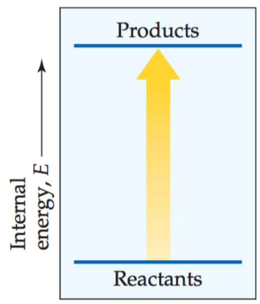
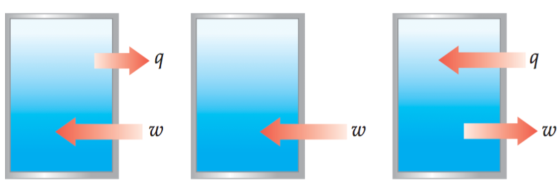
Thermodynamics and Thermochemistry Problem Set

5.1 Imagine a book that is falling from a shelf. At a particular moment during its fall, the book has a kinetic energy of 24 J and a potential energy with respect to the floor of 47 J. **(a)** How does the book's kinetic energy and its potential energy change as it continues to fall? **(b)** What is its total kinetic energy at the instant just before it strikes the floor? **(c)** If a heavier book fell from the same shelf, would it have the same kinetic energy when it strikes the floor? [Section 5.1]

5.3 Consider the accompanying energy diagram. **(a)** Does this diagram represent an increase or decrease in the internal energy of the system? **(b)** What sign is given to ΔE for this process? **(c)** If there is no work associated with the process, is it exothermic or endothermic? [Section 5.2]

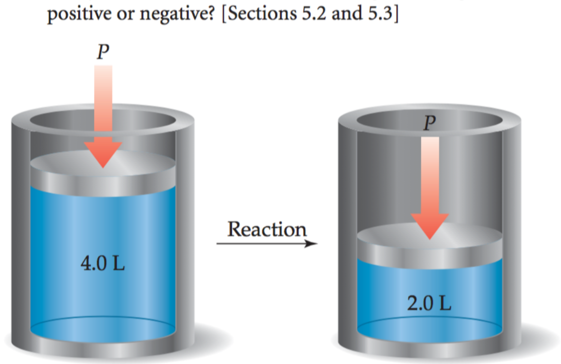


5.4 The contents of the closed box in each of the following illustrations represent a system, and the arrows show the changes to the system during some process. The lengths of the arrows represent the relative magnitudes of q and w. **(a)** Which of these processes is endothermic? **(b)** For which of these processes, if any, is $\Delta E < 0$? **(c)** For which process, if any, does the system experience a net gain in internal energy? [Section 5.2]

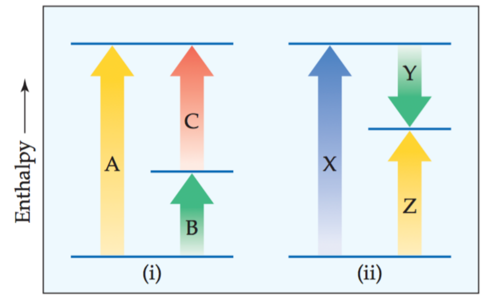


(i) (ii) (iii)

5.8 In the accompanying cylinder diagram a chemical process occurs at constant temperature and pressure. **(a)** Is the sign of w indicated by this change positive or negative? **(b)** If the process is endothermic, does the internal energy of the system within the cylinder increase or decrease during the change and is ΔE positive or negative? [Sections 5.2 and 5.3]



5.11 Consider the two diagrams that follow. **(a)** Based on (i), write an equation showing how ΔH_A is related to ΔH_B and ΔH_C. How do both diagram (i) and your equation relate to the fact that enthalpy is a state function? **(b)** Based on (ii), write an equation relating ΔH_Z to the other enthalpy changes in the diagram. **(c)** How do these diagrams relate to Hess's law? [Section 5.6]



5.13 In what two ways can an object possess energy? How do these two ways differ from one another?

5.14 Suppose you toss a tennis ball upward. **(a)** Does the kinetic energy of the ball increase or decrease as it moves higher? **(b)** What happens to the potential energy of the ball as it moves higher? **(c)** If the same amount of energy were imparted to a ball the same size as a tennis ball but of twice the mass, how high would it go in comparison to the tennis ball? Explain your answers.

5.15 **(a)** Calculate the kinetic energy in joules of a 1200-kg automobile moving at 18 m/s. **(b)** Convert this energy to calories. **(c)** What happens to this energy when the automobile brakes to a stop?

5.18 A watt is a measure of power (the rate of energy change) equal to 1 J/s. **(a)** Calculate the number of joules in a kilowatt-hour. **(b)** An adult person radiates heat to the surroundings at about the same rate as a 100-watt electric incandescent lightbulb. What is the total amount of energy in kcal radiated to the surroundings by an adult in 24 hours?

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?

5.21 **(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?

5.25 **(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).

5.29 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?

5.33 **(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?

5.37 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?

5.39 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.

5.41 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 $3\,O_2(g)$?

5.44 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?

5.47 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.

5.49 **(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?

5.51 **(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?

5.56 **(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?

5.58 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?

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

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:

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

5.63 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:

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

5.67 **(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*?

5.69 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)** $Pb(NO_3)_2(s)$.

5.71 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.

5.76 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 $CaC_2(s)$:

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

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.