Chemistry

Zumdahl, 7th edition

歐亞書局

CH6 Thermochemistry

Hot have flowing into the ocean in Hawaii Volcanoes National Park creates clouds of steam.

Contents

Introduction

- Energy is the essence of our very existence as individuals and as a society.
- The food that we eat furnishes the energy to live, work, and play, just as the coal and oil consumed by manufacturing and transportation systems power our modern industrialized civilization.

6.1 The Nature of Energy

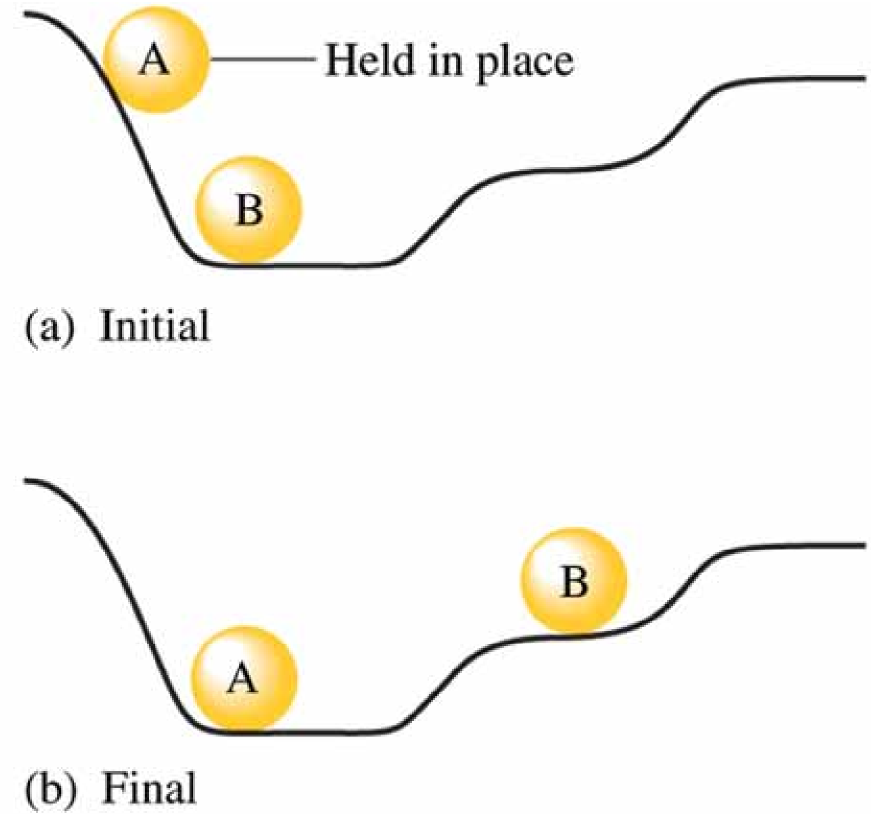
- **energy**: the capacity to do work or to produce heat.
- One of the most important characteristics of energy is that it is conserved.
- The **law of conservation of energy**. Energy can be converted from one form to another but can be neither created nor destroyed.
- That is, the energy of the universe is constant.
- Energy can be classified as either potential or kinetic energy.

- **Potential energy** is energy due to position or composition.
- The **kinetic energy** of an object is energy due to the motion of the object and depends on the mass of the object m and its velocity v: KE = $\frac{1}{2}mv^2$.
- Energy can be converted from one form to anther.
- Consider the two balls in Fig. 6.1(a).
- Ball A, because of its higher position initially, has more potential energy than ball B.

- When A is released, it moves down the hill and strikes B.
- Eventually, the arrangement shown in Fig. 6.1(b) is achieved.
- This transfer of energy is called *frictional heating*.
- The temperature of the hill increases very slightly as the ball rolls down.

Figure 6.1

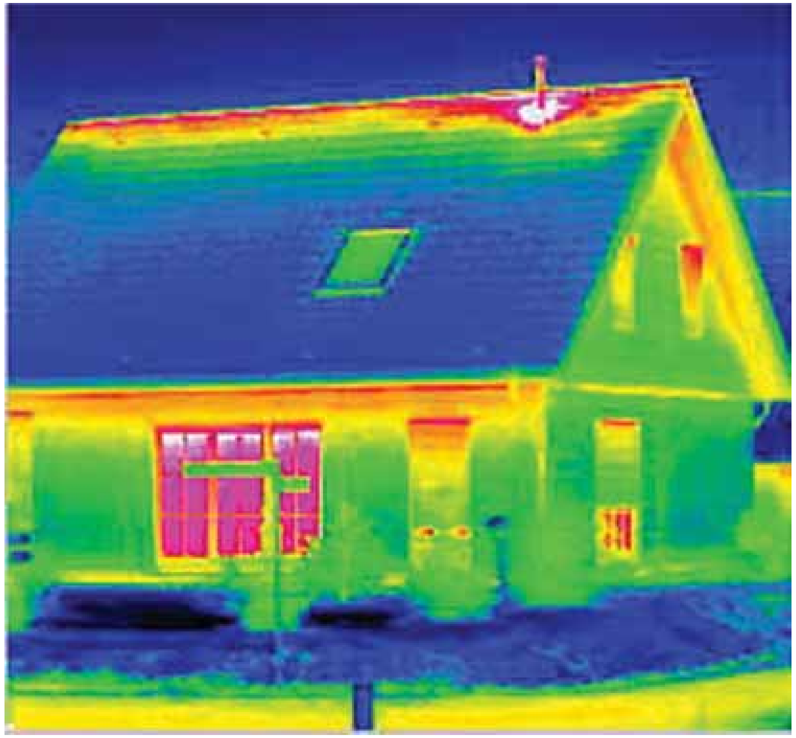
(a) In the initial positions, ball A has a higher potential energy than ball B. (b) After A has rolled down the hill, the potential energy lost by A has been converted to random motions of the components of the hill (frictional heating) and to the increase in the potential energy of B.



- Heat and temperature are decidedly different.
- Temperature is a property that reflects the random motions of the particles in a particular substance.
- **Heat**, involves the transfer of energy between two objects due to a temperature difference.
- Heat is not a substance contained by an object, although we often talk of heat as if this were true.

- Note that in going from the initial to the final arrangements in Fig. 6.1, ball B gains potential energy because work was done by ball A on B.
- **Work** is defined as force acting over a distance.
- This bring us to a very important concept: the **state function** or **state property**.
- A state function refers to a property of the system that depends only on its *present state*.

- A state function (property) does not depend in any way on the system’s past (or future).
- A very important characteristic of a state function: A change in this function (property) in going from one state to another state is independent of the particular pathway taken between the two states.



This infrared photo of a house shows where energy leaks occur. The more red the color, the more energy (heat) is leaving the house.

Chemical Energy

- The system is the part of the universe on which we wish to focus attention; the surroundings include everything else in the universe.
- When a reaction results in the evolution of heat, it is said to be **exothermic** (*exo*- is that is, energy flows out of the system.
- Reactions that absorb energy from the surroundings are said to be endothermic. When the heat flow is into a system, the process is **endothermic**.

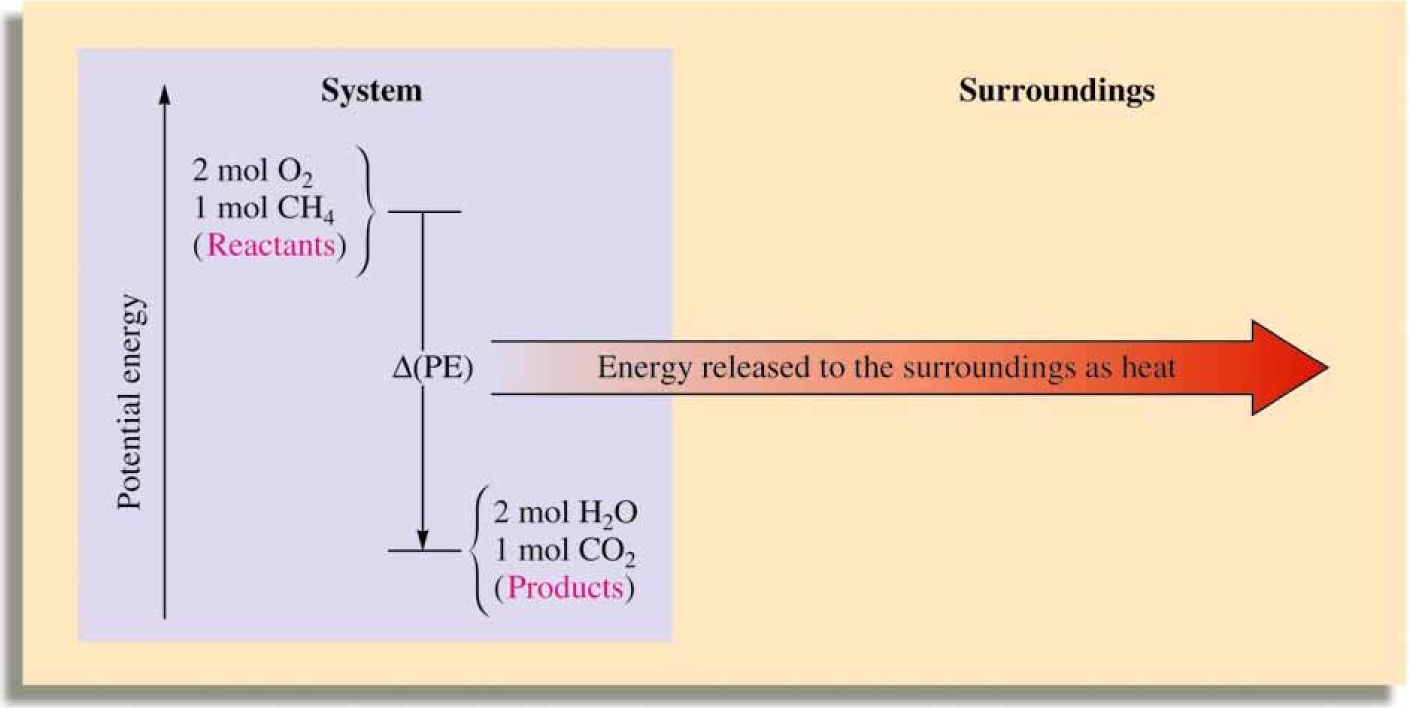
- The formation of nitric oxide from nitrogen and oxygen is endothermic:

$$N_2(g) + O_2(g) + \text{energy (heat)} \longrightarrow 2NO(g)$$

- Total energy is conserved and that energy flows from the system into the surroundings in an exothermic reaction.
- This means that *the energy gained by the surroundings must be equal to the energy lost by the system.*

- *In any exothermic reaction, some of the potential energy stored in the chemical bonds is being converted to thermal energy (random kinetic energy) via heat.*
- The energy diagram for the combustion of methane is shown in Fig. 6.2, where Δ(PE) represents the *change* in potential energy stored in the bonds of the products as compared with the bonds of the reactants.

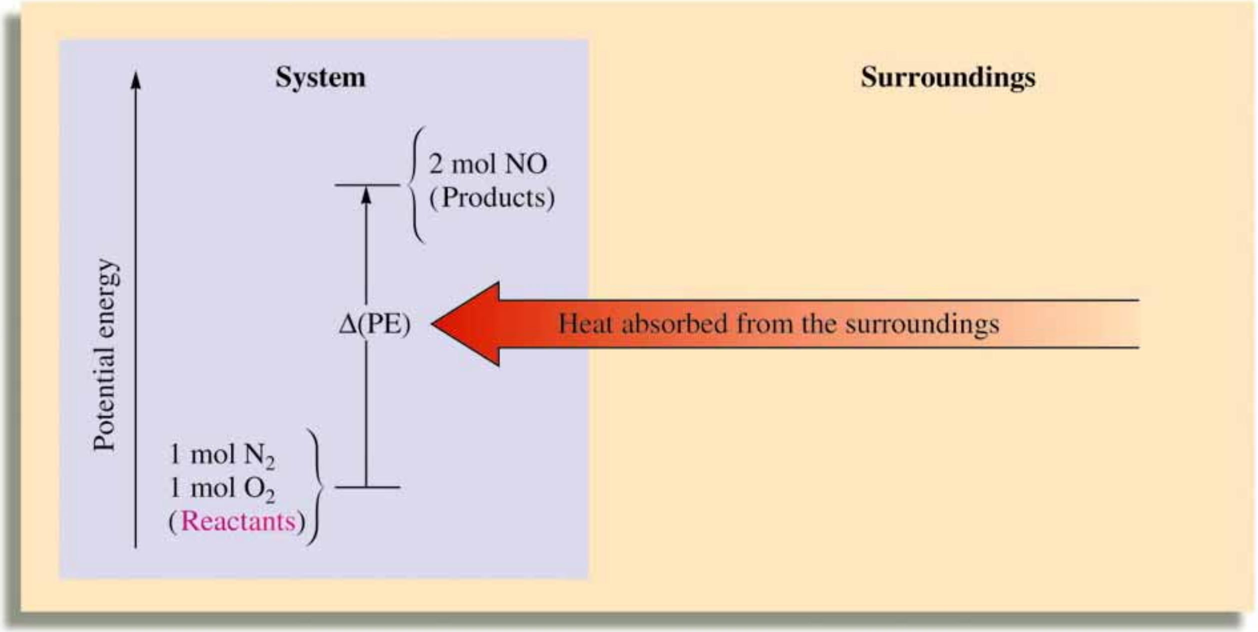
Figure 6.2



The combustion of methane releases the quantity of energy Δ(PE) to the surroundings via heat flow. This is an exothermic process.

- The net result is that the quantity of energy Δ(PE) is transferred to the surroundings through heat.
- For an endothermic reaction, the situation is reversed, as shown in Fig. 6.3.
- The study of energy and its interconversions is called **thermodynamics**.
- The law of conservation of energy is often called the **first law of thermodynamics** and is stated as follows:
- *The energy of the universe is constant.*

Figure 6.3



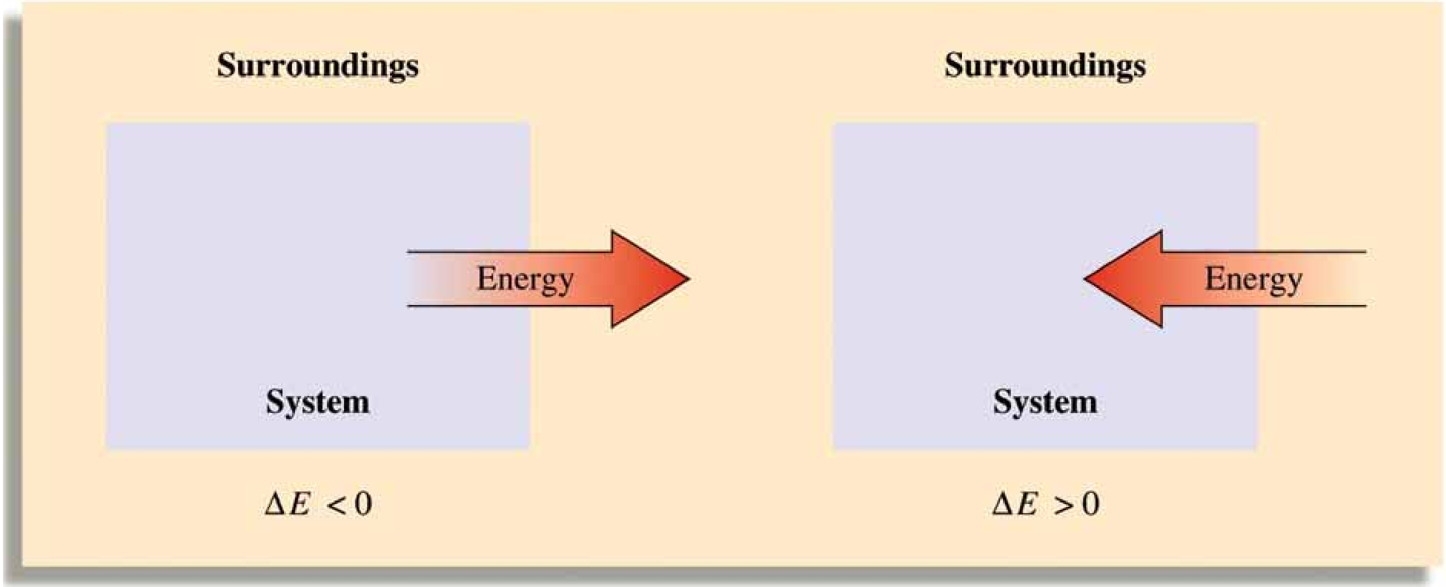
The energy diagram for the reaction of nitrogen and oxygen to form nitric oxide. This is an endothermic process: Heat [equal in magnitude to Δ(PE)] flows into the system from the surroundings.

- The **internal energy** *E* of a system can be defined most precisely as the sum of the kinetic and potential energy of all the "particles" in the system.
- The internal energy of a system can be change by a flow of work, heat, or both. That is,

$$\Delta E = q + w$$

- where ΔE represents the change in the system's internal energy, *q* represents heat, and w represents work.

- Thermodynamic quantities always consist of two parts: a number, giving the magnitude of the change, and a sigh, indicating the direction of the flow.
- *The sigh reflects the system’s point of view.*



- The same conventions also apply to the flow of work.
- If the system does work on the surroundings (energy flows out of the system), w is negative.
- If the surroundings do work on the system (energy flows into the system), w is positive.

$$\Delta E = q + w$$

- The first law of thermodynamics is then written $\Delta E = q - w'$, where w' signifies work from the surroundings' point of view.

Sample Exercise 6.1

Internal Energy

Calculate ΔE for a system undergoing an endothermic process in which 15.6 kJ of heat flows and where 1.4 kJ of work is done on the system.

- A common type of work associated with chemical processes is work done by a gas (through expansion) or work done to a gas (through compression).
- Suppose we have a gas confined to a cylindrical container with a movable piston as shown in Fig. 6.4, where F is the force acting on a piston of area A.
- The pressure of the gas is

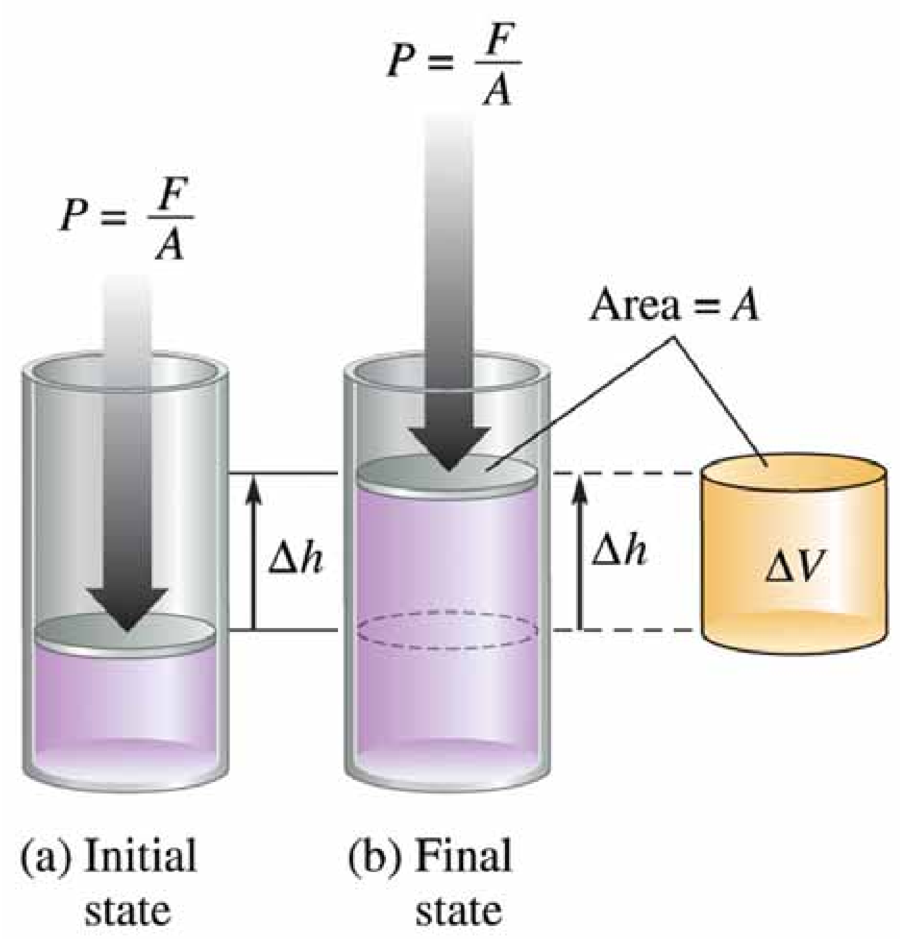
$$P = \frac{F}{A}$$

- Work is defined as force applied over a distance, so if the piston moves a distance Δh, as shown in Fig. 6.4,

$$\text{Work} = \text{force} \times \text{distance} = F \times \Delta h = P \times A \times \Delta h$$

Figure 6.4

(a) The piston, moving a distance Δh against a pressure P, does work on the surroundings. (b) Since the volume of a cylinder is the area of the base times its height, the change in volume of the gas is given by $\Delta h \times A = \Delta V$.



(a) Initial state

(b) Final state

- $\Delta V = A \times \Delta h$

$$\text{Work} = P \times A \times \Delta h = P\Delta V$$

- For an expanding gas, ΔV is a positive quantity because the volume is increasing.
- Thus ΔV and w must have opposite signs, which leads to the equation

$$w = -P\Delta V$$

- Note that for a gas expanding against an external pressure P, w is a negative quantity as required, since work flows out of the system.
- When a gas is compressed, ΔV is a negative quantity (the volume decreases), which makes w a positive quantity (work flows into the system).

Sample Exercise 6.3

Internal Energy, Heat, and Work

A balloon is being inflated to its full extent by heating the air inside it. In the final stages of this process, the volume of the balloon changes from 4.00×10^6 L to 4.50×10^6 L by the addition of 1.3×10^8 J of energy as heat. Assuming that the balloon expands against a constant pressure of 1.0 atm, calculate ΔE for the process. (To convert between L • atm and J, use 1 L • atm = 101.3 J.)

Sample Exercise 6.3

Solution

$$\Delta E = q + w$$

$$q = +1.3 \times 10^8 \text{ J}$$

$$w = -P\Delta V$$

In this case $P = 1.0$ atm and

$$\begin{aligned}\Delta V &= V_{\text{final}} - V_{\text{initial}} \\ &= 4.50 \times 10^6 \text{ L} - 4.00 \times 10^6 \text{ L} = 0.50 \times 10^6 \text{ L} = 5.0 \times 10^5 \text{ L}\end{aligned}$$

Sample Exercise 6.3

Thus

$$w = -1.0\ \text{atm} \times 5.0 \times 10^5\ \text{L} = -5.0 \times 10^5\ \text{L} \cdot \text{atm}$$

$$w = -5.0 \times 10^5\ \cancel{\text{L} \cdot \text{atm}} \times \frac{101.3\ \text{J}}{\cancel{\text{L} \cdot \text{atm}}} = -5.1 \times 10^7\ \text{J}$$

$$\Delta E = q + w = (+1.3 \times 10^8\ \text{J}) + (-5.1 \times 10^7\ \text{J}) = 8 \times 10^7\ \text{J}$$

See Exercises 6.28 through 6.30

6.2 Enthalpy and Calorimetry

Enthalpy

- **enthalpy**, *H*, is defined as

$$H = E + PV$$

- where *E* is the internal energy of the system, *P* is the pressure of the system, and *V* is the volume of the system.
- Since internal energy, pressure, and volume are all state functions, *enthalpy is also a state function*.

- pressure-volume work ($w = -P\Delta V$).

$$\Delta E = q_p + w$$

$$\Delta E = q_p - P\Delta V$$

$$q_p = \Delta E + P\Delta V$$

- where q_p is the heat at constant pressure.
- The definition of enthalpy is $H = E + PV$.

$$\Delta H = \Delta E + \Delta (PV)$$

$$q_p = \Delta E + P\Delta V$$

- at constant pressure

$$\Delta H = q_p$$

- *At constant pressure (where only PV work is allowed), the change in enthalpy ΔH of the system is equal to the energy flow as heat.*

- For a chemical reaction, the enthalpy change is given by the equation

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

Sample Exercise 6.4 Enthalpy

When 1 mole of methane (CH_4) is burned at constant pressure, 890 kJ of energy is released as heat. Calculate ΔH for a process in which a 5.8-g sample of methane is burned at constant pressure.

Solution

At constant pressure, 890 kJ of energy per mole of CH_4 is produced as heat:

$$q_P = \Delta H = -890 \text{ kJ/mol } CH_4$$

Sample Exercise 6.4

In this case, a 5.8-g sample of CH_4 (molar mass = 16.0 g/mol) is burned.

$$5.8\ \cancel{\text{g CH}_4} \times \frac{1\ \text{mol CH}_4}{16.0\ \cancel{\text{g CH}_4}} = 0.36\ \text{mol CH}_4$$

$$0.36\ \cancel{\text{mol CH}_4} \times \frac{-890\ \text{kJ}}{\cancel{\text{mol CH}_4}} = -320\ \text{kJ}$$

$$\Delta H = \text{heat flow} = -320\ \text{kJ}$$

See Exercises 6.35 through 6.38

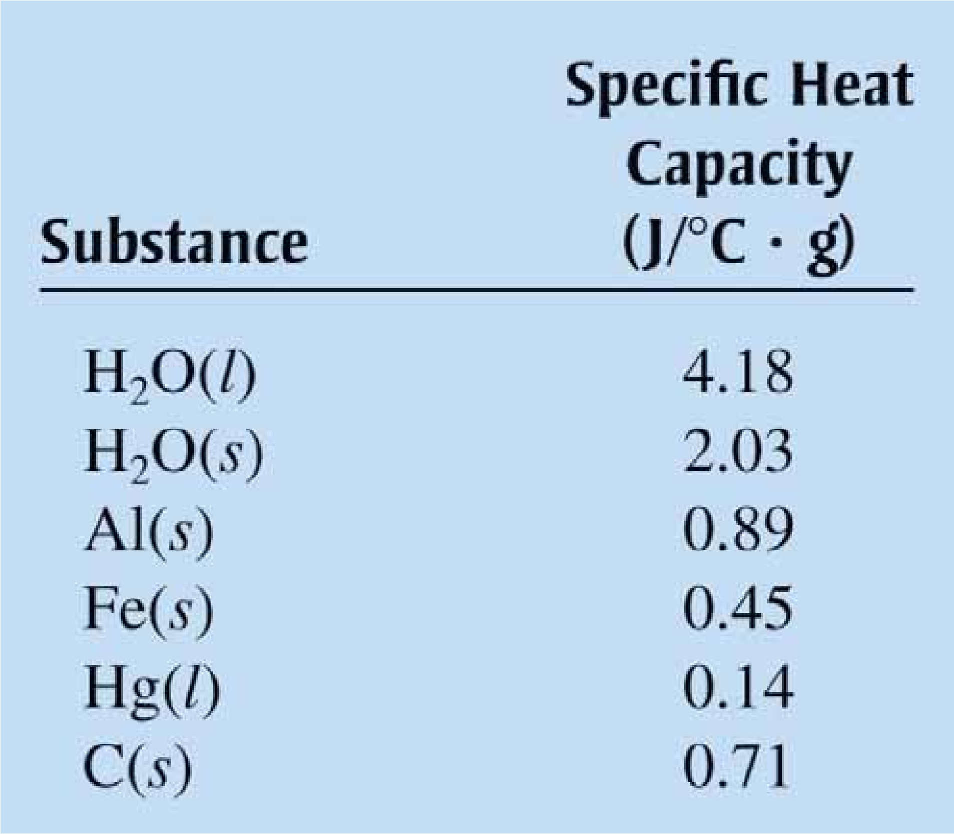
Calorimetry

- The device used experimentally to determine the heat associated with a chemical reaction is called a **calorimetry**.
- **Calorimetry** is based on observing the temperature change when a body absorbs or discharges energy as heat.
- The **heat capacity** *C* of a substance, is defined as

$$C = \frac{\text{heat absorbed}}{\text{increase in temperature}}$$

- If the heat capacity is given per gram of substance, it is called the **specific heat capacity**, and its units are J/℃ • g or J/K • g.
- If the heat capacity is given per mole of the substance, it is called the **molar heat capacity**, and it has the units J/℃ • mol or J/K • mol.
- The specific heat capacities of some common substance are given in Table 6.1.

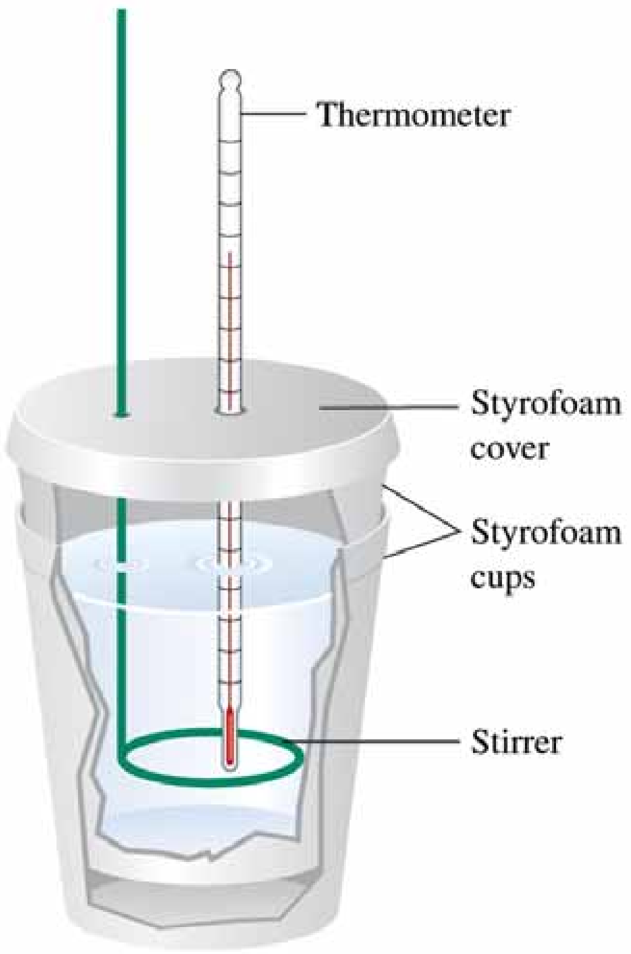
TABLE 6.1 The Specific Heat Capacities of Some Common Substances



Substance	Specific Heat Capacity (J/°C · g)
$H_2O(l)$	4.18
$H_2O(s)$	2.03
$Al(s)$	0.89
$Fe(s)$	0.45
$Hg(l)$	0.14
$C(s)$	0.71

- This device is called a “coffee-cup calorimeter.”
- The measurement of heat using a simple calorimeter such as that shown in Fig. 6.5 is an example of **constant-pressure calorimetry**, since the pressure (atmospheric pressure) remains constant during the process.

Figure 6.5



A coffee-cup calorimeter made of two Styrofoam cups.

- From these assumptions and definitions, we can calculate the heat (change in enthalpy) for the neutralization reaction:
- Energy released by the reaction

  = energy absorbed by the solution

  = specific heat capacity × mass of solution × increase in temperature

  $= s \times m \times \Delta T$

$$\text{Energy released} = s \times m \times \Delta T$$

Sample Exercise 6.5 Constant-Pressure Calorimetry

When 1.00 L of 1.00 M $Ba(NO_3)_2$ solution at 25.0℃ is mixed with 1.00 L of 1.00 M Na_2SO_4 solution at 25℃ in a calorimeter, the white solid $BaSO_4$ forms and the temperature of the mixture increases to 28.1℃. Assuming that the calorimeter absorbs only a negligible quantity of heat, that the specific heat capacity of the solution is 4.18 J/℃・g, and that the density of the final solution is 1.0 g/mL, calculate the enthalpy change per mole of $BaSO_4$ formed.

Sample Exercise 6.5

Solution

Since 1.00 L of each solution is used, the total solution volume is 2.00 L, and

$$\text{Mass of solution} = 2.0 \times 10^3\ \text{g}$$

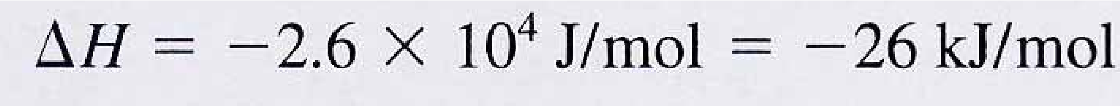
$$\text{Temperature increase} = 28.1^\circ\text{C} - 25.0^\circ\text{C} = 3.1^\circ\text{C}$$

$$\text{Heat evolved} = (4.18\ \text{J}/^\circ\cancel{\text{C}} \cdot \cancel{\text{g}})(2.0 \times 10^3\ \cancel{\text{g}})(3.1^\circ\cancel{\text{C}}) = 2.6 \times 10^4\ \text{J}$$

Thus

$$q = q_P = \Delta H = -2.6 \times 10^4\ \text{J}$$

Sample Exercise 6.5



$$\Delta H = -2.6 \times 10^4 \text{ J/mol} = -26 \text{ kJ/mol}$$

See Exercises 6.51 through 6.54

- Calorimetry experiments also can be performed at **constant volume**.
- To study the energy changes in reactions under conditions of constant volume, a “bomb calorimeter” (Fig. 6.6) is used.
- For a constant-volume process, the change in volume ΔV is equal to zero, so work (which is $-P\Delta V$) is also equal to zero.

- Therefore,

$$\Delta E = q + w = q = q_V \qquad \text{(constant volume)}$$

Figure 6.6

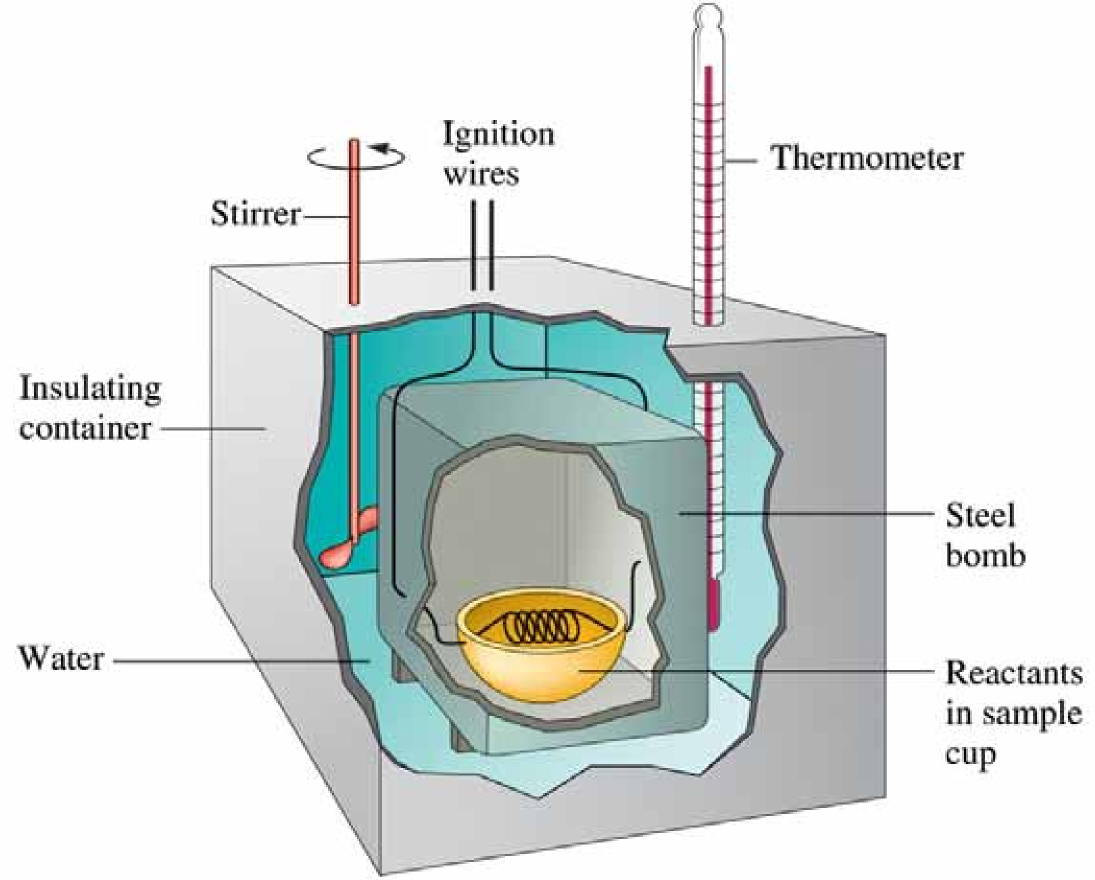

Ignition wires
Thermometer
Stirrer
Insulating container
Steel bomb
Water
Reactants in sample cup

Figure 6.6

A bomb calorimeter. The reaction is carried out inside a rigid steel “bomb” (photo of actual disassemble “bomb” shown on right), and heat evolved is absorbed by the surrounding water and other calorimeter parts. The quantity of energy produced by the reaction can be calculated from the temperature increase.

- Suppose we wish to measure the energy of combustion of octane (C_8H_{18}), a component of gasoline.
- A 0.5269-g sample of octane is placed in a bomb calorimeter known to have a heat capacity of 11.3 kJ/℃.
- Energy released by the reaction

$$= \text{temperature increase} \times \text{energy required to change the temperature by } 1^\circ\text{C}$$

$$= \Delta T \times \text{heat capacity of calorimeter}$$

$$= 2.25\,\cancel{^\circ\mathrm{C}} \times 11.3\ \mathrm{kJ}/\cancel{^\circ\mathrm{C}} = 25.4\ \mathrm{J}$$

- The number of moles of octane is 4.614×10^{-3} mol octane.
- Since 25.4 kJ of energy was released for 4.614×10^{-3} mol octane, the energy released per mole is 5.50×10^{-3} kJ/mol.
- Since the reaction is exothermic, ΔE is negative:

$$\Delta E_{\text{combustion}} = -5.50 \times 10^{-3} \text{ kJ/mol}$$

- Note that since no work is done in this case, ΔE is equal to the heat. $q = -5.50 \times 10^{-3}$ kJ/mol.

6.3 Hess's Law

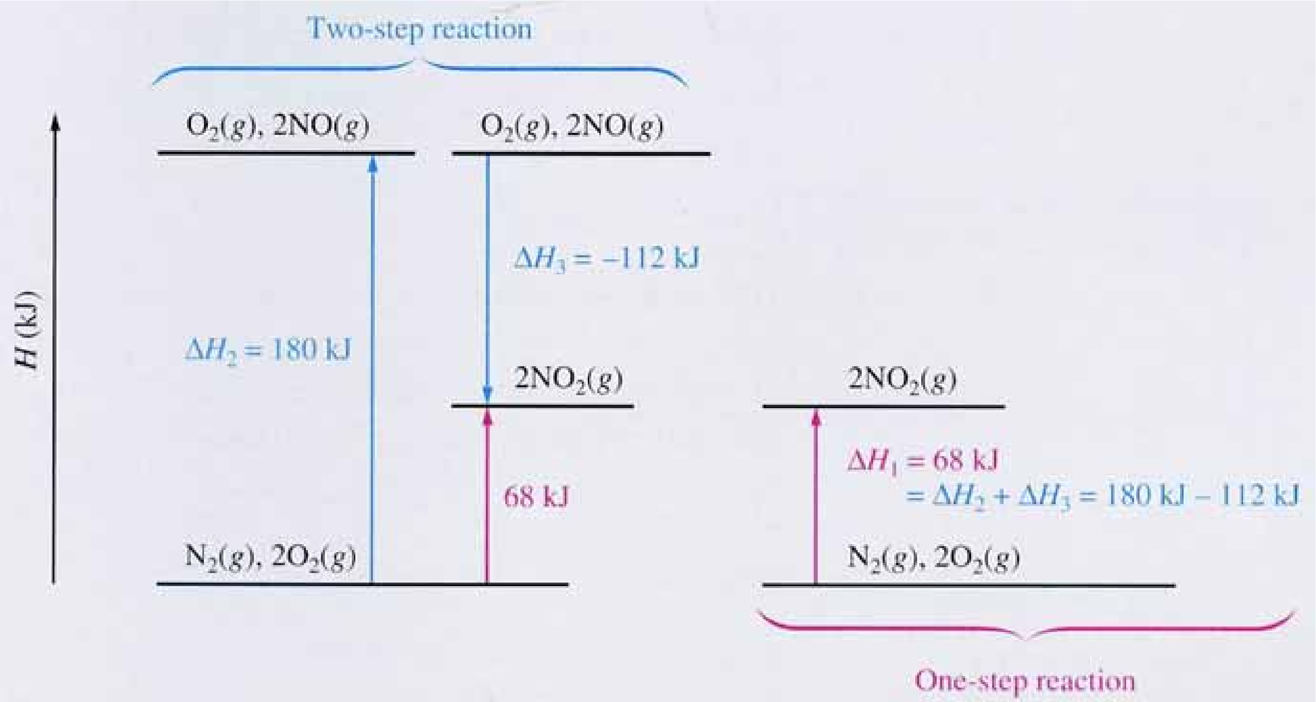
- Since enthalpy is a state function, the change in enthalpy in going from some initial state to some final state is independent of the pathway.
- *In going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.*
- This principle is known as **Hess's law** .

- The overall reaction can be written in one step, where the enthalpy change is represented by ΔH_1.

$$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \quad \Delta H_1 = 68\ \text{kJ}$$

- The principle of Hess's law is shown schematically in Fig. 6.7.

Figure 6.7



The principle of Hess's law. The same change in enthalpy occurs when nitrogen and oxygen react to form nitrogen dioxide, regardless of whether the reaction occurs in one (red) or two (blue) steps.

Characteristic of Enthalpy Changes

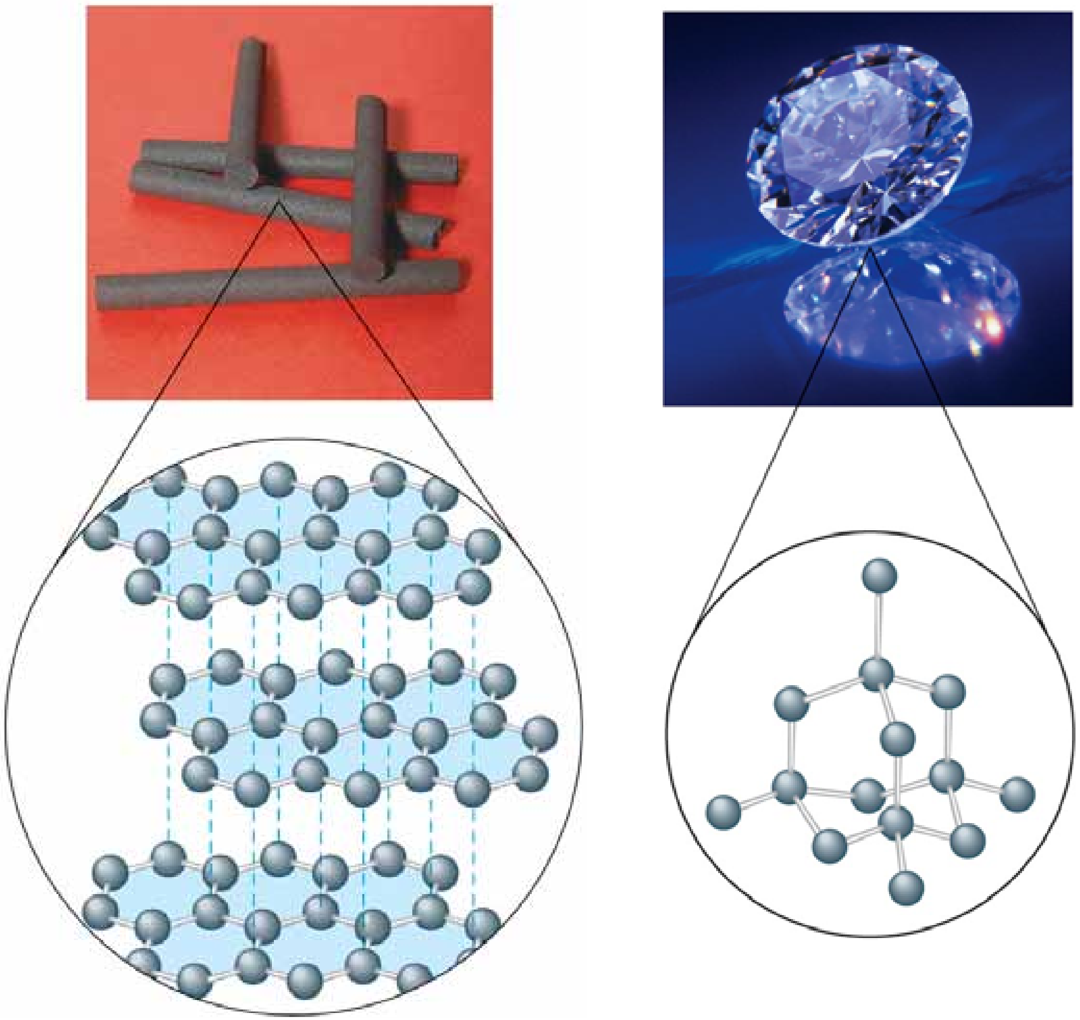
- Two characteristics of ΔH for a reaction:
  1. If reaction is reversed, the sign of ΔH is also reversed.
  2. The magnitude of ΔH is directly proportional to the quantities of reactants and products in a reaction. If the coefficients in a balanced reaction are multiplied by an integer, the value of ΔH is multiplied by the same integer.

- The first rule can be explained by recalling that the sign of ΔH indicates the direction of the heat flow at constant pressure.
- If the direction of the reaction is reversed, the direction of the heat flow also will be reversed.
- The second rule comes from the fact that ΔH is an extensive property, depending on the amount of substances reacting.

Sample Exercise 6.7 Hess's Law Ⅰ

Two forms of carbon are graphite, the soft, black, slippery material used in "lead" pencils and as a lubricant for locks, and diamond, the brilliant, hard gemstone. Using the enthalpies of combustion for graphite (−394 kJ/mol) and diamond (−396 kJ/mol), calculate ΔH for the conversion of graphite to diamond:

$$C_{\text{graphite}}(s) \longrightarrow C_{\text{diamond}}(s)$$



(left) graphite;
(right) diamond.

Hints for Using Hess’s Law

Calculations involving Hess’s law typically require that several reactions be manipulated and combined to finally give the reaction of interest. In doing this procedure you should

- Work *backward* from the required reaction, using the reactants and products to decide how to manipulate the other given reactions at you disposal
- Reverse any reactions as needed to give the required reactants and products
- Multiply reactions to give the correct numbers of reactants and products

- This process involves some trial and error, but it can be very systematic if you always allow the final reaction to guide you.

6.4 Standard Enthalpies of Formation

- For a reaction studied under conditions of constant pressure, we can obtain the enthalpy change using a calorimeter.
- An example is the conversion of solid carbon from its grahite form to its diamond form:

$$C_{\text{graphite}}(s) \longrightarrow C_{\text{diamond}}(s)$$

- The value of ΔH for this process cannot be obtained by direct measurement in a calorimeter because the process is much too slow under normal conditions.

- The **standard enthalpy of formation** (ΔH_f°) of a compound is defined as the change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states.
- A *degree symbol* on a thermodynamic function, for example, ΔH_f°, indicates that the corresponding process has been carried out under standard conditions.
- The **standard state** for a substance is a precisely defined reference state.

Conventional Definitions of Standard States

For a Compound

- The standard state of a gaseous substance is a pressure of exactly 1 atmosphere.

- For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid.

- For a substance present in a solution, the standard state is a concentration of exactly 1 M.

For an Element

- The standard state of an element is the form in which the element exists under conditions of 1 atmosphere and 25℃. (The standard state for oxygen is $O_2(g)$ at a pressure of 1 atmosphere; the standard state for sodium is Na(*s*); the standard state for mercury is Hg(*l*); and so on.)

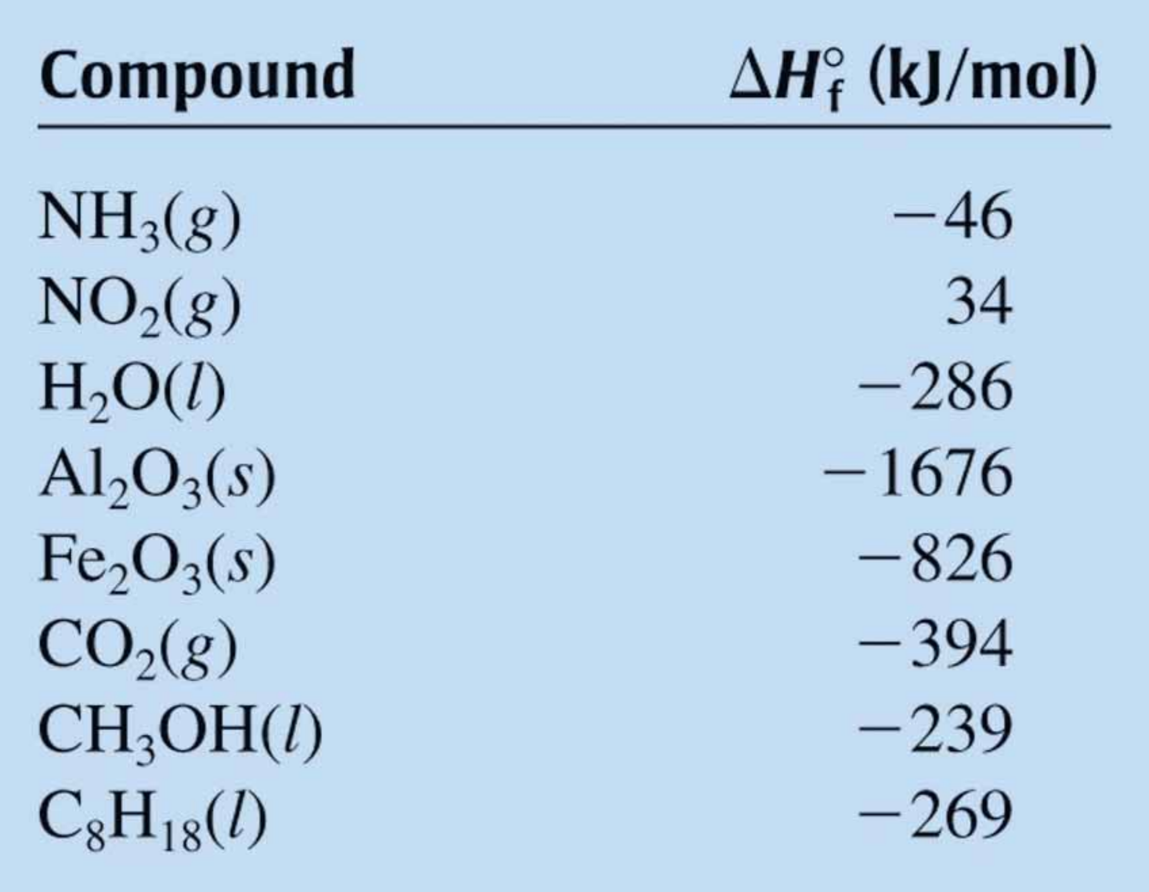
- The standard state of carbon is graphite, the standard states for oxygen and hydrogen are the diatomic gases, and the standard state for methanol is the liquid.
- The ΔH_f° values for some common substances are shown in Table 6.2. More values
- The importance of the tabulated ΔH_f° values is that enthalpies for many reactions can be calculated using these numbers.

- Calculate the standard enthalpy change for the combustion of methane:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

- Enthalpy is a state function, so we can invoke Hess's law and choose any convenient pathway from reactants to products and then sum the enthalpy changes along the chosen pathway.

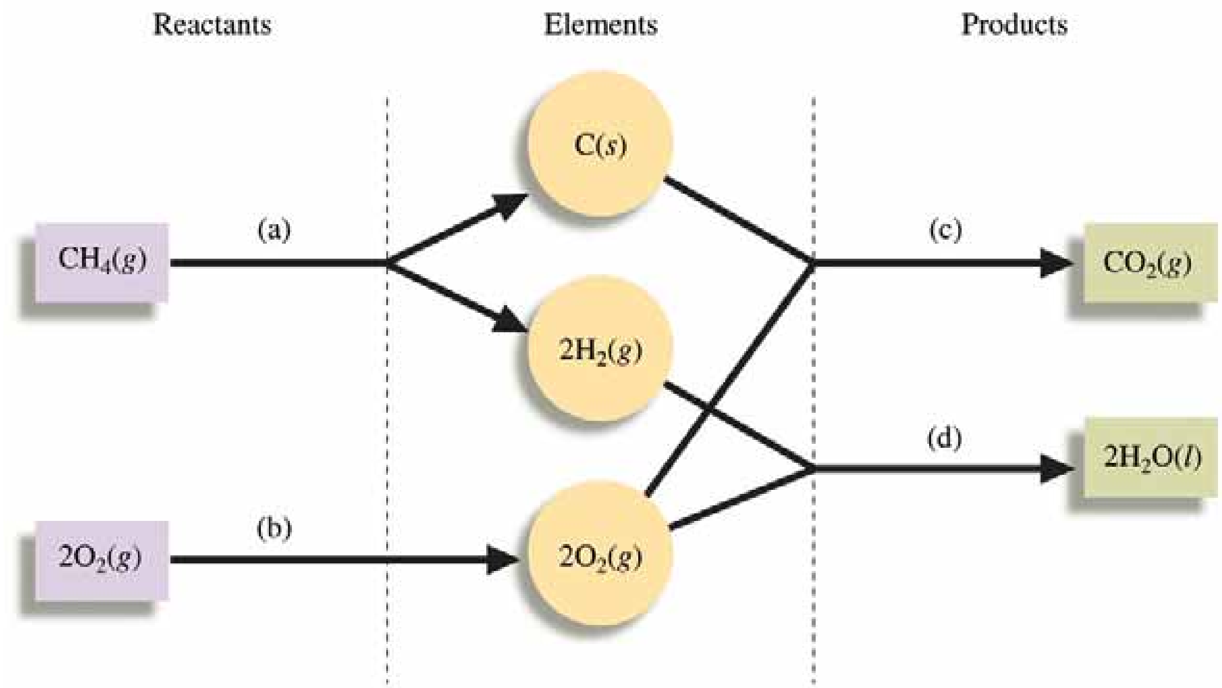
TABLE 6.2 Standard Enthalpies of Formation for Several Compounds at 25 ℃



Compound	ΔH_f° (kJ/mol)
$NH_3(g)$	−46
$NO_2(g)$	34
$H_2O(l)$	−286
$Al_2O_3(s)$	−1676
$Fe_2O_3(s)$	−826
$CO_2(g)$	−394
$CH_3OH(l)$	−239
$C_8H_{18}(l)$	−269

- A convenient pathway, shown in Fig. 6.8, involves taking the reactants apart to the respective elements in their standard states in reactions (a) and (b) and then forming the products from these elements in reactions (c) and (d).

Figure 6.8

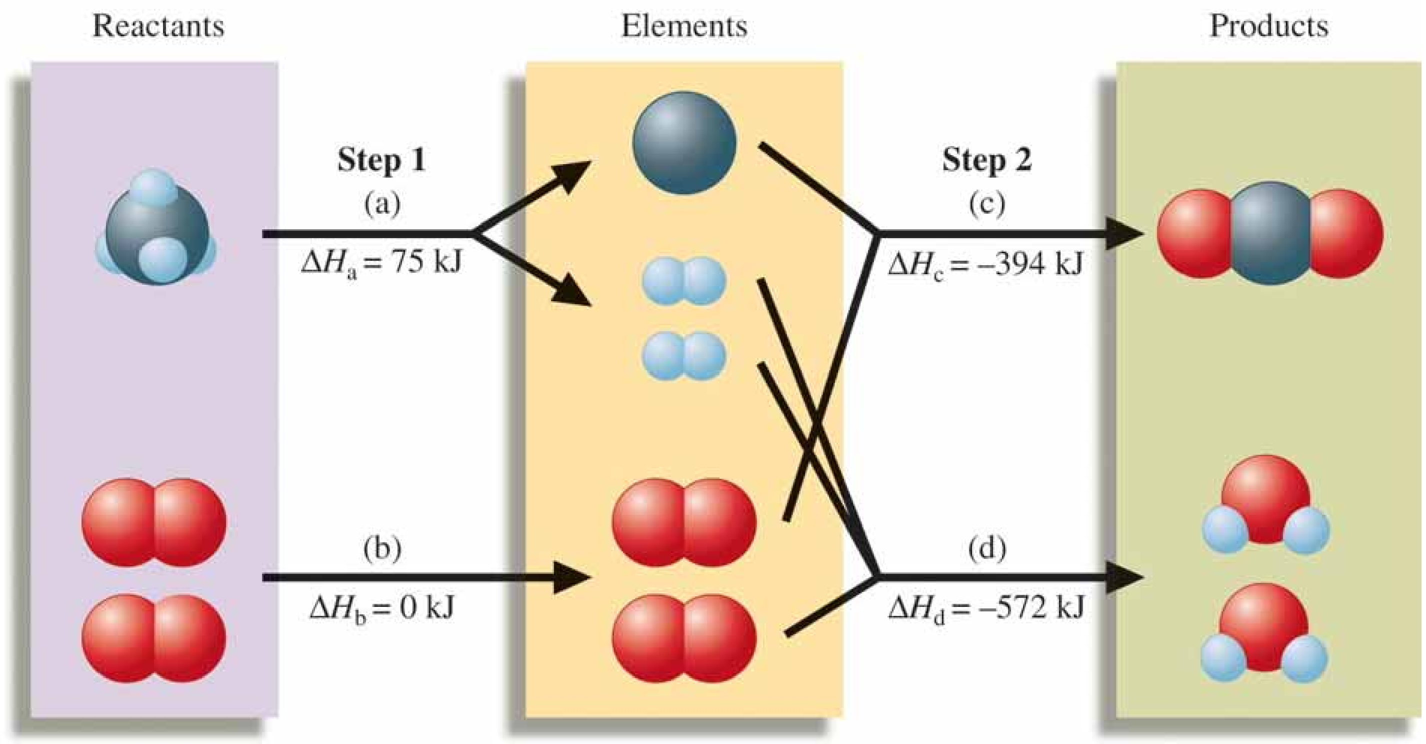


In this pathway for the combustion of methane, the reactants are first taken apart in reactions (a) and (b) to form the constituent elements in their standard states, which are then used to assemble the products in reactions (c) and (d).

- This process is diagramed in Fig. 6.9.
- Notice that the reactants are taken apart and converted to elements [not necessary for $O_2(g)$] that are then used to form products.
- Let's examine carefully the pathway we used in this example.
- First, the reactants were broken down into the elements in their standard states.

- This process involved reversing the formation reactions and switching the signs of the enthalpies of formation.
- The products were then constructed from these elements. This involved formation reactions and thus enthalpies of formation.
- The products were then constructed from these elements.
- This involved formation reactions and thus enthalpies of formation.

Figure 6.9



A schematic diagram of the energy changes for the reaction $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$.

- The enthalpy change for a given reaction can be calculated by subtracting the enthalpies of formation of the reactants from the enthalpies of formation of the products.
- Remember to multiply the enthalpies of formation by integers as required by the balanced equation.
- This statement can be represented symbolically as follows:

$$\Delta H^\circ_{\text{reaction}} = \Sigma n_\text{p} \Delta H^\circ_\text{f}(\text{products}) - \Sigma n_\text{r} \Delta H^\circ_\text{f}(\text{reactants}) \qquad (6.1)$$

- where the symbol Σ (sigma) means "to take the sum of the terms," and n_p and n_r represent the moles of each product or reactant, respectively.
- *Elements are not included in the calculation because elements require no change in form.*

Keep in Mind the Following Key Concepts When Doing Enthalpy Calculations:

- When a reaction is reversed, the magnitude of ΔH remains the same, but its sign changes.

- When the balanced equation for a reaction is multiplied by an integer, the value of ΔH for that reaction must be multiplied by the same integer.

- The change in enthalpy for a given reaction can be calculated from the enthalpies of formation of the reactants and products:

$$\Delta H^\circ_{\text{reaction}} = \Sigma n_p \Delta H^\circ_f(\text{products}) - \Sigma n_r \Delta H^\circ_f(\text{reactants})$$

- Elements in their standard states are not included in the $\Delta H_{\text{reaction}}$ calculations. That is , ΔH°_f for an element in its standard state is zero.

Sample Exercise 6.9

Enthalpies from Standard Enthalpies of Formation Ⅰ

Using the standard enthalpies of formation listed in Table 6.2, calculate the standard enthalpy change for the overall reaction that occurs when ammonia is burned in air to form nitrogen dioxide and water. This is the first step in the manufacture of nitric acid.

$$4NH_3(g) + 7O_2(g) \longrightarrow 4NO_2(g) + 6H_2O(l)$$

Solution

We will use the pathway in which the reactants are broken down into elements in their standard states, which are then used to form the products (see Fig. 6.10).

Sample Exercise 6.9

➡ 1 Decomposition of $NH_3(g)$ into elements (reaction (a) in Fig. 6.10). The first step is to decompose 4 moles of NH_3 into N_2 and H_2:

$$4NH_3(g) \longrightarrow 2N_2(g) + 6H_2(g)$$

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \longrightarrow NH_3(g) \qquad \Delta H_f^\circ = -46\ \text{kJ/mol}$$

$$\Delta H^\circ_{(a)} = 4\ \text{mol}[-(-46\ \text{kJ/mol})] = 184\ \text{kJ}$$

➡ 2 Elemental oxygen (reaction (b) in Fig. 6.10). Since $O_2(g)$ is an element in its standard state, $\Delta H^{\circ}_{(b)} = 0$.

Sample Exercise 6.9

➡ 3 Synthesis of $NO_2(g)$ from elements (reaction (c) in Fig. 6.10). The overall reaction equation has 4 moles of NO_2. Thus the required reaction is 4 times the formation reaction for NO_2:

$$4 \times [\tfrac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g)]$$

$$\Delta H^\circ_{(c)} = 4 \times \Delta H^\circ_f \text{ for } NO_2(g)$$

Form Table 6.2, ΔH°_f for $NO_2(g) = 34$ kJ/mol and

$$\Delta H^\circ_{(c)} = 4 \text{ mol} \times 34 \text{ kJ/mol} = 136 \text{ kJ}$$

Sample Exercise 6.9

➡ 4 Synthesis of $H_2O(l)$ from elements (reaction (d) in Fig. 6.10). Since the overall equation for the reaction has 6 moles of $H_2O(l)$, the required is 6 times the formation reaction for $H_2O(l)$:

$$6 \times [H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)]$$

From Table 6.2, ΔH_f° for $H_2O(l) = -286$ kJ/mol and

$$\Delta H^\circ_{(d)} = 6 \times \Delta H_f^\circ \text{ for } H_2O(l)$$

To summarize, we have done the following:

Sample Exercise 6.9

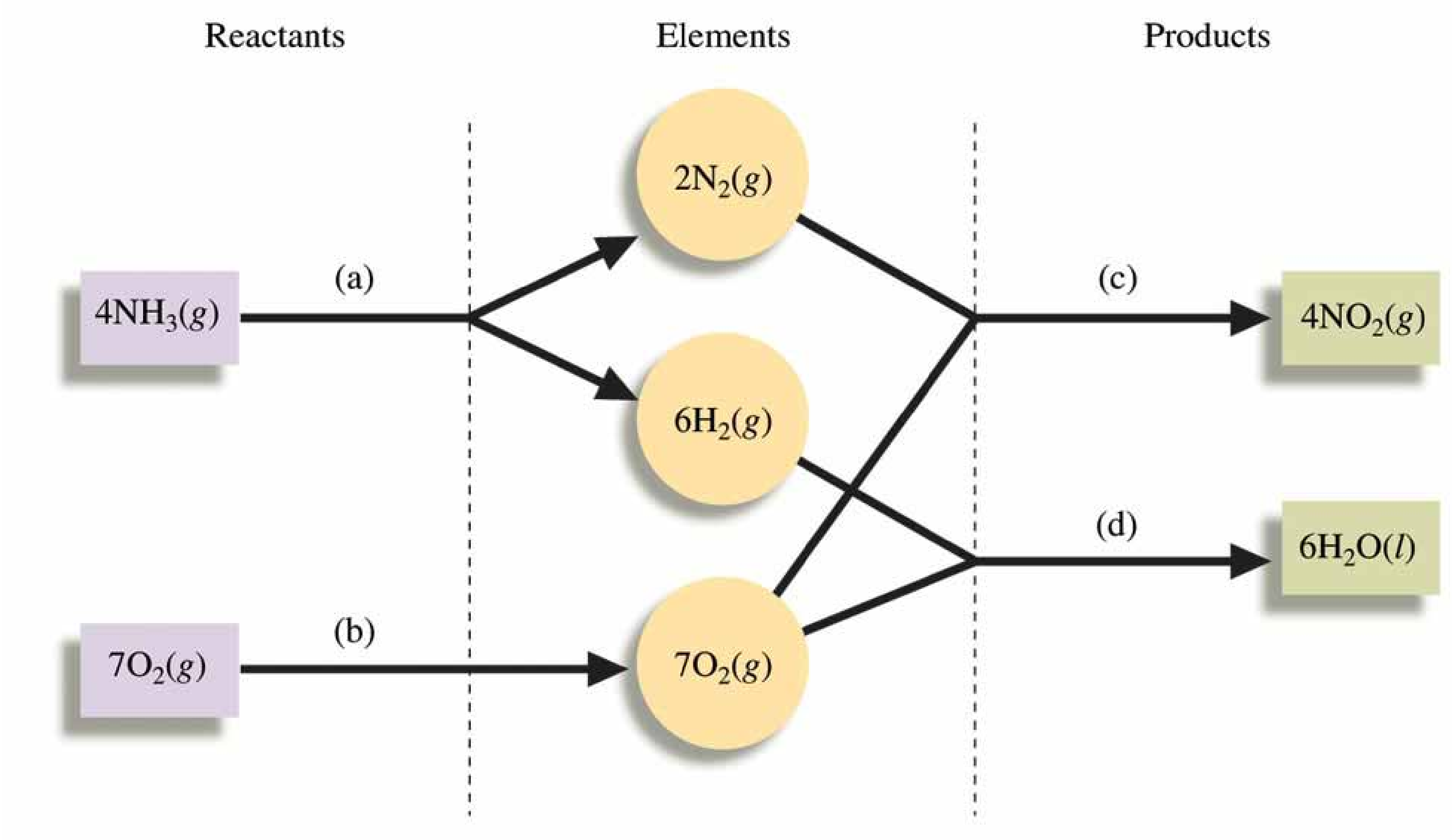
$$\begin{array}{l} 4NH_3(g) \xrightarrow{\Delta H^\circ_{(a)}} \\ 7O_2(g) \xrightarrow{\Delta H^\circ_{(b)}} \end{array} \left\{ \begin{array}{l} 2N_2(g) + 6H_2(g) \\ 7O_2(g) \end{array} \right\} \begin{array}{l} \xrightarrow{\Delta H^\circ_{(c)}} 4NO_2(g) \\ \xrightarrow{\Delta H^\circ_{(d)}} 6H_2O(l) \end{array}$$

$$\Delta H^\circ_{\text{reaction}} = \Delta H^\circ_{(a)} + \Delta H^\circ_{(b)} + \Delta H^\circ_{(c)} + \Delta H^\circ_{(d)}$$

$$\begin{aligned} \Delta H^\circ_{\text{reaction}} &= [4 \times (34\text{ kJ})] + [6 \times (-286\text{ kJ})] - [4 \times (-46\text{ kJ})] \\ &= -1396\text{ kJ} \end{aligned}$$

See Exercises 6.67 and 6.68

Figure 6.10



A pathway for the combustion of ammonla.

Sample Exercise 6.10

Enthalpies from Standard Enthalpies of Formation Ⅱ

Using enthalpies of formation, calculate the standard change in enthalpy for the thermite reaction:

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

This reaction occurs when a mixture of powdered aluminum and iron (Ⅲ) oxide is ignited with a magnesium fuse.

Sample Exercise 6.10

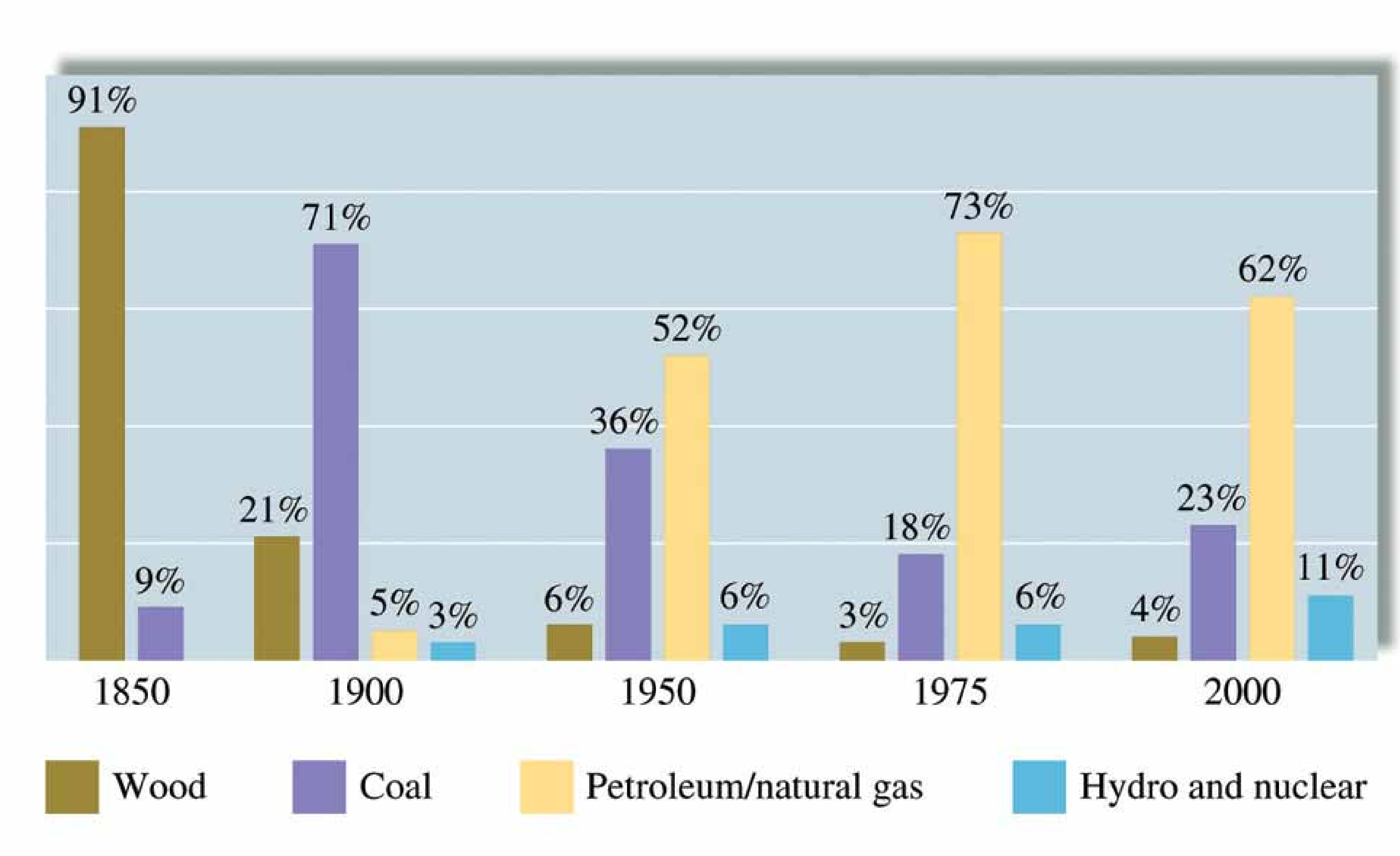
The thermite reaction is one of the most energetic chemical reactions known.

See Exercises 6.71 and 6.72

6.5 Present Sources of Energy

- Woody plants, coal, petroleum, and natural gas hold a vast amount of energy that originally came from the sun.
- By the process of photosynthesis, plants store energy that can be claimed by burning the plants themselves or the decay products that have been converted over millions of years to **fossil fuels**.
- Although the United States currently depends heavily on petroleum for energy, this dependency is a relatively recent phenomenon, as shown in Fig. 6.11.

Figure 6.11

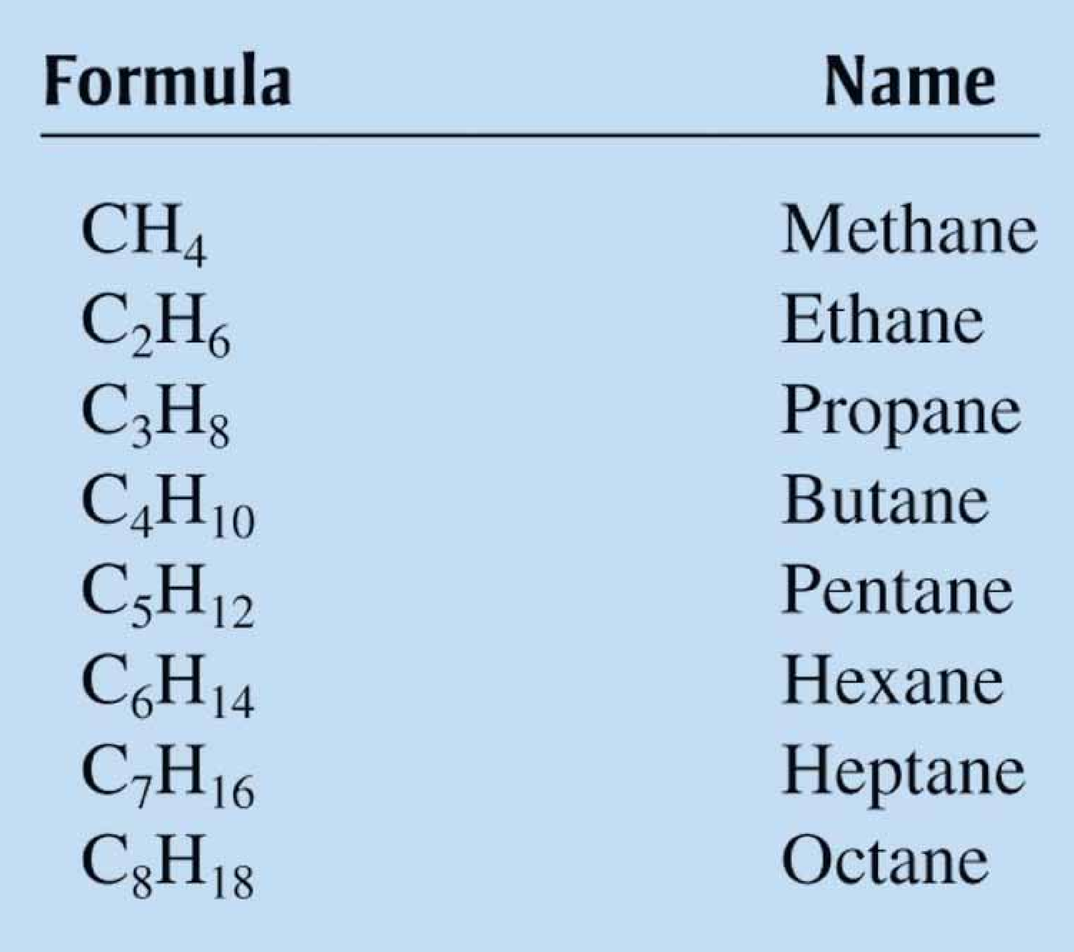


Energy sources used in the United States.

Petroleum and Natural Gas

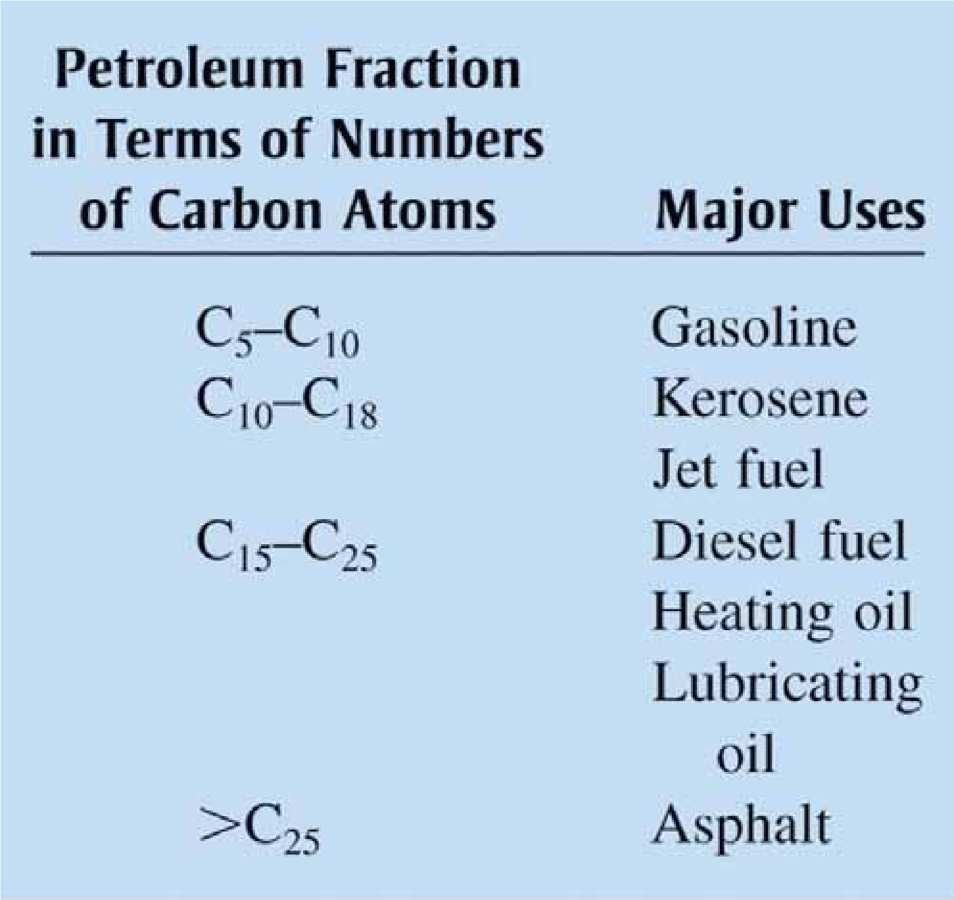
- **Petroleum** is a thick, dark liquid composed mostly of compounds called hydrocarbons that contain carbon and hydrogen.
- Table 6.3 gives the formulas and names for several common hydrocarbons.
- **Natural gas**, usually associated with petroleum deposits, consists mostly of methane, but it also contains significant amounts of ethane, propane, and butane.
- The commercial uses of various petroleum fractions are shown in Table 6.4.

TABLE 6.3 Names and Formulas for Some Common Hydrocarbons



Formula	Name
CH_4	Methane
C_2H_6	Ethane
C_3H_8	Propane
C_4H_{10}	Butane
C_5H_{12}	Pentane
C_6H_{14}	Hexane
C_7H_{16}	Heptane
C_8H_{18}	Octane

TABLE 6.4 Uses of the Various Petroleum Fractions



Petroleum Fraction in Terms of Numbers of Carbon Atoms	Major Uses
C_5–C_{10}	Gasoline
C_{10}–C_{18}	Kerosene Jet fuel
C_{15}–C_{25}	Diesel fuel Heating oil Lubricating oil
$>C_{25}$	Asphalt

- The petroleum era began when the demand for lamp oil during the Industrial Revolution outstripped the traditional sources: animal fats and whale oil.
- In response to this increased demand, Edwin Drake drilled the first oil well in 1859 at Titusville, Pennsylvania.
- The petroleum from this well was refined to produce kerosene (fraction C_{10}—C_{18}), which served as an excellent lamp oil.
- *Gasoline* (fraction C_5—C_{10}) had limited use and was often discarded.

- As gasoline became more important, new ways were sought to increase the yield of gasoline obtained from each barrel of petroleum.
- William Burton invented a process at Standard Oil of Indiana called *pyrolytic* (*high-temperature*) *cracking*.
- In this process, the heavier molecules of the kerosene fraction are heated to about 700℃, causing them to break (crack) into the smaller molecules of hydrocarbons in the gasoline fraction.

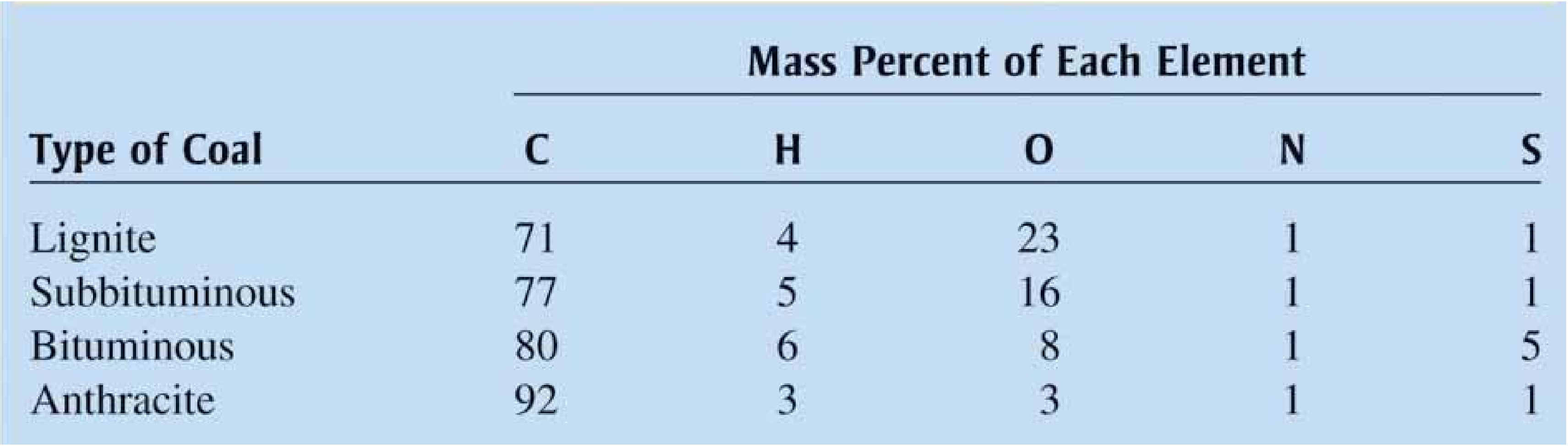
The oil rig in Norway is the largest in the world.

Coal

- Coal was formed from the remains of plants that were buried and subjected to high pressure and heat over long periods of time.
- Coal "matures" through four stages: lignite, subbituminous, bituminous, and anthracite.
- Each stage has a higher carbon-to-oxygen and carbon-to-hydrogen ratio.
- Typical elemental compositions of the various coals are given in Table 6.5.

- The energy available from the combustion of a given mass of coal increase as the carbon content increases.
- Anthracite is the most valuable coal, and lignite the least valuable.

TABLE 6.5 Elemental Composition of Various Types of Coal



	Mass Percent of Each Element				
Type of Coal	**C**	**H**	**O**	**N**	**S**
Lignite	71	4	23	1	1
Subbituminous	77	5	16	1	1
Bituminous	80	6	8	1	5
Anthracite	92	3	3	1	1

Effects of Carbon Dioxide on Climate

- The earth receives a tremendous quantity of radiant energy from the sun, about 30% of which is reflected back into space by the earth's atmosphere.
- The remaining energy passes through the atmosphere to the earth's surface.
- Some of this energy is absorbed by plants for photosynthesis and some by the oceans to evaporate water, but most of it is absorbed by soil, rocks, and water, increasing the temperature of the earth's surface.

- This energy is in turn radiated from the heated surface mainly as *infrared radiation*, often called *heat radiation*.
- The atmosphere, like window glass, is transparent to visible light but does not allow all the infrared radiation to pass back into space.
- As shown in Fig. 6.12, so a net amount of thermal energy is retained by the earth's atmosphere, causing the earth to be much warmer than it would be without its atmosphere.

Figure 6.12

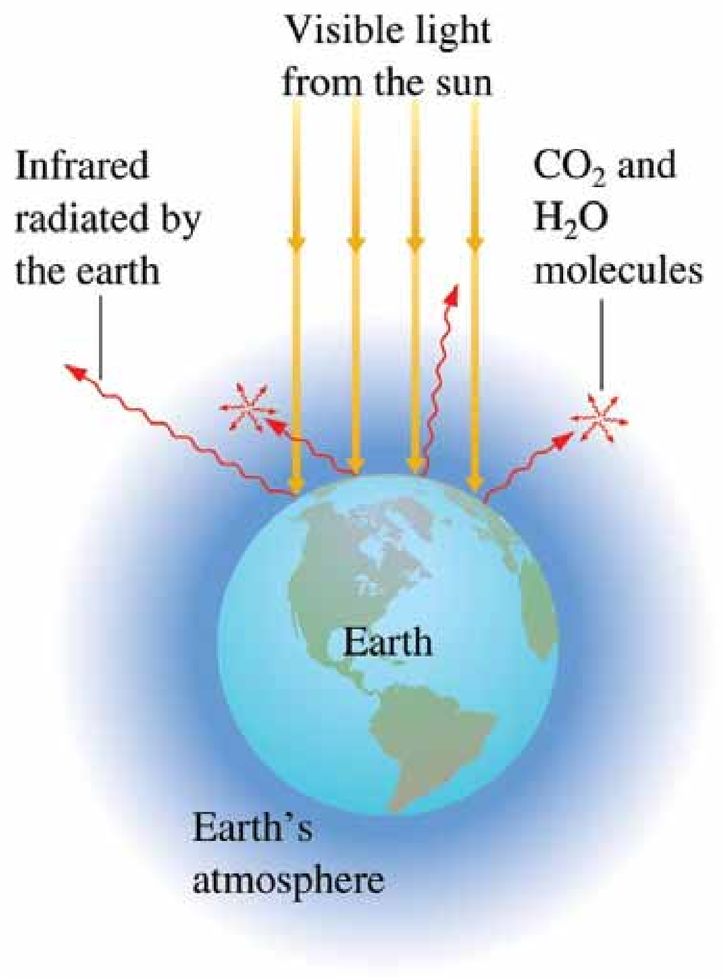

Visible light from the sun
Infrared radiated by the earth
CO_2 and H_2O molecules
Earth
Earth's atmosphere

Figure 6.12

The earth’s atmosphere is transparent to visible light from the sun. This visible light strikes the earth, and part of it is changed to infrared radiation. The infrared radiation from the earth’s surface is strongly absorbed by CO_2, H_2O, and other molecules present in smaller amounts (for example, CH_4 and N_2O) in the atmosphere. In effect, the atmosphere traps some of the energy, acting like the glass in a greenhouse and keeping the earth warmer than it would otherwise be.

- Thus the temperature of the earth’s surface is controlled to a significant extent by the carbon dioxide and water content of the atmosphere.
- In fact, the variation in the earth’s average temperature over the past century is somewhat confusing.
- In the northern latitudes during the past century, the average temperature rose by 0.8°C over a period of 60 years, then cooled by 0.5°C during the next 25 years, and finally warmed by 0.2°C in the succeeding 15 years.

- Such fluctuations do not match the steady increase in carbon dioxide.
- However, in southern latitudes and near the equator during the past century, the average temperature shown a steady rise totaling 0.4℃.
- This figure is in reasonable agreement with the predicted effect of the increasing carbon dioxide concentration over that period.
- Another significant fact is that the past 10 years constitute the warmest decade on record.

Sheep grazing on a ranch in Australia.

- The increase in the atmospheric concentration of carbon dioxide is quite dramatic (see Fig. 6.13).
- Methane is another greenhouse gas that is 21 times more potent than carbon dioxide.
- This fact is particularly significant for countries with lots of animals, because methane is produced by methanogenic archae that live in the animals’ rumen.
- To reduce this level, Australia has initiated a program to vaccinate sheep and cattle to lower the number of archae present in their digestive systems.

Figure 6.13

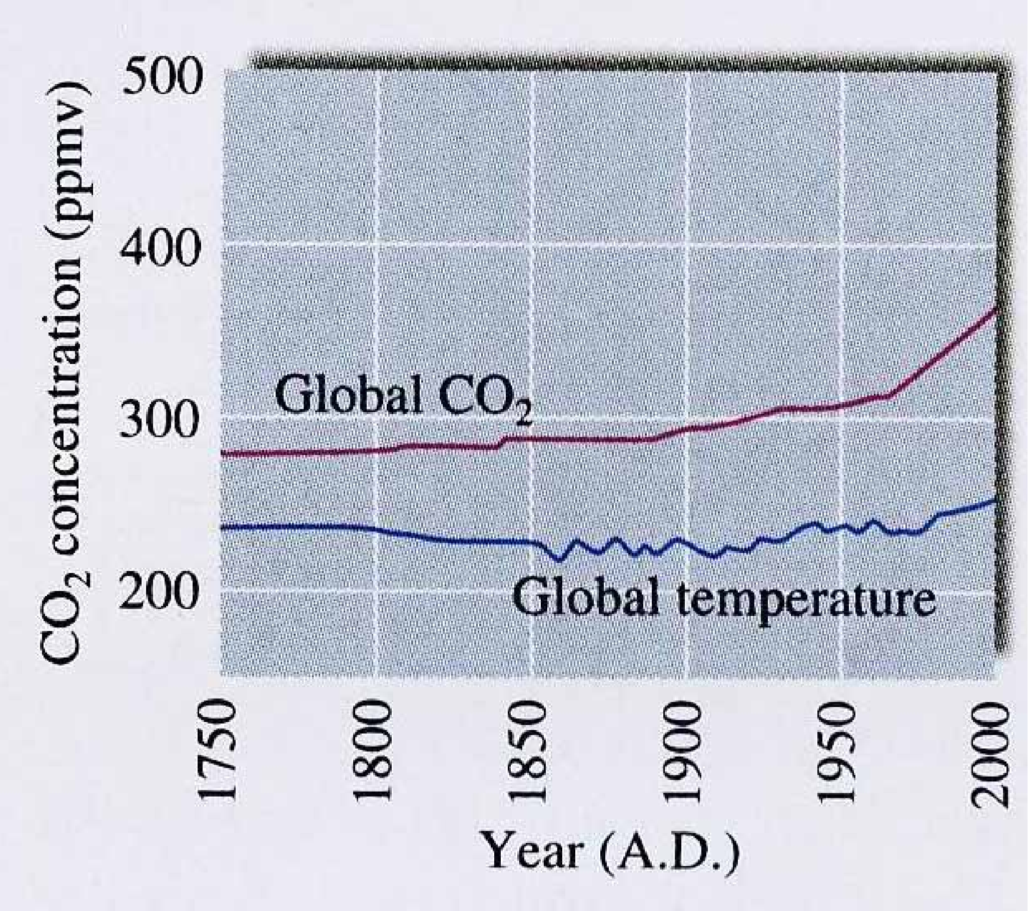

500
400
300
200
CO_2 concentration (ppmv)
Global CO_2
Global temperature
1750
1800
1850
1900
1950
2000
Year (A.D.)

Figure 6.13

The atmospheric CO_2 concentration and the average global temperature over the last 250 years. Note the significant increase in CO_2 concentration in the last 50 years. (Source: National Assessment synthesis Team, Climate Change Impacts on the United States: The Potential Consequences of Climate, Variability and change, Overview, Report for the U.S. Global Change Research Program, Cambridge University Press, Cambridge, UK, p. 13, 2000.)

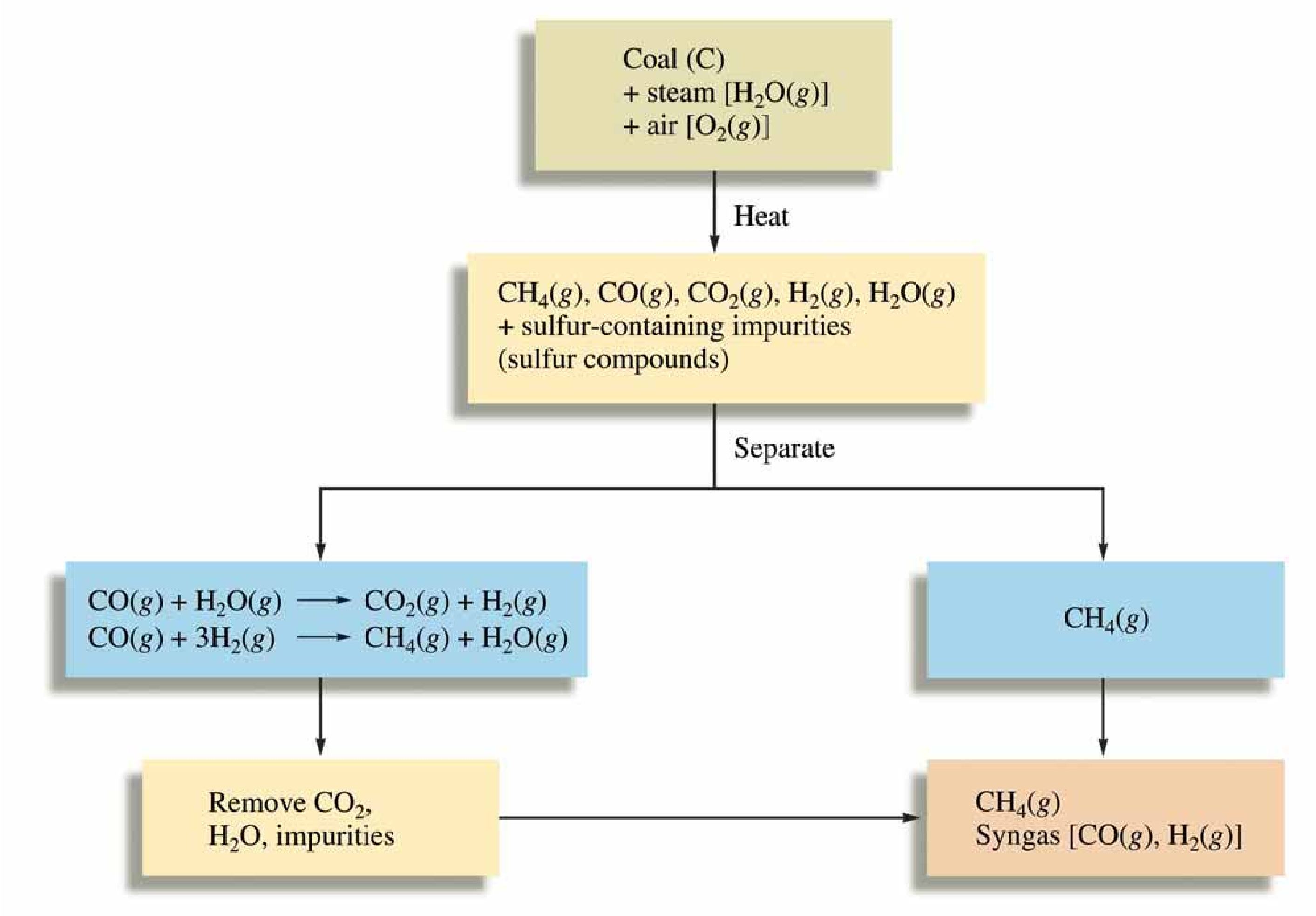
6.6 New Energy Sources

- There are several potential energy sources: the sun (solar), nuclear processes (fission and fusion), biomass (plants), and synthetic fuels.

Coal Conversion

- One alternative energy source involves using a traditional fuel-coal-in new ways.
- Substances like coal that contain large molecules have high boiling points and tend to be solids or thick liquids.
- To convert coal from a solid to a gas therefore requires reducing the size of the molecules; the coal structure must be broken down in a process called coal gasification.
  - The process is represented in Fig. 6.14.

Figure 6.14



Coal (C)
+ steam [$H_2O(g)$]
+ air [$O_2(g)$]

Heat

$CH_4(g)$, $CO(g)$, $CO_2(g)$, $H_2(g)$, $H_2O(g)$
+ sulfur-containing impurities
(sulfur compounds)

Separate

$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$
$CO(g) + 3H_2(g) \longrightarrow CH_4(g) + H_2O(g)$

$CH_4(g)$

Remove CO_2,
H_2O, impurities

$CH_4(g)$
Syngas [$CO(g)$, $H_2(g)$]

Figure 6.14

Coal gasification. Reaction of coal with a mixture of steam and air breaks down the large hydrocarbon molecules in the coal to smaller gaseous molecules, which can be used as fuels.

- The desired product is a mixture of carbon monoxide and hydrogen called synthetic gas, or **syngas**, and methane (CH_4) gas.
- In coal gasification, some of the reactions are exothermic:

$$\begin{aligned}
C(s) + 2H_2(g) &\longrightarrow CH_4(g) & \Delta H^\circ &= -75\text{ kJ}\\
C(s) + \tfrac{1}{2}O_2(g) &\longrightarrow CO(g) & \Delta H^\circ &= -111\text{ kJ}\\
C(s) + O_2(g) &\longrightarrow CO_2(g) & \Delta H^\circ &= -394\text{ kJ}
\end{aligned}$$

- Other gasification reactions are endothermic,

$$C(s) + H_2O(g) \longrightarrow H_2(g) + CO(g) \qquad \Delta H^\circ = 131\text{ kJ}$$

- Although syngas can be used directly as a fuel, it is also important as a raw material to produce other fuels. For example, syngas can be converted directly to methanol:

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

- Methanol is used in the production of synthetic fibers and plastics and also can be used as a fuel. In addition, it can be converted directly to gasoline.
- In addition to coal gasification, the formation of coal slurries is another new use of coal.

Hydrogen as a Fuel

- If you have ever seen a lecture demonstration where hydrogen-oxygen mixtures were ignited, you witnessed a demonstration of hydrogen's potential as a fuel.
- The combustion reaction is

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\circ = -286\ \mathrm{kJ}$$

- There are three main problems: the cost of production, storage, and transport.

The main engines in the space shuttle Endeavour use hydrogen and oxygen as fuel.

- First let's look at the production problem.
- Currently, the main source of hydrogen gas is from the treatment of natural gas with steam:

$$CH_4(g) + 2H_2O(g) \longrightarrow 3H_2(g) + CO(g)$$

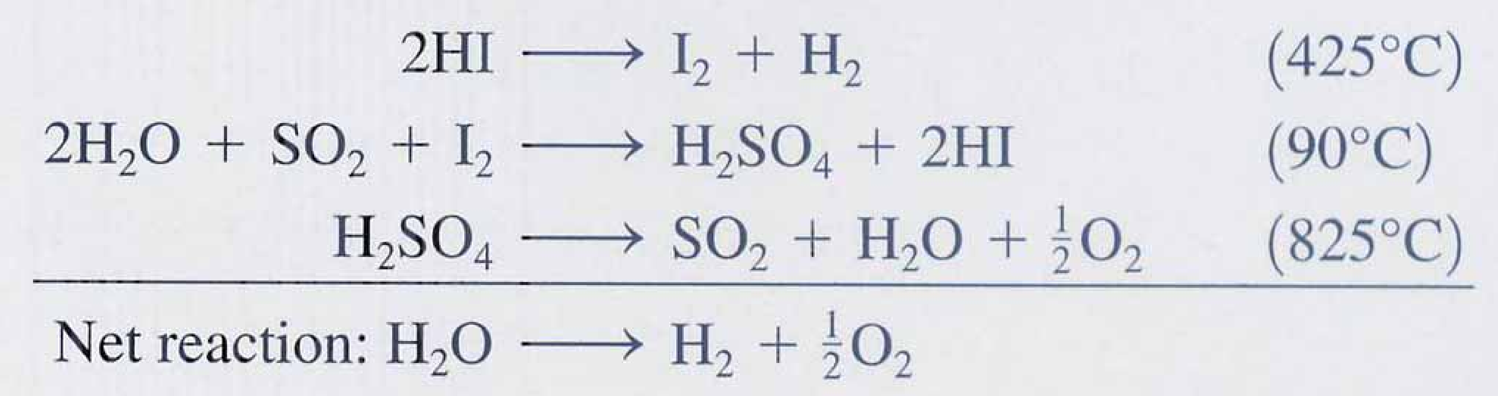
$$\Delta H^\circ = 206 \text{ kJ}$$

- Note that this reaction is highly endothermic; treating methane with steam is not an efficient way to obtain hydrogen for fuel. It would be much more economical to burn the methane directly.

$$H_2O(l) \longrightarrow H_2(g) + \tfrac{1}{2}C_2(g)$$

- Requires 286 kJ of energy per mole of liquid water, and under current circumstances, large-scale production of hydrogen from water is not economically feasible.
- However, several methods for such production are currently being studied: electrolysis of water, thermal decomposition of water, thermochemical decomposition of water, and biological decomposition of water.
- Electrolysis of water involves passing an electric current through it, as shown in Fig. 1.16 in chapter 1.

- Thermal decomposition is another method for producing hydrogen from water.
- In the thermochemical decomposition of water, chemical reactions, as well as heat, are used to “split” water into its components.



$$
\begin{array}{rcll}
2HI & \longrightarrow & I_2 + H_2 & (425°C) \\
2H_2O + SO_2 + I_2 & \longrightarrow & H_2SO_4 + 2HI & (90°C) \\
H_2SO_4 & \longrightarrow & SO_2 + H_2O + \frac{1}{2}O_2 & (825°C) \\
\hline
\text{Net reaction: } H_2O & \longrightarrow & H_2 + \frac{1}{2}O_2 &
\end{array}
$$

- Note that the HI is not consumed in the net reaction. Note also that maximum temperature required is 825℃, a temperature that is feasible if a nuclear reactor is used as a heat source.
- The storage and transportation of hydrogen also present problems.
- An additional problem is the relatively small amount of energy that is available per unit volume of hydrogen gas.

- Although the use of hydrogen as a fuel solves some of the problems associated with fossil fuels, it does present some potential environmental problems of its own.

Sample Exercise 6.12

Enthalpies of Combustion

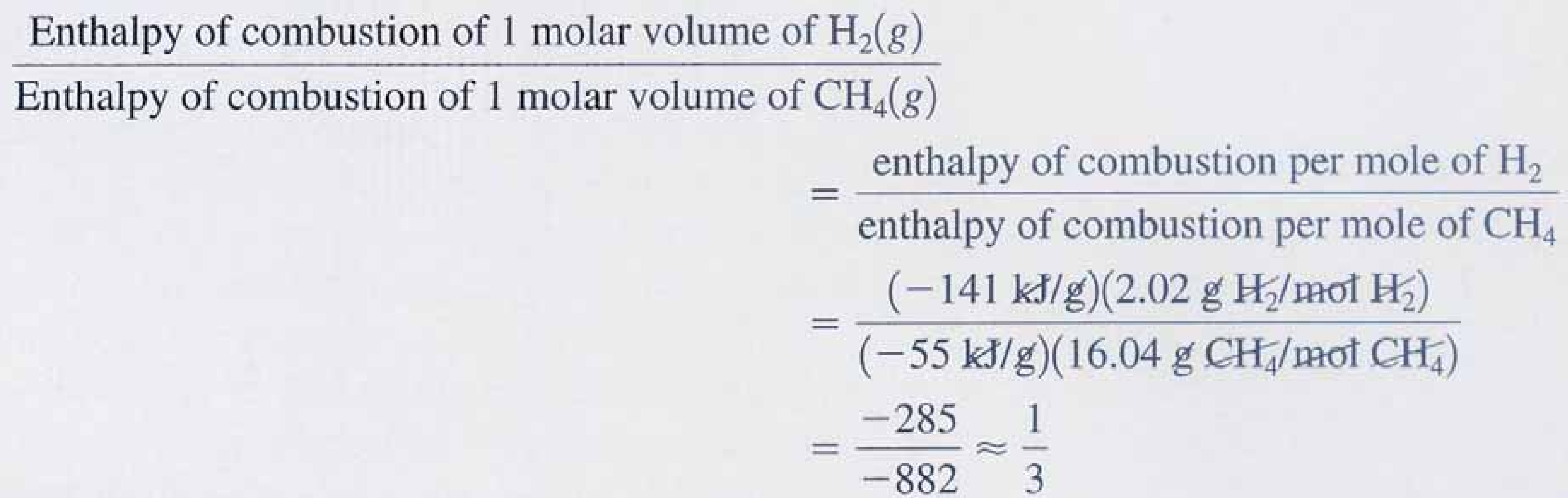
Compare the energy available from the combustion of a given volume of methane and the same volume of hydrogen at the same temperature and pressure.

Solution

In Sample Exercise 6.6 we calculated the heat released for the combustion of methane and hydrogen: 55 kJ/g CH_4 and 141 kJ/g H_2. We also know from our study of gases that 1 mol $H_2(g)$ has the same volume as 1 mol $CH_4(g)$ at the same temperature and pressure (assuming ideal behavior).

Sample Exercise 6.12

Thus, for molar volumes of both gases under the same conditions of temperature and pressure,



$$\frac{\text{Enthalpy of combustion of 1 molar volume of } H_2(g)}{\text{Enthalpy of combustion of 1 molar volume of } CH_4(g)} = \frac{\text{enthalpy of combustion per mole of } H_2}{\text{enthalpy of combustion per mole of } CH_4} = \frac{(-141\ \cancel{kJ}/\cancel{g})(2.02\ \cancel{g}\ \cancel{H_2}/\cancel{mol}\ \cancel{H_2})}{(-55\ \cancel{kJ}/\cancel{g})(16.04\ \cancel{g}\ \cancel{CH_4}/\cancel{mol}\ \cancel{CH_4})} = \frac{-285}{-882} \approx \frac{1}{3}$$

Sample Exercise 6.12

Thus about three times the volume of hydrogen gas is needed to furnish the same energy as a given volume of methane.

See Exercises 6.78

Sample Exercise 6.13

Comparing Enthalpies of Combustion

Assuming that the combustion of hydrogen gas provides three times as much energy per gram as gasoline, calculate the volume of liquid H_2 (density = 0.0710 g/mL) required to furnish the energy contained in 80.0 L (about 20 gas) of gasoline (density = 0.740 g/mL). Calculate also the volume that this hydrogen would occupy as a gas at 1.00 atm and 25℃.

- Thus storage of hydrogen in the individual automobile as a liquid does not seem practical.
- A much better alternative seems to be the use of metals that absorb hydrogen to form solid metal hydrides:

$$H_2(g) + M(s) \longrightarrow MH_2(s)$$

- This hydrogen would then be available for combustion in the engine by release of $H_2(g)$ from the hydride as needed:

$$MH_2(s) \longrightarrow M(s) + H_2(g)$$

- The most likely use of hydrogen in automobiles will be to power fuel cells .
- Ford, Honda, and Toyota are all experimenting with cars powered by hydrogen fuel cells.

Other Energy Alternatives

- Many other energy sources are being considered for future use.
- The western states, especially Colorado, contain huge deposits of *oil shale*, which consists of a complex carbon-based material called *kerogen* contained in porous rock formations.
- *Ethanol* (C_2H_5OH) is another fuel with the potential to supplement, if not replace, gasoline.

- The most common method of producing ethanol is fermentation, a process in which sugar is changed to alcohol by the action of yeast.
- Car engines can burn pure alcohol or *gasohol*, an alcohol-gasoline mixture (10% ethanol in gasoline), with little modification. Gasohol is now widely available in the United States.
- *Methanol* (CH_3OH), an alcohol similar to ethanol, which has been used successfully for many years in race cars, is now being evaluated as a motor fuel in California.

- Another potential source of liquid fuels is oil squeezed from seeds (*seed oil*).
- The main advantage of seed oil as a fuel is that it is renewable. Ideally, fuel would be grown just like food crops.

The sugars in corn are fermented and used to produce ethanol, an additive for gasoline.