Example 6.2

The work done when a gas is compressed in a cylinder like that shown in **Figure 6.4** is 387 J. During this process, there is a heat transfer of 152 J from the gas to the surroundings. Calculate the energy change for this process.

Strategy Compression is work done on the gas, so what is the sign for w? Heat is released by the gas to the surroundings. Is this an endothermic or exothermic process? What is the sign for q?

Solution To calculate the energy change of the gas, we need **Equation (6.1)**. Work of compression is positive and because heat is released by the gas, q is negative. Therefore, we have

$$\begin{aligned}\Delta U &= q + w \\ &= -152\ \text{J} + 387\ \text{J} \\ &= 235\ \text{J}\end{aligned}$$

As a result, the energy of the gas increases by 235 J.

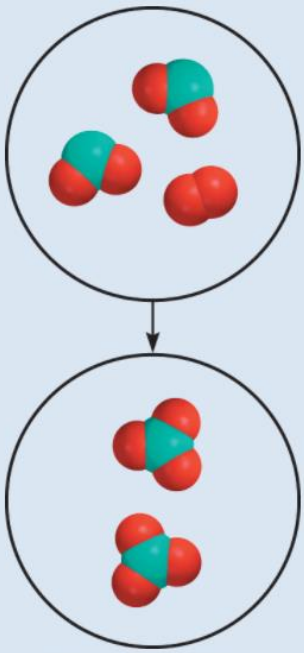
Practice Exercise A gas expands and does P-V work on the surroundings equal to 279 J. At the same time, it absorbs 216 J of heat from the surroundings. What is the change in energy of the system?

Example 6.3

Given the thermochemical equation

$$2SO_2\,(g) + O_2\,(g) \rightarrow 2SO_3\,(g) \qquad \Delta H = -198.2\ \text{kJ/mol}$$

calculate the heat evolved when 93.4 g of SO_2 (molar mass = 64.07 g/mol) is converted to SO_3.



$2SO_2\,(g) + O_2\,(g) \rightarrow 2SO_3\,(g)$

Strategy The thermochemical equation shows that for every 2 moles of SO_2 reacted, 198.2 kJ of heat are given off (note the negative sign). Therefore, the conversion factor is

$$\frac{-198.2 \text{ kJ}}{2 \text{ mol } SO_2}$$

How many moles of SO_2 are in 93.4 g of SO_2? What is the conversion factor between grams and moles?

Solution We need to first calculate the number of moles of SO_2 in 93.4 g of the compound and then find the number of kilojoules produced from the exothermic reaction. The sequence of conversions is as follows:

$$\text{grams of } SO_2 \rightarrow \text{moles of } SO_2 \rightarrow \text{kilojoules of heat generated}$$

Therefore, the enthalpy change for this reaction is given by

$$\Delta H = 93.4 \text{ g } SO_2 \times \frac{1 \text{ mol } SO_2}{64.07 \text{ g } SO_2} \times \frac{-198.2 \text{ kJ}}{2 \text{ mol } SO_2} = -144 \text{ kJ}$$

and the heat released to the surroundings is 144 kJ.

Check Because 93.4 g is less than twice the molar mass of SO_2 (2×64.07 g) as shown in the preceding thermochemical equation, we expect the heat released to be smaller than 198.2 kJ.

Practice Exercise Calculate the heat evolved when 266 g of white phosphorus (P_4) burns in air according to the equation

$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s) \qquad \Delta H = -3013 \text{ kJ/mol}$$

Example 6.5

A 394-g sample of water is heated from 10.75°C to 83.20°C. Calculate the amount of heat absorbed (in kilojoules) by the water.

Strategy We know the quantity of water and the specific heat of water. With this information and the temperature rise, we can calculate the amount of heat absorbed (q).

Solution Using **Equation (6.12)**, we write

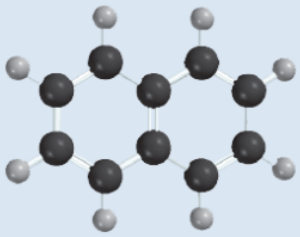
$$\begin{aligned} q &= ms\Delta t \\ &= (394 \text{ g})(4.184 \text{ J/g} \cdot \text{°C})(83.20\text{°C} - 10.75\text{°C}) \\ &= 1.19 \times 10^5 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \\ &= 119 \text{ kJ} \end{aligned}$$

Check The units g and °C cancel, and we are left with the desired unit kJ. Because heat is absorbed by the water from the surroundings, it has a positive sign.

Practice Exercise An iron bar of mass 869 g cools from 94°C to 5°C. Calculate the heat released (in kilojoules) by the metal.

Example 6.6

A quantity of 1.274 g of naphthalene ($C_{10}H_8$), a pungent-smelling substance used in moth repellants, was burned in a constant-volume bomb calorimeter. Consequently, the temperature of the water rose from 21.49°C to 26.52°C. If the heat capacity of the bomb plus water was 10.17 kJ/°C, calculate the heat of combustion of naphthalene on a molar basis; that is, find the molar heat of combustion.



$C_{10}H_8$

Strategy Knowing the heat capacity and the temperature rise, how do we calculate the heat absorbed by the calorimeter? What is the heat generated by the combustion of 1.274 g of naphthalene? What is the conversion factor between grams and moles of naphthalene?

Solution The heat absorbed by the bomb and water is equal to the product of the heat capacity and the temperature change. From **Equation (6.16)**, assuming no heat is lost to the surroundings, we write

$$\begin{aligned} q_{cal} &= C_{cal}\,\Delta t \\ &= (10.17\ \text{kJ/°C})\,(26.52\text{°C} - 21.49\text{°C}) \\ &= 51.16\ \text{kJ} \end{aligned}$$

Because $q_{sys} = q_{cal} + q_{rxn} = 0$, $q_{cal} = -q_{rxn}$. The heat change of the reaction is −51.56 kJ. This is the heat released by the combustion of 1.274 g of $C_{10}H_8$; therefore, we can write the conversion factor as

$$\frac{-51.16\ \text{kJ}}{1.274\ \text{g}\ C_{10}H_8}$$

The molar mass of naphthalene is 128.2 g, so the heat of combustion of 1 mole of naphthalene is

$$\begin{aligned} \text{molar heat of combustion} &= \frac{-51.16\ \text{kJ}}{1.274\ \text{g}\ C_{10}H_8} \times \frac{128.2\ \text{g}\ C_{10}H_8}{1\ \text{mol}\ C_{10}H_8} \\ &= -5.148 \times 10^3\ \text{kJ/mol} \end{aligned}$$

Check Knowing that the combustion reaction is exothermic and that the molar mass of naphthalene is much greater than 1.2 g, is the answer reasonable? Under these conditions, can the heat change (−51.16 kJ) be equated to the enthalpy change of the reaction?

Practice Exercise A quantity of 1.922 g of methanol (CH_3OH) was burned in a constant-volume bomb calorimeter. Consequently, the temperature of the water rose by 4.20°C. If the heat capacity of the bomb plus water was 10.4 kJ/°C, calculate the molar heat of combustion of methanol.

Example 6.9

Calculate the standard enthalpy of formation of acetylene (C_2H_2) from its elements:

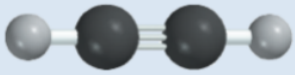
$$2C\,(\text{graphite}) + H_2\,(g) \rightarrow C_2H_2\,(g)$$

The equations for each step and the corresponding enthalpy changes are

(a) $$C\,(\text{graphite}) + O_2\,(g) \rightarrow CO_2\,(g) \qquad \Delta H^\circ_{\text{rxn}} = -393.5 \text{ kJ/mol}$$

(b) $$H_2\,(g) + \tfrac{1}{2}O_2\,(g) \rightarrow H_2O\,(l) \qquad \Delta H^\circ_{\text{rxn}} = -285.8 \text{ kJ/mol}$$

(c) $$2C_2H_2\,(g) + 5O_2\,(g) \rightarrow 4CO_2\,(g) + 2H_2O\,(l) \qquad \Delta H^\circ_{\text{rxn}} = -2598.8 \text{ kJ/mol}$$



C_2H_2

Strategy Our goal here is to calculate the enthalpy change for the formation of C_2H_2 from its elements C and H_2. The reaction does not occur directly, however, so we must use an indirect route using the information given by Equations (a), (b), and (c).

Solution Looking at the synthesis of C_2H_2, we need 2 moles of graphite as reactant. So we multiply Equation (a) by 2 to get

(d) $$2C\,(\text{graphite}) + 2O_2\,(g) \rightarrow 2CO_2\,(g)$$

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= 2\,(-393.5 \text{ kJ/mol}) \\ &= -787.0 \text{ kJ/mol} \end{aligned}$$

Next, we need 1 mole of H_2 as a reactant and this is provided by Equation (b). Last, we need 1 mole of C_2H_2 as a product.

Example 6.10

The thermite reaction involves aluminum and iron(III) oxide

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

This reaction is highly exothermic and the liquid iron formed is used to weld metals. Calculate the heat released in kilojoules per gram of Al reacted with Fe_2O_3. The ΔH_f^o for Fe(l) is 12.40 kJ/mol.



Molten iron formed in a thermite reaction.

Strategy The enthalpy of a reaction is the difference between the sum of the enthalpies of the products and the sum of the enthalpies of the reactants. The enthalpy of each species (reactant or product) is given by the product of the stoichiometric coefficient and the standard enthalpy of formation of the species.

Solution Using the given ΔH_f^o value for Fe(l) and other ΔH_f^o values in **Appendix 2** and **Equation (6.18)**, we write

$$\begin{aligned}\Delta H_{rxn}^o &= \left[\Delta H_f^o\,(Al_2O_3) + 2\Delta H_f^o\,(Fe)\right] - \left[2\Delta H_f^o\,(Al) + 2\Delta H_f^o\,(Fe_2O_3)\right] \\ &= [(-1669.8\text{ kJ/mol}) + 2\,(12.40\text{ kJ/mol})] - [2\,(0) + (-822.2\text{ kJ/mol})] \\ &= -822.8\text{ kJ/mol}\end{aligned}$$

This is the amount of heat released for two moles of Al reacted. We use the following ratio

$$\frac{-822.8\text{ kJ}}{2\text{ mol Al}}$$

to convert to kJ/g Al. The molar mass of Al is 26.98 g, so

$$\begin{aligned}\text{heat released per gram of A} &= \frac{-822.8\text{ kJ}}{2\ \cancel{\text{mol Al}}} \times \frac{1\ \cancel{\text{mol Al}}}{26.98\text{ g Al}} \\ &= -15.25\text{ kJ/g}\end{aligned}$$

Check Is the negative sign consistent with the exothermic nature of the reaction? As a quick check, we see that 2 moles of Al weigh about 54 g and give off about 823 kJ of heat when reacted with Fe_2O_3. Therefore, the heat given off per gram of Al reacted is approximately −830 kJ/54 g or −15.4 kJ/g.

Practice Exercise Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. Calculate the heat released (in kilojoules) per gram of the compound reacted with oxygen. The standard enthalpy of formation of benzene is 49.04 kJ/mol.

Next, we need 1 mole of H_2 as a reactant and this is provided by Equation (b). Last, we need 1 mole of C_2H_2 as a product. Equation (c) has 2 moles of C_2H_2 as a reactant so we need to reverse the equation and divide it by 2:

(e) $$2CO_2\,(g) + H_2O\,(l) \rightarrow C_2H_2\,(g) + \tfrac{5}{2}O_2\,(g) \qquad \Delta H^\circ_{rxn} = \tfrac{1}{2}(2598.8\ \text{kJ/mol}) = 1299.4\ \text{kJ/mol}$$

Adding Equations (d), (b), and (e) together, we get

$$\begin{array}{rcll} 2C\,(\text{graphite}) + 2O_2\,(g) & \rightarrow & CO_2\,(g) & \Delta H^\circ_{rxn} = -787.0\ \text{kJ/mol} \\ H_2\,(g) + \tfrac{1}{2}O_2\,(g) & \rightarrow & H_2O\,(l) & \Delta H^\circ_{rxn} = -285.8\ \text{kJ/mol} \\ 2CO_2\,(g) + H_2O\,(l) & \rightarrow & C_2H_2\,(g) + \tfrac{5}{2}O_2\,(g) & \Delta H^\circ_{rxn} = 1299.4\ \text{kJ/mol} \\ \hline 2C\,(\text{graphite}) + H_2\,(g) & \rightarrow & C_2H_2\,(g) & \Delta H^\circ_{rxn} = 226.6\ \text{kJ/mol} \end{array}$$

Therefore, $\Delta H^\circ_f = \Delta H^\circ_{rxn} = 226.6$ kJ/mol. The ΔH°_f value means that when 1 mole of C_2H_2 is synthesized from 2 moles of C (graphite) and 1 mole of H_2, 226.6 kJ of heat are absorbed by the reacting system from the surroundings. Thus, this is an endothermic process.



An oxyacetylene torch has a high flame temperature (3000°C) and is used to weld metals.

Practice Exercise Calculate the standard enthalpy of formation of carbon disulfide (CS_2) from its elements, given that

$$\begin{array}{rcll} C\,(\text{graphite}) + O_2\,(g) & \rightarrow & CO_2\,(g) & \Delta H^\circ_{rxn} = -393.5\ \text{kJ/mol} \\ S\,(\text{rhombic}) + O_2\,(g) & \rightarrow & SO_2\,(g) & \Delta H^\circ_{rxn} = -296.4\ \text{kJ/mol} \end{array}$$

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