Sample Exercise 5.1 Describing and Calculating Energy Changes

A bowler lifts a 5.4-kg (12-lb) bowling ball from ground level to a height of 1.6 m (5.2 feet) and then drops the ball back to the ground. (a) What happens to the potential energy of the bowling ball as it is raised from the ground? (b) What quantity of work, in J, is used to raise the ball? (c) After the ball is dropped, it gains kinetic energy. If we assume that all of the work done in part (b) has been converted to kinetic energy by the time the ball strikes the ground, what is the speed of the ball at the instant just before it hits the ground? (Note: The force due to gravity is $F = m \times g$, where *m* is the mass of the object and *g* is the gravitational constant; $g = 9.8 \text{ m/s}^2$.)

Solution

Analyze: We need to relate the potential energy of the bowling ball to its position relative to the ground. We then need to establish the relationship between work and the change in potential energy of the ball. Finally, we need to connect the change in potential energy when the ball is dropped with the kinetic energy attained by the ball.

Plan: We can calculate the work done in lifting the ball by using Equation 5.3: $w = F \times d$. The kinetic energy of the ball at the moment of impact equals its initial potential energy. We can use the kinetic energy and Equation 5.1 to calculate the speed, *v*, at impact.

Solve:

(a) Because the bowling ball is raised to a greater height above the ground, its potential energy increases.

(b) The ball has a mass of 5.4 kg, and it is lifted a distance of 1.6 m. To calculate the work performed to raise the ball, we use both Equation 5.3 and $F = m \times g$ for the force that is due to gravity:

$$w = F \times d = m \times g \times d = (5.4 \text{ kg})(9.8 \text{ m/s}^2)(1.6 \text{ m}) = 85 \text{ kg-m}^2/\text{s}^2 = 85 \text{ J}$$



Sample Exercise 5.1 Describing and Calculating Energy Changes

Solution (continued)

Thus, the bowler has done 85 J of work to lift the ball to a height of 1.6 m.

(c) When the ball is dropped, its potential energy is converted to kinetic energy. At the instant just before the ball hits the ground, we assume that the kinetic energy is equal to the work done in part (b), 85 J:

$$E_k = \frac{1}{2}mv^2 = 85 \text{ J} = 85 \text{ kg-m}^2/\text{s}^2$$

We can now solve this equation for *v*:

$$v^{2} = \left(\frac{2E_{k}}{m}\right) = \left(\frac{2(85 \text{ kg-m}^{2}/\text{s}^{2})}{5.4 \text{ kg}}\right) = 31.5 \text{ m}^{2}/\text{s}^{2}$$
$$v = \sqrt{31.5 \text{ m}^{2}/\text{s}^{2}} = 5.6 \text{ m/s}$$

Check: Work must be done in part (b) to increase the potential energy of the ball, which is in accord with our experience. The units are appropriate in both parts (b) and (c). The work is in units of J and the speed in units of m/s. In part (c) we have carried an additional digit in the intermediate calculation involving the square root, but we report the final value to only two significant figures, as appropriate.

Comment: A speed of 1 m/s is roughly 2 mph, so the bowling ball has a speed greater than 10 mph upon impact.

Practice Exercise

What is the kinetic energy, in J, of (a) an Ar atom moving with a speed of 650 m/s, (b) a mole of Ar atoms moving with a speed of 650 m/s (Hint: 1 amu = 1.66×10^{-27} kg) **Answers:** (a) 1.4×10^{-20} J, (b) 8.4×10^3 J



Sample Exercise 5.2 Relating Heat and Work to Changes of Internal Energy

Two gases, A(g) and B(g), are confined in a cylinder-and-piston arrangement like that in Figure 5.3. Substances A and B react to form a solid product: $A(g) + B(g) \rightarrow C(s)$. As the reaction occurs, the system loses 1150 J of heat to the surroundings. The piston moves downward as the gases react to form a solid. As the volume of the gas decreases under the constant pressure of the atmosphere, the surroundings do 480 J of work on the system. What is the change in the internal energy of the system?

Solution

Analyze: The question asks us to determine ΔE , given information about q and w.

Plan: We first determine the signs of *q* and *w* (Table 5.1) and then use Equation 5.5, $\Delta E = q + w$, to calculate ΔE .

Solve: Heat is transferred from the system to the surroundings, and work is done on the system by the surroundings, so *q* is negative and *w* is positive: q = -1150 J and w = 480 kJ. Thus,

$$\Delta E = q + w = (-1150 \text{ J}) + (480 \text{ J}) = -670 \text{ J}$$

The negative value of ΔE tells us that a net quantity of 670 J of energy has been transferred from the system to the surroundings.

Comment: You can think of this change as a decrease of 670 J in the net value of the system's energy bank account (hence the negative sign); 1150 J is withdrawn in the form of heat, while 480 J is deposited in the form of work. Notice that as the volume of the gases decreases, work is being done on the system by the surroundings, resulting in a deposit of energy.

Practice Exercise

Calculate the change in the internal energy of the system for a process in which the system absorbs 140 J of heat from the surroundings and does 85 J of work on the surroundings. *Answer:* +55 J



Sample Exercise 5.3 Determining the Sign of ΔH

Indicate the sign of the enthalpy change, ΔH , in each of the following processes carried out under atmospheric pressure, and indicate whether the process is endothermic or exothermic: (a) An ice cube melts; (b) 1 g of butane (C₄H₁₀) is combusted in sufficient oxygen to give complete combustion to CO₂ and H₂O.

Solution

Analyze: Our goal is to determine whether is positive or negative for each process. Because each process appears to occur at constant pressure, the enthalpy change of each one equals the amount of heat absorbed or released, $\Delta H = q_{\rm P}$.

Plan: We must predict whether heat is absorbed or released by the system in each process. Processes in which heat is absorbed are endothermic and have a positive sign for ΔH ; those in which heat is released are exothermic and have a negative sign for ΔH .

Solve: In (a) the water that makes up the ice cube is the system. The ice cube absorbs heat from the surroundings as it melts, so ΔH is positive and the process is endothermic. In (b) the system is the 1 g of butane and the oxygen required to combust it. The combustion of butane in oxygen gives off heat, so ΔH is negative and the process is exothermic.



Sample Exercise 5.3 Determining the Sign of ΔH

Practice Exercise

Suppose we confine 1 g of butane and sufficient oxygen to completely combust it in a cylinder like that in Figure 5.12. The cylinder is perfectly insulating, so no heat can escape to the surroundings. A spark initiates combustion of the butane, which forms carbon dioxide and water vapor. If we used this apparatus to measure the enthalpy change in the reaction, would the piston rise, fall, or stay the same? *Answer:* The piston must move to maintain a constant pressure in the cylinder. The products contain more molecules of gas than the reactants, as shown by the balanced equation

 $2 C_4 H_{10}(g) + 13 O_2(g) \rightarrow 8 CO_2(g) + 10 H_2 O(g)$

As a result, the piston would rise to make room for the additional molecules of gas. Heat is given off, so the piston would also rise an additional amount to accommodate the expansion of the gases because of the temperature increase.



Sample Exercise 5.4 Relating ΔH to Quantities of Reactants and Products

How much heat is released when 4.50 g of methane gas is burned in a constant pressure system? (Use the information given in Equation 5.18.)

Solution

Analyze: Our goal is to use a thermochemical equation to calculate the heat produced when a specific amount of methane gas is combusted. According to Equation 5.18, 890 kJ is released by the system when 1 mol CH₄ is burned at constant pressure ($\Delta H = -890$ kJ).

Plan: Equation 5.18 provides us with a stoichiometric conversion factor: 1 mol $CH_4 \cong -890$ kJ). Thus, we can convert moles of CH_4 to kJ of energy. First, however, we must convert grams of CH_4 to moles of CH_4 . Thus, the conversion sequence is grams CH_4 (given) \rightarrow moles $CH_4 \rightarrow$ kJ (unknown to be found). **Solve:** By adding the atomic weights of C and 4 H, we have 1 mol $CH_4 = 16.0$ g CH_4 . We can use the appropriate conversion factors to convert grams of CH_4 to moles of CH_4 to kilojoules:

Heat =
$$(4.50 \text{ g CH}_4) \left(\frac{1 \text{ mol CH}_4}{16.0 \text{ g CH}_4}\right) \left(\frac{-890 \text{ kJ}}{1 \text{ mol CH}_4}\right) = -250 \text{ kJ}$$

The negative sign indicates that the system released 250 kJ into the surroundings.

Practice Exercise

Hydrogen peroxide can decompose to water and oxygen by the following reaction:

$$2 \operatorname{H}_2\operatorname{O}_2(l) \to 2 \operatorname{H}_2\operatorname{O}(l) + \operatorname{O}_2(g) \qquad \Delta H = -196 \text{ kJ}$$

Calculate the value of q when 5.00 g of H₂O₂(l) decomposes at constant pressure. *Answer:* -14.4 kJ



Sample Exercise 5.5 Relating Heat, Temperature Change, and Heat Capacity

(a) How much heat is needed to warm 250 g of water (about 1 cup) from 22 °C (about room temperature) to near its boiling point, 98 °C? The specific heat of water is 4.18 J/g-K. (b) What is the molar heat capacity of water?

Solution

Analyze: In part (a) we must find the quantity of heat (q) needed to warm the water, given the mass of water (m), its temperature change (ΔT) , and its specific heat (C_s) . In part (b) we must calculate the molar heat capacity (heat capacity per mole, C_m) of water from its specific heat (heat capacity per gram). **Plan:** (a) Given C_s , m, and ΔT , we can calculate the quantity of heat, q, using Equation 5.22. (b) We can use the molar mass of water and dimensional analysis to convert from heat capacity per gram to heat capacity per mole.

Solve:

(a) The water undergoes a temperature change of

Using Equation 5.22, we have

(b) The molar heat capacity is the heat capacity of one mole of substance. Using the atomic weights of hydrogen and oxygen, we have

From the specific heat given in part (a), we have

$$\Delta T = 98 \,^{\circ}\text{C} - 22 \,^{\circ}\text{C} = 76 \,^{\circ}\text{C} = 76 \,^{\text{K}}$$
$$q = C_s \times m \times \Delta T$$
$$= (4.18 \,^{\text{J}}\text{g}\text{-K})(250 \,^{\text{g}}\text{g})(76 \,^{\text{K}}\text{K}) = 7.9 \times 10^4 \,^{\text{J}}\text{J}$$

1 mol H₂O = 18.0 g H₂O

$$C_m = \left(4.18 \frac{J}{g-K}\right) \left(\frac{18.0 g}{1 \text{ mol}}\right) = 75.2 \text{ J/mol-K}$$



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Practice Exercise

(a) Large beds of rocks are used in some solar-heated homes to store heat. Assume that the specific heat of the rocks is 0.82 J/g-K. Calculate the quantity of heat absorbed by 50.0 kg of rocks if their temperature increases by 12.0 °C.

(b) What temperature change would these rocks undergo if they emitted 450 kJ of heat?

Answers: (a) 4.9×10^5 J, (b) 11 K decrease = 11 °C decrease.



Chemistry: The Central Science, Eleventh Edition By Theodore E. Brown, H. Eugene LeMay, Bruce E. Bursten, and Catherine J. Murphy With contributions from Patrick Woodward

Sample Exercise 5.6 Measuring ΔH Using a Coffee-Cup Calorimeter

When a student mixes 50 mL of 1.0 *M* HCl and 50 mL of 1.0 *M* NaOH in a coffee-cup calorimeter, the temperature of the resultant solution increases from 21.0 °C to 27.5 °C. Calculate the enthalpy change for the reaction in kJ/mol HCl, assuming that the calorimeter loses only a negligible quantity of heat, that the total volume of the solution is 100 mL, that its density is 1.0 g/mL, and that its specific heat is 4.18 J/g-K.

Solution

Analyze: Mixing solutions of HCl and NaOH results in an acid–base reaction:

 $\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{H}_2\text{O}(l) + \text{NaCl}(aq)$

We need to calculate the heat produced per mole of HCl, given the temperature increase of the solution, the number of moles of HCl and NaOH involved, and the density and specific heat of the solution. **Plan:** The total heat produced can be calculated using Equation 5.23. The number of moles of HCl consumed in the reaction must be calculated from the volume and molarity of this substance, and this amount then used to determine the heat produced per mol HCl.

Solve:

Because the total volume of the solution is 100 mL,	(100 mL)(1.0 g/mL) = 100 g
its mass is	$\Delta T = 27.5 ^{\circ}\text{C} - 21.0 ^{\circ}\text{C} = 6.5 ^{\circ}\text{C} = 6.5 \text{K}$
The temperature change is	$q_{\rm rxn} = -C_s \times m \times \Delta T$ $= (4.18 {\rm J/z} {\rm K})(100 {\rm z})((5 {\rm K}) = -2.7 {\rm K} 10^3 {\rm J} = -2.7 {\rm K})$
Using Equation 5.23, we have	$= -(4.18 \text{ J/g-K})(100 \text{ g})(6.5 \text{ K}) = -2.7 \times 10^3 \text{ J} = -2.7 \text{ kJ}$ $\Delta H = q_P = -2.7 \text{ kJ}$



Sample Exercise 5.6 Measuring ΔH Using a Coffee-Cup Calorimeter

Solution (continued)

Because the process occurs at constant pressure,

To express the enthalpy change on a molar basis, we use the fact that the number of moles of HCl is given by the product of the respective solution volumes (50 mL = 0.050 L) and concentrations (1.0 M = 1.0 mol/L):

Thus, the enthalpy change per mole of HCl is

 $\Delta H = -2.7 \text{ kJ}/0.050 \text{ mol} = -54 \text{ kJ/mol}$ **Check:** ΔH is negative (exothermic), which is expected for the reaction of an acid with a base and evidenced by the fact that the reaction causes the temperature of the solution to increase. The molar magnitude of the heat produced seems reasonable.

(0.050 L)(1.0 mol/L) = 0.050 mol

Practice Exercise

When 50.0 mL of 0.100 M AgNO₃ and 50.0 mL of 0.100 M HCl are mixed in a constant-pressure calorimeter, the temperature of the mixture increases from 22.30 °C to 23.11 °C. The temperature increase is caused by the following reaction:.

$$\operatorname{AgNO}_3(aq) + \operatorname{HCl}(aq) \rightarrow \operatorname{AgCl}(s) + \operatorname{HNO}_3(aq)$$

Calculate ΔH for this reaction in kJ/mol AgNO₃, assuming that the combined solution has a mass of 100.0 g and a specific heat of $4.18 \text{ J/g} \degree \text{C}$. *Answer:* -68,000 J/mol = -68 kJ/mol



Sample Exercise 5.7 Measuring q_{rxn} Using a Bomb Calorimeter

Methylhydrazine (CH_6N_2) is used as a liquid rocket fuel. The combustion of methylhydrazine with oxygen produces $N_2(g)$, $CO_2(g)$, and $H_2O(l)$:

 $2 \operatorname{CH}_6\operatorname{N}_2(l) + 5 \operatorname{O}_2(g) \to 2 \operatorname{N}_2(g) + 2 \operatorname{CO}_2(g) + 6 \operatorname{H}_2\operatorname{O}(l)$

When 4.00 g of methylhydrazine is combusted in a bomb calorimeter, the temperature of the calorimeter increases from 25.00 °C to 39.50 °C. In a separate experiment the heat capacity of the calorimeter is measured to be 7.794 kJ/°C. Calculate the heat of reaction for the combustion of a mole of CH_6N_2 .

Solution

Analyze: We are given a temperature change and the total heat capacity of the calorimeter. We are also given the amount of reactant combusted. Our goal is to calculate the enthalpy change per mole for combustion of the reactant.

Plan: We will first calculate the heat evolved for the combustion of the 4.00-g sample. We will then convert this heat to a molar quantity.

Solve:

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For combustion of the 4.00-g sample of methylhydrazine, the temperature change of the
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calorimeter is

We can use ΔT and the value for C_{cal} to calculate the heat of reaction (Equation 5.24): We can readily convert this value to the heat of reaction for a mole of CH₆N₂: $\Delta T = (39.50 \,^{\circ}\text{C} - 25.00 \,^{\circ}\text{C}) = 14.50 \,^{\circ}\text{C}$ $q_{\text{rxn}} = -C_{\text{cal}} \times \Delta T = -(7.794 \,\text{kJ/}^{\circ}\text{C})(14.50 \,^{\circ}\text{C}) = -113.0 \,\text{kJ}$ $\left(\frac{-113.0 \,\text{kJ}}{4.00 \,\text{g} \,\text{CH}_6\text{N}_2}\right) \times \left(\frac{46.1 \,\text{g} \,\text{CH}_6\text{N}_2}{1 \,\text{mol} \,\text{CH}_6\text{N}_2}\right) = -1.30 \times 10^3 \,\text{kJ/mol} \,\text{CH}_6\text{N}_2$

Check: The units cancel properly, and the sign of the answer is negative as it should be for an exothermic reaction.



Sample Exercise 5.7 Measuring q_{rxn} Using a Bomb Calorimeter

Practice Exercise

A 0.5865-g sample of lactic acid (HC₃H₅O₃) is burned in a calorimeter whose heat capacity is 4.812 kJ/°C. The temperature increases from 23.10 °C to 24.95 °C. Calculate the heat of combustion of lactic acid (**a**) per gram and (**b**) per mole. *Answers:* (**a**) –15.2 kJ/g, (**b**) –1370 kJ/mol.



Sample Exercise 5.8 Using Hess's Law to Calculate ΔH

The enthalpy of reaction for the combustion of C to CO_2 is -393.5 kJ/mol C, and the enthalpy for the combustion of CO to CO_2 is -283.0 kJ/mol CO:

(1)	$C(s) + O_2(g) \longrightarrow CO_2(g)$	$\Delta H_1 = -393.5 \text{ kJ}$
(2)	$\operatorname{CO}(g) + \frac{1}{2}\operatorname{O}_2(g) \longrightarrow \operatorname{CO}_2(g)$	$\Delta H_2 = -283.0 \text{ kJ}$
Using these data, calculate the enthalpy for the combustion of C to CO:		
(3)	$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$	$\Delta H_3 = ?$

Solution

Analyze: We are given two thermochemical equations, and our goal is to combine them in such a way as to obtain the third equation and its enthalpy change.

Plan: We will use Hess's law. In doing so, we first note the numbers of moles of substances among the reactants and products in the target equation, (3). We then manipulate equations (1) and (2) to give the same number of moles of these substances, so that when the resulting equations are added, we obtain the target equation. At the same time, we keep track of the enthalpy changes, which we add.

Solve: To use equations (1) and (2), we arrange them so that C(s) is on the reactant side and CO(g) is on the product side of the arrow, as in the target reaction, equation (3). Because equation (1) has C(s) as a reactant, we can use that equation just as it is. We need to turn equation (2) around, however, so that CO(g) is a product. Remember that when reactions are turned around, the sign of ΔH is reversed. We arrange the two equations so that they can be added to give the desired equation:

$C(s) + O_2(g) \longrightarrow CO_2(g)$	$\Delta H_1 = -393.5 \text{ kJ}$
$\operatorname{CO}_2(g) \longrightarrow \operatorname{CO}(g) + \frac{1}{2}\operatorname{O}_2(g)$	$-\Delta H_2 = 283.0 \text{ kJ}$
$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$	$\Delta H_3 = -110.5 \text{ kJ}$



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Sample Exercise 5.8 Using Hess's Law to Calculate ΔH

Solution (continued)

When we add the two equations, $CO_2(g)$ appears on both sides of the arrow and therefore cancels out. Likewise, $\frac{1}{2}O_2(g)$ is eliminated from each side.

Comment: It is sometimes useful to add subscripts to the enthalpy changes, as we have done here, to keep track of the associations between the chemical reactions and their ΔH values.

Practice Exercise

Carbon occurs in two forms, graphite and diamond. The enthalpy of the combustion of graphite is –393.5 kJ/mol and that of diamond is –395.4 kJ/mol:

$C(graphite) + O_2(g) \longrightarrow CO_2(g)$	$\Delta H_1 = -393.5 \text{ kJ}$
$C(diamond) + O_2(g) \longrightarrow CO_2(g)$	$\Delta H_2 = -395.4 \text{ kJ}$

Calculate for the conversion of graphite to diamond:

$$C(graphite) \longrightarrow C(diamond) \qquad \Delta H_3 = ?$$

Answer: $\Delta H_3 = +1.9 \text{ kJ}$



Sample Exercise 5.9 Using Three Equations with Hess's Law to Calculate ΔH

Calculate ΔH for the reaction

$$2 \operatorname{C}(s) + \operatorname{H}_2(g) \to \operatorname{C}_2\operatorname{H}_2(g)$$

given the following chemical equations and their respective enthalpy changes

$$\begin{array}{ll} C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2 \operatorname{CO}_2(g) + H_2O(l) & \Delta H = -1299.6 \text{ kJ} \\ C(s) + O_2(g) \longrightarrow \operatorname{CO}_2(g) & \Delta H = -393.5 \text{ kJ} \\ H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) & \Delta H = -285.8 \text{ kJ} \end{array}$$

Solution

Analyze: We are given a chemical equation and asked to calculate its ΔH using three chemical equations and their associated enthalpy changes.

Plan: We will use Hess's law, summing the three equations or their reverses and multiplying each by an appropriate coefficient so that they add to give the net equation for the reaction of interest. At the same time, we keep track of the ΔH values, reversing their signs if the reactions are reversed and multiplying them by whatever coefficient is employed in the equation.

Solve: Because the target equation has C_2H_2 as a product, we turn the first equation around; the sign of ΔH is therefore changed. The desired equation has 2 C(*s*) as a reactant, so we multiply the second equation and its ΔH by 2. Because the target equation has H_2 as a reactant, we keep the third equation as it is. We then add the three equations and their enthalpy changes in accordance with Hess's law:

$2\operatorname{CO}_2(g) + \operatorname{H}_2\operatorname{O}(l) \longrightarrow \operatorname{C}_2\operatorname{H}_2(g) + \frac{5}{2}\operatorname{O}_2(g)$	$\Delta H = 1299.6 \text{ kJ}$
$2 \operatorname{C}(s) + 2 \operatorname{O}_2(g) \longrightarrow 2 \operatorname{CO}_2(g)$	$\Delta H = -787.0 \text{ kJ}$
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	$\Delta H = -285.8 \text{ kJ}$
$2 \operatorname{C}(s) + \operatorname{H}_2(g) \longrightarrow \operatorname{C}_2\operatorname{H}_2(g)$	$\Delta H = 226.8 \text{ kJ}$



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Sample Exercise 5.9 Using Three Equations with Hess's Law to Calculate ΔH

Solution (continued)

When the equations are added, there are 2 CO_2 , $\frac{5}{2} \text{ O}_2$, and H_2O on both sides of the arrow. These are canceled in writing the net equation.

Check: The procedure must be correct because we obtained the correct net equation. In cases like this you should go back over the numerical manipulations of the ΔH values to ensure that you did not make an inadvertent error with signs.

Practice Exercise

Calculate ΔH for the reaction

$$NO(g) + O(g) \rightarrow NO_2(g)$$

given the following information:

$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$	$\Delta H = -198.9 \text{ kJ}$
$O_3(g) \longrightarrow \frac{3}{2}O_2(g)$	$\Delta H = -142.3 \text{ kJ}$
$O_2(g) \longrightarrow 2 O(g)$	$\Delta H = 495.0 \text{ kJ}$

Answer: -304.1 kJ



Sample Exercise 5.10 Identifying Equations Associates with Enthalpies of Formation

For which of the following reactions at 25°C would the enthalpy change represent a standard enthalpy of formation? For each that does not, what changes are needed to make it an equation whose ΔH is an enthalpy of formation?

(a) $2 \operatorname{Na}(s) + \frac{1}{2} \operatorname{O}_2(g) \longrightarrow \operatorname{Na}_2\operatorname{O}(s)$ (b) $2 \operatorname{K}(l) + \operatorname{Cl}_2(g) \longrightarrow 2 \operatorname{KCl}(s)$ (c) $\operatorname{C}_6\operatorname{H}_{12}\operatorname{O}_6(s) \longrightarrow 6 \operatorname{C}(diamond) + 6 \operatorname{H}_2(g) + 3 \operatorname{O}_2(g)$

Solution

Analyze: The standard enthalpy of formation is represented by a reaction in which each reactant is an element in its standard state and the product is one mole of the compound.

Plan: We need to examine each equation to determine, first, whether the reaction is one in which one mole of substance is formed from the elements. Next, we need to determine whether the reactant elements are in their standard states.

Solve: In (a) 1 mol Na₂O is formed from the elements sodium and oxygen in their proper states, solid Na and O_2 gas, respectively. Therefore, the enthalpy change for reaction (a) corresponds to a standard enthalpy of formation. In (b) potassium is given as a liquid. It must be changed to the solid form, its standard state at room temperature. Furthermore, two moles of product are formed, so the enthalpy change for the reaction as written is twice the standard enthalpy of formation of KCl(*s*). The equation for the formation reaction of 1 mol of KCl(*s*) is

$$K(s) + \frac{1}{2}Cl(g) \longrightarrow KCl(s)$$



Sample Exercise 5.10 Identifying Equations Associates with Enthalpies of Formation

Solution (continued)

Reaction (c) does not form a substance from its elements. Instead, a substance decomposes to its elements, so this reaction must be reversed. Next, the element carbon is given as diamond, whereas graphite is the standard state of carbon at room temperature and 1 atm pressure. The equation that correctly represents the enthalpy of formation of glucose from its elements is

 $6 \operatorname{C}(graphite) + 6 \operatorname{H}_2(g) + 3 \operatorname{O}_2(g) \longrightarrow \operatorname{C}_6 \operatorname{H}_{12} \operatorname{O}_6(s)$

Practice Exercise

Write the equation corresponding to the standard enthalpy of formation of liquid carbon tetrachloride (CCl₄). *Answer:* $C(graphite) + 2 Cl_2(g) \rightarrow CCl_4(l)$



Sample Exercise 5.11 Calculating an Enthalpy of Reaction from Enthalpies of Formation

(a) Calculate the standard enthalpy change for the combustion of 1 mol of benzene, $C_6H_6(l)$, to form $CO_2(g)$ and $H_2O(l)$. (b) Compare the quantity of heat produced by combustion of 1.00 g propane to that produced by 1.00 g benzene.

Solution

Analyze: (a) We are given a reaction [combustion of $C_6H_6(l)$ to form $CO_2(g)$ and $H_2O(l)$] and asked to calculate its standard enthalpy change, ΔH° . (b) We then need to compare the quantity of heat produced by combustion of 1.00 g C_6H_6 with that produced by 1.00 g C_3H_8 , whose combustion was treated above in the text. (See Equations 5.29 and 5.30.)

Plan: (a) We need to write the balanced equation for the combustion of C_6H_6 . We then look up ΔH_f° values in Appendix C or in Table 5.3 and apply Equation 5.31 to calculate the enthalpy change for the reaction. (b) We use the molar mass of C_6H_6 to change the enthalpy change per mole to that per gram. We similarly use the molar mass of C_3H_8 and the enthalpy change per mole calculated in the text above to calculate the enthalpy change per gram of that substance.

Solve:

(a)We know that a combustion reaction involves $O_2(g)$ as a reactant. Thus, the balanced equation for the combustion reaction of 1 mol $C_6H_6(l)$ is

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6 CO_2(g) + 3 H_2O(l)$$



Sample Exercise 5.11 Calculating an Enthalpy of Reaction from Enthalpies of Formation

Solution

Solve:

We can calculate ΔH for this reaction by using Equation 5.31 and data in Table 5.3. Remember to multiply the ΔH_{f}° value for each substance in the reaction by that substance's stoichiometric coefficient. Recall also that $\Delta H_{f}^{\circ} = 0$ for any element in its most stable form under standard conditions, so $\Delta H_{f}^{\circ}[O_{2}(g)] = 0$

(b) From the example worked in the text, $\Delta H^{\circ} = -2220 \text{ kJ}$ for the combustion of 1 mol of propane. In part (a) of this exercise we determined that $\Delta H^{\circ} = -3267 \text{ kJ}$ for the combustion of 1 mol benzene. To determine the heat of combustion per gram of each substance, we use the molar masses to convert moles to grams: $\Delta H_{rxn}^{\circ} = [6\Delta H_{f}^{\circ}(CO_{2}) + 3\Delta H_{f}^{\circ}(H_{2}O)] - [\Delta H_{f}^{\circ}(C_{6}H_{6}) + \frac{15}{2}\Delta H_{f}^{\circ}(O_{2})]$ = [6(-393.5 kJ) + 3(-285.8 kJ)] - [(49.0 kJ) + \frac{15}{2}(0 kJ)] = (-2361 - 857.4 - 49.0) kJ = -3267 kJ

 $C_{3}H_{8}(g): \quad (-2220 \text{ kJ/mol})(1 \text{ mol}/44.1 \text{ g}) = -50.3 \text{ kJ/g}$ $C_{6}H_{6}(l): \quad (-3267 \text{ kJ/mol})(1 \text{ mol}/78.1 \text{ g}) = -41.8 \text{ kJ/g}$

Comment: Both propane and benzene are hydrocarbons. As a rule, the energy obtained from the combustion of a gram of hydrocarbon is between 40 and 50 kJ. **Practice Exercise**

Using the standard enthalpies of formation listed in Table 5.3, calculate the enthalpy change for the combustion of 1 mol of ethanol: *Answer:* -1367 kJ. $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$



Sample Exercise 5.12 Calculating an Enthalpy of Formation Using an Enthalpy of Reaction

The standard enthalpy change for the reaction

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

is 178.1 kJ. From the values for the standard enthalpies of formation of CaO(s) and $CO_2(g)$ given in Table 5.3, calculate the standard enthalpy of formation of $CaCO_3(s)$.

Solution

Analyze: We need to obtain ΔH°_{f} (CaCO₃). **Plan:** We begin by writing the expression for the standard enthalpy change for the reaction:

Solve: Inserting the ΔH°_{rxn} given and the known ΔH°_{f} values from Table 5.3 or Appendix C, we have

Solving for ΔH°_{f} (CaCO3) gives

$$\Delta H_{\rm rxn}^{\circ} = \left[\Delta H_f^{\circ}({\rm CaO}) + \Delta H_f^{\circ}({\rm CO}_2)\right] - \Delta H_f^{\circ}({\rm CaCO}_3)$$

$$178.1 \text{ kJ} = -635.5 \text{ kJ} - 393.5 \text{ kJ} - \Delta H_f^{\circ}(\text{CaCO}_3)$$
$$\Delta H_f^{\circ}(\text{CaCO}_3) = -1207.1 \text{ kJ/mol}$$

Check: We expect the enthalpy of formation of a stable solid such as calcium carbonate to be negative, as obtained.

Practice Exercise

Given the following standard enthalpy change, use the standard enthalpies of formation in Table 5.3 to calculate the standard enthalpy of formation of CuO(s):

 $CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(l) \qquad \Delta H^\circ = -129.7 \text{ kJ}$

Answer: -156.1 kJ/mol



Sample Exercise 5.13 Comparing Fuel Values

A plant such as celery contains carbohydrates in the form of starch and cellulose. These two kinds of carbohydrates have essentially the same fuel values when combusted in a bomb calorimeter. When we consume celery, however, our bodies receive fuel value from the starch only. What can we conclude about the difference between starch and cellulose as foods?

Solution

If cellulose does not provide fuel value, we must conclude that it is not converted in the body into CO_2 and H_2O , as starch is. A slight, but critical, difference in the structures of starch and cellulose explains why only starch is broken down into glucose in the body. Cellulose passes through without undergoing significant chemical change. It serves as fiber, or roughage, in the diet, but provides no caloric value.

Practice Exercise

The nutritional label on a bottle of canola oil indicates that 10 g of the oil has an energy value of 86 kcal. A similar label on a bottle of pancake syrup indicates that 60 mL (about 60 g) has an energy value of 200 kcal. Account for the difference.

Answer: The oil has a fuel value of 8.6 kcal/g, whereas the syrup has a fuel value of about 3.3 kcal/g. The higher fuel value for the canola oil arises because the oil is essentially pure fat, whereas the syrup is a solution of sugars (carbohydrates) in water. The oil has a higher fuel value per gram; in addition, the syrup is diluted by water.



Sample Exercise 5.14 Estimating the Fuel Value of a food from Its Composition

(a) A 28-g (1-oz) serving of a popular breakfast cereal served with 120 mL of skim milk provides 8 g protein, 26 g carbohydrates, and 2 g fat. Using the average fuel values of these kinds of substances, estimate the energy value (caloric content) of this serving.

(**b**) A person of average weight uses about 100 Cal/mi when running or jogging. How many servings of this cereal provide the energy value requirements for running 3 mi?

Solution

(a) Analyze: The energy value of the serving will be the sum of the energy values of the protein, carbohydrates, and fat.

Plan: We are given the masses of the protein, carbohydrates, and fat contained in the combined. We can use the data in Table 5.4 to convert these masses to their energy values, which we can sum to get the total energy value.

Solve: (8 g protein)
$$\left(\frac{17 \text{ kJ}}{1 \text{ g protein}}\right)$$
 + (26 g carbohydrate) $\left(\frac{17 \text{ kJ}}{1 \text{ g carbohydrate}}\right)$ + (2 g fat) $\left(\frac{38 \text{ kJ}}{1 \text{ g fat}}\right)$ = 650 kJ (to two significant figures)

This corresponds to 160 kcal:

$$(650 \text{ kJ})\left(\frac{1 \text{ kcal}}{4.18 \text{ kJ}}\right) = 160 \text{ kcal}$$



Sample Exercise 5.14 Estimating the Fuel Value of a food from Its Composition

Solution (continued)

Recall that the dietary Calorie is equivalent to 1 kcal. Thus, the serving provides 160 Cal.

(b) Analyze: Here we are faced with the reverse problem, calculating the quantity of food that provides a specific energy value.

Plan: The problem statement provides a conversion factor between Calories and miles. The answer to part (a) provides us with a conversion factor between servings and Calories.

Solve: We can use these factors in a straightforward dimensional analysis to determine the number of servings needed, rounded to the nearest whole number:

Servings =
$$(3 \text{ mi})\left(\frac{100 \text{ Cal}}{1 \text{ mi}}\right)\left(\frac{1 \text{ serving}}{160 \text{ Cal}}\right) = 2 \text{ servings}$$

Practice Exercise

(a) Dry red beans contain 62% carbohydrate, 22% protein, and 1.5% fat. Estimate the fuel value of these beans. (b) During a very light activity, such as reading or watching television, the average adult uses about 7 kJ/min. How many minutes of such activity can be sustained by the energy provided by a serving of chicken noodle soup containing 13 g protein, 15 g carbohydrate, and 5 g fat? *Answer:* (a) 15 kJ/g, (b) 95 min



Sample Integrative Exercise | Putting Concepts Together

Trinitroglycerin, $C_3H_5N_3O_9$ (usually referred to simply as nitroglycerin), has been widely used as an explosive. Alfred Nobel used it to make dynamite in 1866. Rather surprisingly, it also is used as a medication, to relieve angina (chest pains resulting from partially blocked arteries to the heart) by dilating the blood vessels. The enthalpy of decomposition at 1 atm pressure of trinitroglycerin to form nitrogen gas, carbon dioxide gas, liquid water, and oxygen gas at 25 °C is -1541.4 kJ/mol. (a) Write a balanced chemical equation for the decomposition of trinitroglycerin. (b) Calculate the standard heat of formation of trinitroglycerin. (c) A standard dose of trinitroglycerin for relief of angina is 0.60 mg. If the sample is eventually oxidized in the body (not explosively, though!) to nitrogen gas, carbon dioxide gas, and liquid water, what number of calories is released? (d) One common form of trinitroglycerin melts at about 3 °C. From this information and the formula for the substance, would you expect it to be a molecular or ionic compound? Explain. (e) Describe the various conversions of forms of energy when trinitroglycerin is used as an explosive to break rockfaces in highway construction.

Solution

(a) The general form of the equation we must balance is

 $C_3H_5N_3O_9(l) \rightarrow N_2(g) + CO_2(g) + H_2O(l) + O_2(g)$

We go about balancing in the usual way. To obtain an even number of nitrogen atoms on the left, we multiply the formula for $C_3H_5N_3O_9$ by 2. This then gives us 3 mol of N_2 , 6 mol of CO_2 and 5 mol of H_2O . Everything is balanced except for oxygen. We have an odd number of oxygen atoms on the right. We can balance the oxygen by adding mol of O_2 on the right:

 $2 C_3 H_5 N_3 O_9(l) \longrightarrow 3 N_2(g) + 6 CO_2(g) + 5 H_2 O(l) + \frac{1}{2} O_2(g)$



Sample Integrative Exercise | Putting Concepts Together

Solution (continued)

We multiply through by 2 to convert all coefficients to whole numbers:

 $4 \operatorname{C_3H_5N_3O_9}(l) \to 6 \operatorname{N_2}(g) + 12 \operatorname{CO_2}(g) + 10 \operatorname{H_2O}(l) + \operatorname{O_2}(g)$

(At the temperature of the explosion, water is a gas. The rapid expansion of the gaseous products creates the force of an explosion.)

(b) The heat of formation is the enthalpy change in the balanced chemical equation:

 $3 C(s) + \frac{3}{2} N_2(g) + \frac{5}{2} H_2(g) + \frac{9}{2} O_2(g) \longrightarrow C_3 H_5 N_3 O_9(l) \qquad \Delta H_f^\circ = ?$

We can obtain the value of ΔH_{f}° by using the equation for the heat of decomposition of trinitroglycerin:

$$4 C_3 H_5 N_3 O_9(l) \to 6 N_2(g) + 12 CO_2(g) + 10 H_2 O(l) + O_2(g)$$

The enthalpy change in this reaction is 4(-1541.4 kJ) = -6165.6 kJ. [We need to multiply by 4 because there are 4 mol of $C_3H_5N_3O_9(l)$ in the balanced equation.] This enthalpy change is given by the sum of the heats of formation of the products minus the heats of formation of the reactants, each multiplied by its coefficient in the balanced equation:

$$-6165.6 \text{ kJ} = \{6\Delta H_f^{\circ}[N_2(g)] + 12\Delta H_f^{\circ}[CO_2(g)] + 10\Delta H_f^{\circ}[H_2O(l)] + \Delta H_f^{\circ}[O_2(g)]\} - 4\Delta H_f^{\circ}(C_3H_5N_3O_9(l)]$$

The ΔH_f° values for N₂(g) and O₂(g) are zero, by definition. We look up the values for H₂O(l) and CO₂(g) from Table 5.3 and find that

$$-6165.6 \text{ kJ} = 12(-393.5 \text{ kJ}) + 10(-285.8 \text{ kJ}) - 4\Delta H_f^{\circ}(C_3H_5N_3O_9(l))$$

$$\Delta H_f^{\circ}(C_3H_5N_3O_9(l)) = -353.6 \text{ kJ/mol}$$



Sample Integrative Exercise | Putting Concepts Together

Solution (continued)

(c) We know that on oxidation 1 mol of $C_3H_5N_3O_9(l)$ yields 1541.4 kJ. We need to calculate the number of moles of in $C_3H_5N_3O_9(l)$ in 0.60 mg:

$$0.60 \times 10^{-3} \text{ g } \text{C}_3\text{H}_5\text{N}_3\text{O}_9 \left(\frac{1 \text{ mol } \text{C}_3\text{H}_5\text{N}_3\text{O}_9}{227 \text{ g } \text{C}_3\text{H}_5\text{N}_3\text{O}_9}\right) \left(\frac{1541.4 \text{ kJ}}{1 \text{ mol } \text{C}_3\text{H}_5\text{N}_3\text{O}_9}\right) = 4.1 \times 10^{-3} \text{ kJ}$$
$$= 4.1 \text{ J}$$

(d) Because trinitroglycerin melts below room temperature, we expect that it is a molecular compound. With few exceptions, ionic substances are generally hard, crystalline materials that melt at high temperatures. (Sections 2.5 and 2.6) Also, the molecular formula suggests that it is likely to be a molecular substance. All the elements of which it is composed are nonmetals.

(e) The energy stored in trinitroglycerin is chemical potential energy. When the substance reacts explosively, it forms substances such as carbon dioxide, water, and nitrogen gas, which are of lower potential energy. In the course of the chemical transformation, energy is released in the form of heat; the gaseous reaction products are very hot. This very high heat energy is transferred to the surroundings; the gases expand against the surroundings, which may be solid materials. Work is done in moving the solid materials and imparting kinetic energy to them. For example, a chunk of rock might be impelled upward. It has been given kinetic energy by transfer of energy from the hot, expanding gases. As the rock rises, its kinetic energy is transformed into potential energy. Eventually, it again acquires kinetic energy as it falls to Earth. When it strikes Earth, its kinetic energy is converted largely to thermal energy, though some work may be done on the surroundings as well.

