanes*. One of the cleanest-burning octanes is a compound called 2,3,4-trimethylpentane, which has the following structural formula:



The complete combustion of one mole of this compound to $CO_2(g)$ and $H_2O(g)$ leads to $\Delta H^\circ = -5064.9$ kJ/mol. **(a)** Write a balanced equation for the combustion of 1 mol of $C_8H_{18}(l)$. **(b)** Write a balanced equation for the formation of $C_8H_{18}(l)$ from its elements. **(c)** By using the information in this problem and data in Table 5.3, calculate ΔH_f° for 2,3,4-trimethylpentane.

5.78 Diethyl ether, $C_4H_{10}O(l)$, a flammable compound that has long been used as a surgical anesthetic, has the structure

$$CH_3{-}CH_2{-}O{-}CH_2{-}CH_3$$

The complete combustion of 1 mol of $C_4H_{10}O(l)$ to $CO_2(g)$ and $H_2O(l)$ yields $\Delta H^\circ = -2723.7$ kJ. **(a)** Write a balanced equation for the combustion of 1 mol of $C_4H_{10}O(l)$. **(b)** Write a balanced equation for the formation of $C_4H_{10}O(l)$ from its elements. **(c)** By using the information in this problem and data in Table 5.3, calculate ΔH_f° for diethyl ether.

5.79 Ethanol (C_2H_5OH) is currently blended with gasoline as an automobile fuel. **(a)** Write a balanced equation for the combustion of liquid ethanol in air. **(b)** Calculate the standard enthalpy change for the reaction, assuming $H_2O(g)$ as a product. **(c)** Calculate the heat produced per liter of ethanol by combustion of ethanol under constant pressure. Ethanol has a density of 0.789 g/mL. **(d)** Calculate the mass of CO_2 produced per kJ of heat emitted.

5.80 Methanol (CH_3OH) is used as a fuel in race cars. **(a)** Write a balanced equation for the combustion of liquid methanol in air. **(b)** Calculate the standard enthalpy change for the reaction, assuming $H_2O(g)$ as a product. **(c)** Calculate the heat produced by combustion per liter of methanol. Methanol has a density of 0.791 g/mL. **(d)** Calculate the mass of CO_2 produced per kJ of heat emitted.