3.0 INTRODUCTION

Almost all reactions involve energy changes because the potential energy of the products and the reactants usually differ. If the potential energy of the products is greater than that of the reactants, energy must be supplied to the reaction to make the reaction proceed. However, if the products are at lower potential energy, energy is released during reaction. The released energy can be used to drive turbines and pistons, run batteries, and even supply the energy used by our bodies while we work and play. An understanding of the energy changes that take place during a reaction allows us to determine how best to run the reaction and even how much product we can expect under various conditions. The study of the energy changes that accompany chemical reactions is known as thermochemistry, which is a branch of the more general field of thermodynamics - the study of energy and its transformations. In this chapter, we discuss the first law of thermodynamics, define some important terms, and demonstrate some valuable tools that can be used to determine the energy requirements of reactions.

THE OBJECTIVES OF THIS CHAPTER ARE TO:

- define energy, heat, and work and to show the relationship between them;
- discuss the first law of thermodynamics and apply it to some simple systems;
- define state functions;
- relate the enthalpy of reaction to the energy change of the reaction;
- define standard states;
- discuss Hess’ law and demonstrate its use;
- define enthalpies of formation and bond energies and demonstrate their use;
- explain how the energy content in food is determined; and
- discuss how enthalpies of reaction are determined experimentally.
3.1 SOME DEFINITIONS AND CONVENTIONS

In our study of thermodynamics, we will be interested in the changes in the thermodynamic properties that accompany a process. A change is designated by the symbol “Δ”. For example, “ΔX” means a change in the quantity X. The sign of ΔX indicates the direction of the change because ΔX ≡ X_{\text{final}} - X_{\text{initial}}. Consequently, ΔE = 50 J means that the final energy is 50 J greater than the initial energy (i.e., the energy increased by 50 J). Similarly, ΔE = -50 J means that the energy of the final state is 50 J lower than the initial state or that the energy decreased by 50 J.

Indicating that the energy changed by 50 J means little without knowledge of what it is that experienced the change. Consequently, an important part of any thermodynamic problem is precisely defining the system, the reference object or process. Everything that interacts with the system is known as the surroundings. Together, the system and its surroundings comprise the thermodynamic universe; that is, thermodynamic universe = system + surroundings. Thus, we can write ΔE_{\text{univ}} = ΔE + ΔE_{\text{sur}}. Note that subscripts are used to specify changes in the universe and the surroundings, but none are used for the system. Thus, ΔE = -50 J implies that the energy of the system dropped by 50 J, while ΔE_{\text{sur}} = +50 J means that the energy of the surroundings increased by 50 J.

Let’s apply these ideas to a cash flow problem in which you write a check to a friend for $50. The first step in “setting up the books” is to define the system, which is taken as your account. Only your friend’s account interacts with (accepts money from) the system, so it can be thought of as the surroundings. If ΔB is the change in the balance of your account (the system), then ΔB = -$50 because money transferred out of the system, which caused your balance to decrease by $50. Similarly, ΔB_{\text{sur}} = +$50 because money transferred into the surroundings, which increased the balance in your friend’s account by $50. Money was conserved in the process because money was neither created nor destroyed, ΔB_{\text{univ}} = ΔB + ΔB_{\text{sur}} = -50 + 50 = 0. Money was simply transferred from the system to the surroundings. Note that, ΔB = +$50 if the system is defined as your friend's account, and, if both accounts are in the same bank, ΔB = 0 if the bank is the system. Consequently, it is very important to clearly define the system in any process.

3.2 WORK, HEAT, AND ENERGY

Work is a force through a distance and is represented by the symbol w. As shown in Figure 3.1, the sign of w simply indicates whether the work was done on or by the system.

\[ w = \text{work done on the system} \quad -w = \text{work done by the system} \]

Figure 3.1 Work and the sign of w

As the large mass M drops, its potential energy decreases. Part of the lost potential energy is used to do work as the smaller mass m is lifted. If mass m is the system, \( w > 0 \) as work is done on it, but if mass M is the system, \( w < 0 \) as work is done by it.
Thus, \( w = +50 \text{ J} \) is read ‘50 joules of work was done on the system’. However, a minus sign is not read explicitly, rather it is indicated by the use of the word by. Consequently, \( w = -50 \text{ J} \) is usually read as ‘50 joules of work was done by the system.’

Heat is that form of energy that is transferred as a result of temperature differences and is represented by the symbol \( q \). The sign of \( q \) indicates the direction of the heat flow.

\[ q = \text{heat absorbed by the system} \quad -q = \text{heat given off by the system} \]

Thus, \( q = +50 \text{ J} \) is read ‘50 J of heat was absorbed by the system.’ Once again, a minus sign is not read explicitly, and \( q = -50 \text{ J} \) is read ‘50 J of heat was given off by the system.’ When \( q > 0 \), heat enters the system, and the process is said to be endothermic. Endothermic processes increase the energy of the system (Figure 3.2a). When \( q < 0 \), heat exits the system, and the process is said to be exothermic. Exothermic processes reduce the energy of the system (Figure 3.2b).

When heat is added to a chemical system, it usually results in either a temperature rise or a phase change (vaporization, sublimation, or melting). If the \textit{heat results only in a temperature rise}, then the amount of heat absorbed by a system is proportional to the temperature change it undergoes. The proportionality constant is called the \textit{heat capacity}, \( C \), of the system. Equation 3.1 is used to determine the amount of heat transferred when the temperature of a system with a heat capacity \( C \) changes by \( \Delta T \) degrees.

\[ q = C\Delta T \quad \text{Eq. 3.1} \]

In Equation 3.1, the temperature change \( \Delta T \) ( \( T_{\text{final}} - T_{\text{initial}} \) ) has the same numerical value in either Celsius or Kelvin, and the most common units for the heat capacity are J·°C\(^{-1}\). The heat capacity depends not only on the substance but on its mass as well. Water does not have a unique heat capacity but a specified mass of water does. For example, the heat capacity of 12 g of water is 50 J·°C\(^{-1}\). Tabulated values are usually given for the heat capacities of one gram of material. This quantity is called the \textit{specific heat}, \( s \). Specific heats are normally given in J·g\(^{-1}·°C\(^{-1}\). Table 3.1 shows the specific heats of several substances. A high specific heat implies that the substance can absorb a substantial amount of heat with a relatively small temperature rise. Heat capacity \( (C) \) is related to the specific heat \( (s) \) and mass \( (m) \) of the sample by Equation 3.2.

\[ C = ms \quad \text{Eq. 3.2} \]

The \textit{molar heat capacity}, \( \bar{C} \), is the heat capacity of a mole of substance and has units of J·mol\(^{-1}·°C\(^{-1}\).
**Example 3.1**

How much heat is required to heat 17 g of ice from -12 °C to 0 °C? The specific heat of ice is 2.0 J·g⁻¹·°C⁻¹.

Combining Equations 3.1 and 3.2 we can write

\[ q = ms\Delta T \]

where \( \Delta T = T_{\text{final}} - T_{\text{initial}} = 0 - (-12) = +12 \, ^\circ\text{C}, \) so

\[ q = (17 \, \text{g})(2.0 \, \text{J} \cdot \text{g}^{-1} \cdot \text{°C}^{-1})(12 \, \text{°C}) = +4.1 \times 10^2 \, \text{J} = 0.41 \, \text{kJ} \]

If 0.41 kJ of heat is added to 17 g of ice at -12 °C, the ice would warm to 0 °C, but more heat would be required to melt it.

**Energy** is the capacity to do work or to transfer heat. It can take the form of either kinetic or potential energy. **Kinetic energy (KE)** is energy of motion. Any particle that is moving has the capacity to do work or to transfer heat. For example, the kinetic energy of a moving truck has the capacity to do work by simply colliding with another object and moving the object through a distance. It also has the capacity to transfer heat through the brake drums and tires when the brakes are applied. Recall that one of the postulates of the kinetic molecular theory of gases is that temperature is a measure of the average kinetic energy of the molecules. Thus, increasing the temperature of a system increases the kinetic energy (speed) of the particles in the system.

**Potential energy** is energy of position. A truck parked at the top of a hill has potential energy due to its position. It has no kinetic energy when it is parked, but when the brake is released, it begins to move as its potential energy is converted into kinetic energy. The truck rolls downhill because doing so reduces its potential energy. Similarly, chemical bonds form because the potential energy of the bound atoms is lower than the potential energy of the separated atoms. Molecules like trinitrotoluene (TNT), sugar, and octane (a component of gasoline) release energy when they react with oxygen because the potential energy of the bonds they form is lower than the potential energy of the original bonds. Gases also condense to liquids because the potential energy of the molecules is lower in the liquid (intermolecular interactions) than in the gas (no interactions).

**PRACTICE EXAMPLE 3.1**

A person lifts a 70 kg mass to a height of 2.0 m. The effort requires 1.4 kJ of work.

If the person is the system, \( w = \_ \_ \_ \_ \_ \_ \_ \_ \_ \).  
If the mass is the system, \( w = \_ \_ \_ \_ \_ \_ \_ \_ \).  

Fill in the following blanks with on or by.  
1.4 kJ of work was done \_ \_ \_ \_ \_ \_ the person, and 1.4 kJ of work was done \_ \_ \_ \_ \_ \_ the mass.

A piece of metal is placed into hot water. 120 J of heat is transferred from the water to the metal.

If the metal is the system, \( q = \_ \_ \_ \_ \_ \_ \_ \_ \_ \) and the process is said to be \_ \_ \_ \_ \_ \_ \_ \_ \_ thermic.  
If the water is the system, \( q = \_ \_ \_ \_ \_ \_ \_ \_ \_ \) and the process is said to be \_ \_ \_ \_ \_ \_ \_ \_ \_ thermic.  

Fill in the following blanks with absorbed or given off. 
120 J of heat were \_ \_ \_ \_ \_ \_ \_ \_ \_ \_ \_ \_ \_ \_ \_ \_ by the metal and 
120 J of heat were \_ \_ \_ \_ \_ \_ \_ \_ \_ \_ \_ \_ \_ \_ \_ \_ by the water.
3.3 THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics states that energy is conserved in all processes.*

\[ \Delta E_{\text{univ}} = 0 \]  
Eq. 3.3

Another common statement is that energy cannot be created or destroyed. The energy change in the universe is simply the sum of the energy changes in the system and its surroundings, so Equation 3.3 can also be expressed in the following form:

\[ \Delta E + \Delta E_{\text{sur}} = 0 \]

Solving for the energy change in the system, we arrive at Equation 3.4.

\[ \Delta E = -\Delta E_{\text{sur}} \]  
Eq. 3.4

Energy cannot be created or destroyed, but it can be transferred between a system and its surroundings (Equation 3.4). We conclude that all energy leaving a system enters the surroundings, and all energy entering a system comes from the surroundings.

Heat and work are the two most common ways of transferring energy between a system and its surroundings. The energy of a system increases when work is done on it \((w > 0)\) and/or it absorbs heat \((q > 0)\), but its energy decreases when it does work \((w < 0)\) and/or gives off heat \((q < 0)\). These relationships are summarized in Equation 3.5, which is another common expression of the first law of thermodynamics.

\[ \Delta E = q + w \]  
Eq. 3.5

Example 3.2

What energy change is experienced by a system that absorbs 358 J of heat and does 412 J of work?

The energy of a system increases when it absorbs heat, but its energy decreases when it does work, so the energy change of the system equals the heat absorbed by the system minus the work done by the system: \(\Delta E = 358 - 412 = -54\) J.

Alternatively, we can use Equation 3.5. The system absorbs 358 J of heat so \(q = +358\) J. The system also does 412 J of work, so \(w = -412\) J. Thus, we obtain the following:

\[ \Delta E = q + w = 358 - 412 = -54\] J

The energy of the system drops by 54 J, which means that the energy of the surroundings increases by 54 J.

As an example of energy transfer with heat and work, consider the experiment shown in Figure 3.3: A green object of mass \(M\) falls a distance \(d\) from a table to the floor while...
lifting a smaller red object with mass $m$. We assume that all of the kinetic energy of mass $M$ is converted into heat when it strikes the floor.* We divide the surroundings into a thermal and mechanical components. The thermal surroundings exchange energy with a system in the form of heat. The floor is the thermal surroundings in Figure 3.3. The faster the system (mass $M$) hits the floor, the greater is the amount of energy that is transferred to the thermal surroundings. The mechanical surroundings exchange energy with a system in the form of work. The red mass $m$ is the mechanical surroundings in Figure 3.3. The amount of energy transferred to the mechanical surroundings increases as $m$ increases.

Consider the how energy transfer varies as a function of the smaller mass $m$ when mass $M$ falls a distance $d$ as shown in Figure 3.3. We assume that $\Delta E = -100$ J for the fall.

- If $m = 0$ (no smaller mass), no work is done ($w = 0$) and the entire 100 J is transferred to the thermal surroundings, $\Delta E = q = -100$ J.
- If $m$ is such that the system must do 70 J of work to lift the smaller mass ($w = -70$ J), then only 30 J can be transferred to the thermal surroundings: $q = \Delta E - w = -100 - (-70) = -30$ J.
- If $m = M$, all of the energy change would be transferred to the mechanical surroundings ($\Delta E = w = -100$ J) leaving none to transfer to the thermal surroundings. No work could actually be done because a system cannot move without kinetic energy. This system is at equilibrium.

In the above experiments, we examined the transition between the same initial and final states by three different thermodynamic paths that differed in their distributions of $q$ and $w$. $\Delta E$ was the same for each path because $\Delta E$ depends only upon the initial and final states - not on how they were achieved: $\Delta E = E_{\text{final}} - E_{\text{initial}}$. Properties, like energy, that depend only upon the state of the system are called state functions.† The fact that energy is a state function means that $\Delta E$ for a chemical process depends only upon the states of the reactants and products, not on the manner in which they react! This is an important property because it allows us to determine $\Delta E$ for a reaction using any path - even one that is unreasonable - as long as the reactants and products remain the same. Both $q$ and $w$ are path dependent, so they are not state functions. $q$ and $w$ for a reaction depend not only on the reactants and products; they also depend on how the reaction is carried out.

Almost all chemical reactions that are not insulated from their surroundings exchange energy with the thermal surroundings, but those that consume or produce gases can also exchange energy with the mechanical surroundings. We now show how to partition the energy change of such reactions into their heat and work components. We begin by expressing the ideal gas law for a mixture of gases.

$$PV = nRT$$

* The kinetic energy of the system is transferred to the molecules in the floor, which causes their temperature to rise. Cars are stopped by brakes in a similar manner as the kinetic energy of the car is converted into heat by the friction in the brake pads.

† $n$, $P$, $V$, and $T$ are also state functions. Any property whose change is denoted with a “$\Delta$” is a state function. Thus, a volume change is represented as $\Delta V$ because it depends only upon the initial and final volumes.
\( n_g \) is the total number of moles of gas in the mixture. If the mixture is a reaction mixture, then \( n_g \) may vary during the reaction as gases are either consumed or produced. However, most reactions are carried out at constant temperature and pressure, so \( P, T, \) and \( R \) are all constant. Thus, the change in the number of moles of gas requires a change in the volume, which is expressed in Equation 3.6.

\[ P \Delta V = \Delta n_g RT \quad \text{Eq. 3.6} \]

\( \Delta V \) is the volume change caused by a change in the number of moles of gas, which is determined as follows:

\[ \Delta n_g = \text{moles of gas produced} - \text{moles of gas consumed} \quad \text{Eq. 3.7} \]

**Example 3.3**

Determine \( \Delta n_g \) for each of the following processes.

- **a)** \( \text{N}_2(g) + 3 \text{H}_2(g) \rightarrow 2 \text{NH}_3(g) \)
  \[ \Delta n_g = 2 \text{ mol produced (2NH}_3) - 4 \text{ mol consumed (1N}_2 + 3 \text{H}_2) = -2 \text{ mol gas} \]

- **b)** \( \text{Cl}_2(g) + \text{H}_2(g) \rightarrow 2 \text{HCl}(g) \)
  \[ \Delta n_g = 2 \text{ mol produced (2HCl)} - 2 \text{ mol consumed (1Cl}_2 + 1 \text{H}_2) = 0 \]

- **c)** \( \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) \)
  \[ \Delta n_g = 1 \text{ mol produced - 0 mol gas consumed (reactant is a liquid)} = 1 \text{ mol gas} \]

- **d)** \( \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \)
  \[ \Delta n_g = 1 \text{ mol produced (CO}_2) - 0 \text{ mol consumed} = 1 \text{ mol gas} \]

\( \Delta n_g \), which is moles of gas-phase products – moles of gas-phase reactants, is the actual change in the number of moles of gas during the process, not necessarily the number determined from the balanced chemical equation. Thus, \( \Delta n_g = -2 \) moles as determined in Example 3.3a is the change in the number of moles of gas when 1 mol \( \text{N}_2 \) reacts with 3 mol \( \text{H}_2 \) to produce 2 mol \( \text{NH}_3 \). The fact that it is negative means that gas is consumed during the reaction. \( \Delta n_g \) for the process in which 4.0 g \( \text{H}_2 \) react would be determined as follows:

\[ \Delta n_g = 4.0 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.0 \text{ g H}_2} \times \frac{-2 \text{ mol gas change}}{3 \text{ mol H}_2 \text{ reacting}} = -1.3 \text{ mol gas change} \]

We next consider the transfer of energy between a reaction and its surroundings by examining the combustion of propane carried out at constant temperature and pressure.* Conditions of constant temperature and pressure are so common in chemical reactions that we restrict our discussions in this and the next chapter to the thermodynamics of systems at these conditions.
inside of a cylinder and piston (Figure 3.4). The reaction is

\[
\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})
\]

\[\Delta n_g = +1 \text{ mol} \quad (7 \text{ mol gas produced} - 6 \text{ mol gas consumed}), \] so one mole of gas is created during the reaction of one mole of propane. The reaction temperature is high enough to assure that the water is a gas. We make two observations during the reaction: 1) the reaction vessel gets very hot,* and 2) the volume of the container increases (the piston rises). The first observation indicates that the reaction is exothermic \((q < 0)\), and the second observation indicates that work is being done by the piston \((w < 0)\). Thus, the energy change of the reaction is transferred to the surroundings as both heat and work. We now focus on the work term.

The surroundings exert an opposing pressure \((P_{op})\) on the piston, which results in an opposing force \((F_{op})\) that is equal to the opposing pressure times the cross-sectional area of the piston \((A)\). The piston does work when it moves a distance \((d)\) against the opposing force.

\[
\text{work done by the piston} = (F_{op})(d) = (P_{op}A)(d) = (P_{op})(Ad)
\]

\(Ad\) is the cross-sectional area times the distance moved by the piston, which is the volume change of the gas; \(i.e., Ad = \Delta V\). The piston is being moved by the system, so

\[
\text{work done by the system} = P_{op}\Delta V
\]

We use the fact that \(w\) is the work done on (not by) the system to arrive at Equation 3.8.

\[
w = -P_{op}\Delta V \quad \text{Eq. 3.8}
\]

Equation 3.8 indicates that \(w < 0\) when \(\Delta V > 0\), which means that work is done by a system during an expansion. Similarly, work is done on a system during a compression \((\Delta V < 0)\). The reaction is run at constant temperature and pressure, so the volume change in Figure 3.4 is due to an increase in the number of moles of gas inside the cylinder \((\Delta n_g = 1 \text{ mol gas})\), so Equation 3.6 applies. Substitution of \(\Delta n_gRT\) for P\(\Delta V\) into Equation 3.8 yields Equation 3.9, which relates the work done on the system \((w)\) as the result of changing the number of moles of gas.

\[
w = -\Delta n_gRT \quad (R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \quad \text{Eq. 3.9}
\]

Thus, work is done by a system \((w < 0)\) that produces more gas than it consumes, work is done on a system \((w > 0)\) that consumes more gas than it produces, and no work is done during reactions that do not change the number of moles of gas. In the combustion of propane given above, \(\Delta n_g = 1 \text{ mol gas}\). The positive sign of \(\Delta n_g\) means that \(w < 0\) and work is done by the gas as it pushes the piston against the opposing atmospheric pressure.

* The cylinder gets very hot during the reaction, but the reaction can still be considered at constant temperature because energy is a state function. \(\Delta E\) depends only on the initial and final states, so temperatures that are reached during the reaction are irrelevant so long as the temperatures are the same when the initial and final measurements are made.

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Example 3.4

How much work is done during the ...

a) combustion of 25.0 g of propane at 298 K?

At 298 K, the water that is produced would be a liquid not a gas.* The reaction is

\[
\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})
\]

\(\Delta n_g = 3 \text{ mol gas formed} - 6 \text{ mol gas consumed} = -3 \text{ mol gas/mole propane.}

We determine \(\Delta n_g\) for the reaction of 25 g as follows:

\[
\Delta n_g = \frac{25.0 \text{ g C}_3\text{H}_8}{44.09 \text{ g C}_3\text{H}_8} \times \frac{1 \text{ mol C}_3\text{H}_8}{1 \text{ mol C}_3\text{H}_8} = -1.70 \text{ mol gas}
\]

Next use Equation 3.9 to determine \(w\).

\[w = -\Delta n_g RT = -(1.70 \text{ mol})(8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K}) = 4.21 \times 10^3 \text{ J} = 4.21 \text{ kJ}
\]

4.21 kJ of work is done on the gases \((w > 0)\) by the atmosphere as the piston is pushed down by the atmosphere, decreasing the volume \((\Delta V < 0)\).

b) evaporation of 12 g of water at 25 °C?

\(\Delta n_g = +1 \text{ mol for the evaporation of 1 mol H}_2\text{O: H}_2\text{O}(\text{l}) \rightarrow H_2\text{O}(\text{g})\), \(\Delta n_g\) for the evaporation of 12 g of water is determined as follows:

\[
\Delta n_g = \frac{12 \text{ g H}_2\text{O}}{18 \text{ g H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol H}_2\text{O}} = 0.67 \text{ mol}
\]

Next, use Equation 3.9 to determine the work.

\[w = -\Delta n_g RT = -(0.67 \text{ mol})(8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K}) = -1.7 \times 10^3 \text{ J}
\]

1.7 kJ of work is done by 0.67 mole of escaping water molecules.

3.4 ENTHALPY

The work described in Equation 3.9 is only one part of the energy change of reaction, and we now consider the other, heat. The heat absorbed† by a reaction at constant pressure \((q_p)\) is called the enthalpy of reaction, \(\Delta H\); i.e., \(\Delta H = q_p\). The enthalpy (heat) of reaction can be related to the energy change by substituting \(\Delta H\) for \(q\) and \(-\Delta n_g RT\) for \(w\) into \(\Delta E = q + w\).

\[
\Delta E = \Delta H - \Delta n_g RT \quad \text{Eq. 3.10a}
\]

Solving for the enthalpy change, we obtain Equation 3.10b.

\[
\Delta H = \Delta E + \Delta n_g RT \quad \text{Eq. 3.10b}
\]

According to Equations 3.10a and 3.10b, \(\Delta E = \Delta H\) for reactions in which the number of

* The water would be produced as a gas due to the large amount of heat produced during the reaction, but after the reaction cooled to room temperature, the water would liquefy. Remember, it is only the initial and final conditions that matters.

† Defining enthalpy as the heat absorbed by the reaction allows us to specify the direction of the heat flow with the sign of the enthalpy change. When \(\Delta H > 0\), the reaction absorbs heat, but when \(\Delta H < 0\), the reaction releases heat.
moles of gas does not change; that is, $\Delta E = \Delta H$ for reactions in which $\Delta n_g = 0$.

Reactions are often run in sealed containers that do not undergo volume change (referred to as bombs). If there is no volume change, no work is done. The generation or consumption of gas results in a pressure change but not work. We may then substitute $q = q_V$, the heat absorbed at constant volume, and $w = 0$ into $\Delta E = q + w$ to obtain $\Delta E = q_V$.

To summarize, the enthalpy of reaction is the heat absorbed when a process is carried out at constant pressure ($\Delta H = q_p$), while the energy change is the heat absorbed when the same process is carried out at constant volume ($\Delta E = q_v$). Equation 3.10a can then be read as: the heat absorbed by a reaction carried out at constant volume ($\Delta E$) is equal to the heat absorbed when the reaction is carried out at constant pressure ($\Delta H$) plus the work done on the reaction as a result of a change in the number of moles of gas ($-\Delta n_g RT$).

**Example 3.5**

The enthalpy of vaporization of water at 25 °C is 44.0 kJ·mol$^{-1}$. What is $\Delta E$ for the vaporization of 12 g of water at 25 °C?

The thermochemical expression for the evaporation of one mole of H$_2$O at 25 °C is

$$\text{H}_2\text{O}(l, 25 \degree C) \rightarrow \text{H}_2\text{O}(g, 25 \degree C) \quad \Delta H = 44.0 \text{ kJ}$$

The amount of work done by the gas is $\Delta n_g RT = 2.5$ kJ (see Example 3.4). Applying Equation 3.10a to this process, we obtain

$$\Delta E = \Delta H - \Delta n_g RT = 44.0 - 2.5 = 41.5 \text{ kJ}$$

Thus, a mole of water vapor at 25 °C has 41.5 kJ more energy than does a mole of liquid water at 25 °C, but the vaporization of a mole of water requires 44.0 kJ of heat because 2.5 kJ is extracted by the escaping molecules doing work as they push back the atmosphere. The work done by the gases is of no use to us; it is lost. What is important is that we must supply 44.0 kJ of energy to vaporize a mole of water.

We now take into account the fact that only 0.67 mole (12 g) of water actually evaporated. Although the units of $\Delta E$ as determined above are kJ, it is implied from the balanced equation that 41.5 kJ of energy are absorbed in the evaporation of one mole of water. Consequently, we can write

$$\Delta E = (41.5 \text{ kJ·mol}^{-1})(0.67 \text{ mol}) = 28 \text{ kJ}$$

The energy of 12 g H$_2$O is 28 kJ greater in the gas phase than in the liquid phase.

**PRACTICE EXAMPLE 3.4**

$\Delta E = -244.9$ kJ for the combustion of 5.000 g of butane at 25 °C. What is $\Delta H_{\text{comb}}$ for a mole of butane?

$$\text{C}_4\text{H}_{10}(g) + \frac{13}{2} \text{O}_2(g) \rightarrow 4 \text{CO}_2(g) + 5 \text{H}_2\text{O}(l)$$

moles of butane ($M_m = 58.12$ g·mol$^{-1}$)

$n = \frac{m}{M_m} = \frac{5.000 \text{ g}}{58.12 \text{ g·mol}^{-1}} = 0.0859 \text{ mol}$

work term

$\Delta n_g = 0$

$\Delta n_g RT = 0$

$\Delta H_{\text{comb}} = \Delta E_{\text{comb}} = 0$

The remainder of this chapter is devoted to discussing ways of obtaining enthalpies of reaction and showing how they are used.
3.5 STANDARD STATES AND PROPERTIES OF ENTHALPY CHANGE

Enthalpy tables can be very useful when trying to make predictions about a reaction, but thermodynamic properties, such as enthalpy, vary with the state of the substance, its concentration if it is in solution, or its pressure if it is a gas. To assure that tabulated enthalpies are consistent, they are typically reported for processes in which the reactants and products are all in their **standard states**.

- The standard state of a pure substance is its most stable form at 1 atm pressure and the specified temperature. Unless indicated otherwise, it is assumed that solids and liquids are pure. Gases can be assumed pure even in mixtures because the molecules in the gas are far apart and have no significant effect on one another. Thus, the standard state of a gas is the gas at 1 atm pressure.

- The standard state of a dissolved substance is the substance at a concentration of 1 M at 1 atm pressure and the specified temperature.

_There is no standard temperature_, so the temperature should be specified. If no temperature is specified, then exactly 25 °C (298.15 K) should be assumed. However, 25 °C is simply the most common temperature; it is not the standard temperature. The standard state of a substance depends upon the temperature. For example, the standard state of water is a liquid at 1 atm and 25 °C, but it is a solid at 1 atm and -25 °C and a gas at 1 atm and 125 °C. A superscript zero is used to indicate that the thermodynamic property corresponds to the standard state value. Hence, \( \Delta H^\circ \) indicates the **standard enthalpy** of the process, which is the enthalpy of reaction when all reactants and products are in their standard states. All values of enthalpy given in this chapter are standard enthalpies.

A **thermochemical equation** is a chemical equation that also indicates a thermodynamic property of the reaction. Consider the thermochemical equation for the thermite reaction

\[
\text{Fe}_2\text{O}_3(s) + 2\text{Al}(s) \rightarrow \text{Al}_2\text{O}_3(s) + 2\text{Fe}(s) \quad \Delta H^\circ = -852 \text{ kJ}
\]

The value of \( \Delta H \) in the above equation indicates that 852 kJ of heat are **liberated** (\( \Delta H < 0 \)) when one mole of solid \( \text{Fe}_2\text{O}_3 \) reacts with two moles of solid \( \text{Al} \) to produce one mole of solid \( \text{Al}_2\text{O}_3 \) and two moles of solid \( \text{Fe} \). No temperature is given, so we assume a temperature of 298 K. The enthalpy change of the reaction is the standard enthalpy of reaction (as indicated by the superscript \( ^\circ \)) because all of the substances are solids, and the solid is the standard state of each at 298 K.

The units of \( \Delta H \) in a thermochemical equation are kJ, but it is important to realize that
the value applies to the reaction of the number of moles specified in the balanced equation. Some enthalpy changes are associated with the reaction of one mole of a named substance. In these cases, the enthalpy change is given in kJ·mol⁻¹ when the reaction is not written. Thus, we would say that the heat of vaporization of water is 44.0 kJ·mol⁻¹, but we write the thermochemical equation for the vaporization as

\[ \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) \quad \Delta H^\circ = 44.0 \text{ kJ} \]

That is, the per mole is not included when the reaction is written because the chemical equation shows that the 44.0 kJ corresponds to the heat absorbed when 1 mol evaporates.

**Example 3.6**

Use the thermochemical equation for the thermite reaction to determine the standard enthalpies for the following:

a) The reaction of 1.0 mol of Al with an excess of Fe₂O₃.

We recognize that \( \Delta H^\circ = -852 \text{ kJ} \) for the reaction of 2 mol Al, so we write

\[ 1 \text{ mol Al} \times \frac{-852 \text{ kJ}}{2 \text{ mol Al}} = -426 \text{ kJ} \]

Rewriting the thermochemical equation for the new quantity, we obtain

\[ \frac{1}{2} \text{Fe}_2\text{O}_3(s) + \text{Al}(s) \rightarrow \frac{1}{2} \text{Al}_2\text{O}_3(s) + \text{Fe}(s) \quad \Delta H^\circ = -426 \text{ kJ} \]

b) The reaction of 2.0 mol of Fe with an excess of Al₂O₃.

Enthalpy is a state function, so the amount of energy required to convert the products of the original reaction back to the reactants, must be the same as the energy released when the reactants were first converted to products. The thermochemical equation is

\[ \text{Al}_2\text{O}_3(s) + 2\text{Fe}(s) \rightarrow 2\text{Fe}_2\text{O}_3(s) + 2\text{Al}(s) \quad \Delta H^\circ = +852 \text{ kJ} \]

Example 3.6 demonstrates two important properties of \( \Delta H \).

1) If a reaction is multiplied by a number, so too, is the enthalpy change.

\[
\text{C}_8\text{H}_{18}(g) + \frac{25}{2} \text{O}_2(g) \rightarrow 8 \text{ CO}_2(g) + 9 \text{ H}_2\text{O}(l) \quad \Delta H^\circ = -5500 \text{ kJ} \\
2 \text{C}_8\text{H}_{18}(g) + 25 \text{O}_2(g) \rightarrow 16 \text{ CO}_2(g) + 18 \text{ H}_2\text{O}(l) \quad \Delta H^\circ = 2(-5500) = -11,100 \text{ kJ}
\]

The amount of energy released is doubled when the amount of octane is doubled.

2) If a reaction is reversed, then the sign of the enthalpy of reaction is changed.

\[ \text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H^\circ = +6 \text{ kJ} \quad \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s) \quad \Delta H^\circ = -6 \text{ kJ} \]

Thus, 6 kJ are absorbed when one mole of ice melts at its melting point, but 6 kJ are released (\( \Delta H < 0 \)) when one mole of water freezes.

* The heat or enthalpy of combustion is another important example that we will use frequently. The heat of combustion of a substance is defined as the heat absorbed when one mole of the substance reacts with oxygen at constant pressure. The statement, “The standard heat of combustion of propane is -2220 kJ·mol⁻¹ at 298K,” implies the following thermochemical equation:

\[
\text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(l) \quad \Delta H^\circ = -2220 \text{ kJ}
\]

**PRACTICE EXAMPLE 3.5**

Use the thermochemical equation for the combustion of butane from Practice Example 3.4 to determine \( \Delta H \) for the following at 298 K:

a) \( 8\text{CO}_2(g) + 10\text{H}_2\text{O}(l) \rightarrow 2\text{C}_4\text{H}_{10}(g) + 13\text{O}_2(g) \)

\[ \Delta H = \underline{\phantom{00000}} \text{ kJ} \]

b) combustion of 25.0 g of butane (\( M_m = 58.12 \text{ g mol}^{-1} \)).

\[ \Delta H = \underline{\phantom{00000}} \text{ kJ} \]
3.6 **HESS’ LAW OF HEAT SUMMATION**

Enthalpy is a state function, so the enthalpy of reaction is independent of the path used to convert the reactants into products. This means that we can choose any path, even one that is unrealistic as long as it takes the initial state (reactants) to the final state (products). This fact coupled with Hess’ law of heat summation allows us to determine enthalpies of reactions from tabulated data.

**Hess’ Law of heat summation.** If a process can be expressed as the sum of several steps, then the enthalpy change of the process is the sum of the enthalpy changes of the steps.

Example 3.7 is an application of this very useful thermodynamic law.

---

**Example 3.7**

*How much heat is required to convert 20.0 g of water at 25 °C to steam at 150 °C?*

Refer to Table 3.2 for the thermal properties of water. The overall process can be expressed as \( \text{H}_2\text{O}(l, 25 \degree \text{C}) \rightarrow \text{H}_2\text{O}(g, 150 \degree \text{C}) \), which can be broken down into three steps as shown in the heating curve in Figure 3.5 and by the following three steps:

1. **Warm the liquid to the boiling point**
   \[
   \text{H}_2\text{O}(l, 25 \degree \text{C}) \rightarrow \text{H}_2\text{O}(l, 100 \degree \text{C}) \quad \Delta H_1
   \]
   Heating the liquid increases the temperature to the boiling point.

2. **Vaporize the liquid at its boiling point**
   \[
   \text{H}_2\text{O}(l, 100 \degree \text{C}) \rightarrow \text{H}_2\text{O}(g, 100 \degree \text{C}) \quad \Delta H_2
   \]
   Heating at the boiling point vaporizes the liquid without changing its temperature.

3. **Warm the steam to 150 °C**
   \[
   \text{H}_2\text{O}(g, 100 \degree \text{C}) \rightarrow \text{H}_2\text{O}(g, 150 \degree \text{C}) \quad \Delta H_3
   \]
   Heating beyond the boiling point again results in a temperature increase.

When the three steps are summed, the boxed items cancel* and are, therefore, not included in the net reaction. Thus, the liquid at 100 °C formed in Step 1 is consumed in Step 2, and the gas at 100 °C formed in Step 2 is consumed in Step 3. Only the initial and final states do not cancel.

Addition of the three steps results in the overall reaction. Hess’ law of heat summation tells us that the enthalpy of the overall reaction is the sum of the three enthalpies:

\[
\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3
\]

We must now determine the three enthalpies.

---

* A substance can never appear as both a reactant and a product in a balanced chemical equation. Each molecule that is formed cancels one molecule that reacts. Thus, if a reaction shows 3A on the reactant side and 1A on the product side, the net equation would show (3-1)A = 2A as reactants. We will use this fact many times.
Step 1 is a 75 °C temperature rise, and the heat absorbed is determined in a manner similar to Example 3.1. Using, the specific heat of liquid water in Table 3.2, we obtain
\[ \Delta H_1 = m \cdot s \Delta T = (20.0 \text{ g})(4.18 \text{ J} \cdot \text{g}^{-1} \cdot \text{°C}^{-1})(75 \text{ °C}) = 6.3 \times 10^3 \text{ J} = 6.3 \text{ kJ} \]

Step 2 is vaporization. The heat of vaporization of water is 40.7 kJ mol\(^{-1}\) at its boiling point (Table 3.2). The molar heat of vaporization must be multiplied by the number of moles to obtain the enthalpy of the process.
\[ \Delta H_2 = 20.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} \times 40.7 \text{ kJ} \text{ mol H}_2\text{O} = 45.2 \text{ kJ} \]

Step 3 is a 50 °C temperature increase, and the heat absorbed is determined in a manner similar to Step 1. The specific heat of steam is 2.0 J g\(^{-1}\)°C\(^{-1}\) (Table 3.2).
\[ \Delta H_3 = m \cdot s \Delta T = (20.0 \text{ g})(2.0 \text{ J} \cdot \text{g}^{-1} \cdot \text{°C}^{-1})(50 \text{ °C}) = 2.0 \times 10^3 \text{ J} = 2.0 \text{ kJ} \]

We obtain the answer by summing the three contributions:
\[ \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = 6.3 + 45.2 + 2.0 = 53.5 \text{ kJ} \]

**Example 3.8**

Use the following three thermochemical reactions:

1. \( \text{C(s)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H_1 = -393.51 \text{ kJ} \)
2. \( \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H_2 = -285.83 \text{ kJ} \)
3. \( 2\text{C(s)} + 3\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{C}_2\text{H}_5\text{OH}(l) \quad \Delta H_3 = -277.69 \text{ kJ} \)

and Hess’ Law to determine the enthalpy of combustion of ethanol:
\( \text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l) \)

Our goal is to arrange the three given reactions in such a way that their sum is the combustion reaction. The combustion produces two moles of \( \text{CO}_2 \) while Reaction 1 produces only one. Reaction 1 must therefore be multiplied by two, which means that its enthalpy change must also be multiplied by two.

**Reaction A:** \( 2\text{C(s)} + 2\text{O}_2(g) \rightarrow 2\text{CO}_2(g) \quad \Delta H_A = 2\Delta H_1 = -787.02 \text{ kJ} \)

Reaction 2 must be multiplied by three to supply the required three moles of water.

**Reaction B:** \( 3\text{H}_2(g) + \frac{3}{2} \text{O}_2(g) \rightarrow 3\text{H}_2\text{O}(l) \quad \Delta H_B = 3\Delta H_2 = -857.49 \text{ kJ} \)

Reaction 3 forms one mole of ethanol, but the combustion consumes one mole, so Reaction 1 must be written in the reverse direction. When the direction of a reaction is reversed, the sign of the enthalpy change is also reversed. Thus we write,

**Reaction C:** \( \text{C}_2\text{H}_5\text{OH}(l) \rightarrow 2\text{C(s)} + 3\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \quad \Delta H_C = -\Delta H_3 = +277.69 \text{ kJ} \)
Summing Reactions A, B and C results in the desired combustion reaction:

\[
\begin{align*}
2C(s) + 2O_2(g) &\rightarrow 2CO_2(g) \\
3H_2(g) + \frac{3}{2}O_2(g) &\rightarrow 3H_2O(l) \\
C_2H_5OH(l) &\rightarrow 2C(s) + 3H_2(g) + O_2(g) \\
C_2H_5OH(l) + 3O_2(g) &\rightarrow 2CO_2(g) + 3H_2O(l)
\end{align*}
\]

Consequently, the enthalpy of combustion is the sum of the three enthalpies.

\[
\Delta H = \Delta H_A + \Delta H_B + \Delta H_C = 2\Delta H_1 + 3\Delta H_2 - \Delta H_3 = -787.02 -857.49 +277.69
\]

\[
\Delta H = -1366.82 \text{ kJ}
\]

### 3.7 ENTHALPIES (OR HEATS) OF FORMATION

Hess’ law is a valuable tool in thermodynamics, but finding a set of thermochemical reactions that sum to the desired reaction can be a formidable task. The task is simplified with the use of a series of thermochemical reactions known as formation reactions. The standard enthalpy (or heat) of formation, $$\Delta H^\circ$$, is defined as follows:

The standard heat of formation of a substance is the enthalpy change for the reaction that produces one mole of the substance from its elements in their standard states.

The enthalpies given for reactions 1, 2 and 3 in Example 3.8 are the standard enthalpies of formation of CO$_2$(g), H$_2$O(l), and C$_2$H$_5$OH(l), respectively. Heats of formation are given for substances, but it is important to realize that the heat of formation is the enthalpy change for the formation reaction. For example, the statement that the heat of formation of CO$_2$(g) is -393.51 kJ.mol$^{-1}$ implies the following thermochemical equation:

\[
C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.51 \text{ kJ}
\]

The standard state of carbon is graphite, which is represented as C(s), and the standard state of oxygen is O$_2$(g). Note that the heat of formation of any element in its standard state is zero because there is no change in the formation of an element in its standard state. Consider the formation reaction of oxygen gas, O$_2$(g) $\rightarrow$ O$_2$(g). Clearly there is no enthalpy change in a reaction with the same initial and final states. Selected standard enthalpies of formation at 25 °C can be found in Appendix B.

### PRACTICE EXAMPLE 3.6

Given the following thermochemical equations for combustion,

1) \( C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 5H_2O(l) + 4CO_2(g) \quad \Delta H_1 = -2856 \text{ kJ} \)

2) \( C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_2 = -394 \text{ kJ} \)

3) \( H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H_3 = -286 \text{ kJ} \)

determine the enthalpy change for the following reaction, which is known as the enthalpy of formation of butane:

\( 4C(s) + 5H_2 \rightarrow C_4H_{10}(g) \)

Rearrange and/or multiply each of the given chemical equations by an integer so that their sum equals the formation reaction.

Rewrite Equation 1 so that the correct number of butane molecules appear in the correct place and determine the enthalpy of reaction for the resulting equation A.

\[
\text{Eq A.} \quad \Delta H_A = \ldots \text{ kJ}
\]

Rewrite Equation 2 so that the correct number of carbon atoms appear in the correct place and determine the enthalpy of reaction for the resulting equation B.

\[
\text{Eq B.} \quad \Delta H_B = \ldots \text{ kJ}
\]

Rewrite Equation 3 so that the correct number of water molecules appear in the correct place and determine the enthalpy of reaction for the resulting equation C.

\[
\text{Eq C.} \quad \Delta H_C = \ldots \text{ kJ}
\]

Sum equations A,B, and C to obtain Equation D, which should be the formation reaction of butane, and use Hess’ Law to determine the enthalpy of formation ($$\Delta H_f$$) of butane.

\[
\text{Eq D.} \quad \Delta H_f = \ldots \text{ kJ}
\]
Example 3.9

The standard heat of formation of ammonium dichromate, \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\text{(s)}\), is \(-1807\text{ kJ.mol}^{-1}\). Write the process to which this number applies.

The heat of formation is the enthalpy change when one mole of the substance is formed. We therefore start with

\[
\rightarrow \ 1 \ (\text{NH}_4)_2\text{Cr}_2\text{O}_7\text{(s)}
\]

The coefficient of one is not normally used, but it is placed in the above for emphasis; the coefficient of the product cannot be changed. The substance is formed from its elements in their standard states. The standard states of nitrogen, hydrogen and oxygen are the diatomic gases at 1 atm pressure while that of chromium is the solid metal. The process to which the heat of formation of \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\text{(s)}\) applies is

\[
\text{N}_2\text{(g)} + 4\text{H}_2\text{(g)} + \frac{7}{2}\text{O}_2\text{(g)} + 2\text{Cr}(s) \rightarrow (\text{NH}_4)_2\text{Cr}_2\text{O}_7\text{(s)} \quad \Delta H^\circ = -1807 \text{ kJ}
\]

Multiplying the above equation by two to get rid of the fraction results in a reaction with an enthalpy equal to the heat of formation of 2\((\text{NH}_4)_2\text{Cr}_2\text{O}_7\). The reaction must be balanced using a coefficient of one for the substance whose heat of formation is being reported.

PRACTICE EXAMPLE 3.7

Write the formation reactions for the following.

a) \(\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{(s)}\)

b) \(\text{Na}_2\text{O}\text{(s)}\)

c) \(\text{NH}_3\text{(g)}\)

Tabulated standard enthalpies of formation can be used to calculate standard enthalpies of a large number of reactions by the application of Hess’ law of heat summation as demonstrated in Example 3.8. The procedure can be simplified by using the expression given in Equation 3.11.

\[
\Delta H = \sum \ c[\text{product}] \times \Delta H^\circ[\text{product}] - \sum \ c[\text{reactant}] \times \Delta H^\circ[\text{reactant}] \quad \text{Eq. 3.11}
\]

\(c[\text{product}]\) is the coefficient of the product in the balanced equation whose heat of formation is \(\Delta H^\circ[\text{product}]\). Thus, the enthalpy of any reaction can be determined as the sum of the heats of formation of the products, each multiplied by its coefficient in the balanced equation, minus the sum of the heats of formation of the reactants, each multiplied by its coefficient in the balanced equation.*

The enthalpies of formation of most compounds cannot be determined directly. As an example, consider the reaction pertaining to the heat of formation of sucrose:

\[
12 \text{C(s)} + 11 \text{H}_2\text{(g)} + \frac{11}{2}\text{O}_2\text{(g)} \rightarrow \text{C}_{12}\text{H}_{22}\text{O}_{11}\text{(s)}
\]

Under no circumstances would \(\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{(s)}\) be the sole product of the reaction of carbon, hydrogen and oxygen. Rather, a large number of compounds containing those elements would result, and the enthalpy of reaction could not be associated with any single compound. Consequently, enthalpies of formation are often determined indirectly as shown in Example 3.11 and Practice Example 3.9.

* Tabulated values of heats of formation are given in kJ.mol\(^{-1}\), but each coefficient is the number of moles of the substance in the balanced equation. Therefore, the product of the coefficient and the enthalpy of formation of the substance has units of kJ. Thus, enthalpy changes for reactions determined with Equation 3.11 have units of kJ.
Example 3.10

Determine the standard heat of combustion of C₂H₅OH using Equation 3.11.

This is the same problem done in Example 3.8. This time, however, we use Equation 3.11 instead of rearranging a series of reactions. The chemical equation for the combustion reaction is:

\[ \text{C}_2\text{H}_5\text{OH}(l) + 3\ \text{O}_2(g) \rightarrow 2\ \text{CO}_2(g) + 3\ \text{H}_2\text{O}(l) \]

We apply Equation 3.11 to the above as follows:

\[ \Delta H^\circ = 2\Delta H_f^\circ[\text{CO}_2(g)] + 3\Delta H_f^\circ[\text{H}_2\text{O}(l)] - \Delta H_f^\circ[\text{C}_2\text{H}_5\text{OH}(l)] - 3\Delta H_f^\circ[\text{O}_2(g)] \]

Inserting the tabulated values for the heats of formation, we obtain:

\[ \Delta H = 2(-393.51) + 3(-285.83) -(-277.69) -3(0) = -1366.82\ \text{kJ} \]

The above is the same value as obtained in Example 3.8. Thus, the application of Equation 3.11 is equivalent to rearranging the formation reactions so that they sum to the desired reaction; i.e., Equation 3.11 is just an application of Hess’ law.

Example 3.11

The standard enthalpy of combustion of octane (C₈H₁₈) is -5494 kJ·mol⁻¹. What is the standard enthalpy of formation of octane?

The enthalpy of combustion is the heat absorbed when one mole of a substance reacts with oxygen at constant pressure.

\[ 1\text{C}_8\text{H}_{18}(l) + 25/2\ \text{O}_2(g) \rightarrow 8\text{CO}_2(g) + 9\text{H}_2\text{O}(l) \]

Δ\(H^\circ\) = -5494 kJ

Applying Equation 3.11 to the combustion reaction we obtain:

\[ \Delta H^\circ = -5494 = 8\Delta H_f^\circ[\text{CO}_2(g)] + 9\Delta H_f^\circ[\text{H}_2\text{O}(l)] - 1\Delta H_f^\circ[\text{C}_8\text{H}_{18}(l)] - 12.5\Delta H_f^\circ[\text{O}_2(g)] \]

We next solve for the enthalpy of formation of octane.

\[ 1\Delta H_f^\circ[\text{C}_8\text{H}_{18}(l)] = 8\Delta H_f^\circ[\text{CO}_2(g)] + 9\Delta H_f^\circ[\text{H}_2\text{O}(l)] - 12.5\Delta H_f^\circ[\text{O}_2(g)] - \Delta H^\circ \]

We are given Δ\(H^\circ\) and values for the standard enthalpies of formation of CO₂, H₂O, and O₂ can be obtained from Appendix B. Consequently, the standard enthalpy of formation of octane is:

\[ 1\Delta H_f^\circ[\text{C}_8\text{H}_{18}(l)] = 8(-393.51) + 9(-285.83) - 12.5(0) -(-5494) = -227\ \text{kJ} \]

Divide by the one mole to obtain the heat of formation of octane, Δ\(H_f^\circ\) = -227 kJ·mol⁻¹. It is through reactions like combustion that most enthalpies of formation are determined.

Practice Example 3.8

Determine the heat of combustion of propane gas (C₃H₈) from tabulated heats of formation.

The chemical equation for the combustion of propane at 298 K:

\[ 1\text{C}_3\text{H}_8(l) + 5\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(l) \]

The relevant heats of formation:

\[ \Delta H_f[\text{CO}_2(g)] = -393.5 \text{kJ·mol}^{-1} \]

\[ \Delta H_f[\text{H}_2\text{O}(l)] = -285.8 \text{kJ·mol}^{-1} \]

\[ \Delta H_f[\text{C}_3\text{H}_8(g)] = -103.8 \text{kJ·mol}^{-1} \]

The heat of combustion of propane as determined from heats of formation:

\[ \Delta H_{\text{comb}} = \text{___________ kJ·mol}^{-1} \]

Practice Example 3.9

The standard heat of combustion of butane at 298 K is –2856 kJ·mol⁻¹. Use other tabulated heats of formation to determine the standard heat of formation of C₄H₁₀?

The combustion reaction is:

\[ 1\text{C}_4\text{H}_{10}(l) + 13/2\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 5\text{H}_2\text{O}(l) \]

The standard heat of combustion in terms of the heats of formations of reactants and products is

\[ \Delta H^\circ = \]

Solving for the heat of formation of butane yields

\[ \Delta H_f^\circ = \]

Inserting the known enthalpies one obtains

\[ \Delta H_f^\circ = \text{_______________ kJ·mol}^{-1} \]
3.8 BOND DISSOCIATION ENERGIES

Heats of formation offer an excellent way to determine enthalpies of reaction. However, it is quite possible that the reaction of interest may involve molecules for which heats of formation have not been reported. In these cases, bond energies can be used to approximate enthalpy changes.

The bond dissociation energy, which is also referred to as the bond energy or dissociation energy, is given the symbol D. It is the energy required to break one mole of bonds in the gas phase. Table 3.3 shows some common bond energies. Note that they are always positive because energy is always required to break bonds. The bond energy of an H-Cl bond is 431 kJ·mol⁻¹, so we can write the following:

\[
\text{HCl}(g) \rightarrow \text{H}(g) + \text{Cl}(g) \quad \Delta H^\circ = +431 \text{ kJ} = D_{\text{H-Cl}}
\]

In the preceding reaction, the HCl molecule is atomized. Atomization is the process of breaking all of the bonds in a molecule to produce the atoms, and the energy required is the enthalpy of atomization, \( \Delta H_{\text{atom}} \). Thus, the bond energy of HCl is the same as its atomization energy. The atomization energy of a large molecule is equal to the sum of the bond energies of all of the bonds in the molecule. Consequently, bond energies can be determined from enthalpies of atomization. Consider the atomization of a water molecule

\[
\text{H}_2\text{O}(g) \rightarrow 2\text{H}(g) + \text{O}(g) \quad \Delta H_{\text{atom}} = 927 \text{ kJ}
\]

Atomization requires the breaking of two O-H bonds, so the average O-H bond energy is

\[
D_{\text{O-H}} = \frac{\Delta H_{\text{atom}}}{\text{moles of bonds}} = \frac{927 \text{ kJ}}{2 \text{ mol}} = 463 \text{ kJ} \cdot \text{mol}^{-1}
\]

Enthalpies of atomization can be determined from enthalpies of formation (Example 3.12 and Practice Example 3.10).

Another path that can be used to convert the reactants to the products is to atomize the reactants and then recombine the atoms to make the products. Application of Hess’ Law of heat summation to this path produces the following valuable procedure to use in estimating heats of reactions.

\[
\Delta H \approx \sum D_{\text{broken bonds}} - \sum D_{\text{formed bonds}} \quad \text{Eq. 3.12}
\]

When using Equation 3.12 to determine the enthalpy of a reaction, you should always draw Lewis structures for the reactants and products to assure that you have the correct number and bond order of each type of bond.

Table 3.3 Bond energies of some common bonds (kJ/mol)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single bonds</td>
<td></td>
</tr>
<tr>
<td>H-H</td>
<td>436</td>
</tr>
<tr>
<td>C-H</td>
<td>413</td>
</tr>
<tr>
<td>N-H</td>
<td>391</td>
</tr>
<tr>
<td>O-H</td>
<td>463</td>
</tr>
<tr>
<td>S-H</td>
<td>347</td>
</tr>
<tr>
<td>H-F</td>
<td>565</td>
</tr>
<tr>
<td>C-F</td>
<td>485</td>
</tr>
<tr>
<td>N-F</td>
<td>272</td>
</tr>
<tr>
<td>O-F</td>
<td>190</td>
</tr>
<tr>
<td>S-F</td>
<td>327</td>
</tr>
<tr>
<td>H-Cl</td>
<td>431</td>
</tr>
<tr>
<td>C-Cl</td>
<td>328</td>
</tr>
<tr>
<td>N-Cl</td>
<td>200</td>
</tr>
<tr>
<td>O-Cl</td>
<td>203</td>
</tr>
<tr>
<td>S-Cl</td>
<td>271</td>
</tr>
<tr>
<td>H-Br</td>
<td>366</td>
</tr>
<tr>
<td>C-Br</td>
<td>276</td>
</tr>
<tr>
<td>N-Br</td>
<td>243</td>
</tr>
<tr>
<td>O-Br</td>
<td>235</td>
</tr>
<tr>
<td>S-Br</td>
<td>218</td>
</tr>
<tr>
<td>H-I</td>
<td>299</td>
</tr>
<tr>
<td>C-I</td>
<td>234</td>
</tr>
<tr>
<td>N-I</td>
<td>159</td>
</tr>
<tr>
<td>O-I</td>
<td>234</td>
</tr>
<tr>
<td>S-I</td>
<td>170</td>
</tr>
<tr>
<td>F-F</td>
<td>159</td>
</tr>
<tr>
<td>C-N</td>
<td>305</td>
</tr>
<tr>
<td>N-O</td>
<td>201</td>
</tr>
<tr>
<td>O-P</td>
<td>351</td>
</tr>
<tr>
<td>S-S</td>
<td>266</td>
</tr>
<tr>
<td>Cl-Cl</td>
<td>243</td>
</tr>
<tr>
<td>C-O</td>
<td>358</td>
</tr>
<tr>
<td>N-P</td>
<td>209</td>
</tr>
<tr>
<td>O-S</td>
<td>265</td>
</tr>
<tr>
<td>Br-Br</td>
<td>193</td>
</tr>
<tr>
<td>C-S</td>
<td>259</td>
</tr>
<tr>
<td>I-I</td>
<td>151</td>
</tr>
<tr>
<td>Multiple bonds</td>
<td></td>
</tr>
<tr>
<td>C=C</td>
<td>612</td>
</tr>
<tr>
<td>C=N</td>
<td>615</td>
</tr>
<tr>
<td>N=N</td>
<td>418</td>
</tr>
<tr>
<td>O=O</td>
<td>495</td>
</tr>
<tr>
<td>C=O</td>
<td>820</td>
</tr>
<tr>
<td>C=N</td>
<td>891</td>
</tr>
<tr>
<td>N=N</td>
<td>941</td>
</tr>
<tr>
<td>C=O</td>
<td>799</td>
</tr>
<tr>
<td>N=O</td>
<td>607</td>
</tr>
<tr>
<td>C=O</td>
<td>1072</td>
</tr>
</tbody>
</table>

† The bond energy of a bond depends upon its environment. Thus, the C-H bond energy in CHF₃ is slightly different from the one in CH₄. Consequently, Equation 3.12 is only an approximation because a tabulated bond energy is usually an average of several different examples of the bond, which may be slightly different than the bond energy in the molecule to which it is applied. In addition, bond energies are sometimes used for reactions in solution, but they apply only to gas-phase reactions.
Example 3.12

a) Use the data in Appendix B to determine the average P-Cl bond energy.

The easiest way to obtain the P-Cl bond energy is from the enthalpy of atomization of the gas-phase molecule that contains only P-Cl bonds. PCl$_3$ is a good choice, so we write its atomization equation and use Appendix B to determine its enthalpy of atomization.

$$\text{PCl}_3(g) \rightarrow \text{P}(g) + 3\text{Cl}(g)$$

$$\Delta H_{\text{atom}} = \Delta H_f[\text{P}(g)] + 3\Delta H_f[\text{Cl}(g)] - \Delta H_f[\text{PCl}_3(g)] = 316 + 3(122) - (-288) = 970 \text{ kJ}$$

Atomization of PCl$_3$ requires breaking three P-Cl bonds, so the average P-Cl bond energy in PCl$_3$ is

$$D_{\text{P-Cl}} = \frac{\Delta H_{\text{atom}}}{\text{moles of bonds}} = \frac{970 \text{ kJ}}{3 \text{ mol}} = 323 \text{ kJ mol}^{-1}$$

b) Use the results of Part a and the data in Appendix B to determine the P-O bond strength in POCl$_3$.

Start by determining the enthalpy of atomization.

$$\text{POCl}_3(g) \rightarrow \text{P}(g) + \text{O}(g) + 3\text{Cl}(g)$$

$$\Delta H_{\text{atom}} = \Delta H_f[\text{P}(g)] + \Delta H_f[\text{O}(g)] + 3\Delta H_f[\text{Cl}(g)] - \Delta H_f[\text{POCl}_3(g)]$$

$$\Delta H_{\text{atom}} = 316 + 249 + 3(122) - (-542) = 1473 \text{ kJ}$$

Atomization of POCl$_3$ requires breaking 3 P-Cl bonds and one P-O bond

$$\Delta H_{\text{atom}} = 3D_{\text{P-Cl}} + D_{\text{P-O}} = 1473 \text{ kJ}$$

The one is retained in front of $D_{\text{P-O}}$ as a reminder that the bond energy in kJ mol$^{-1}$ is multiplied by one mole to produce units of kJ. The energy of three P-Cl bonds was determined in Example 3.12, so we can solve the above for $D_{\text{P-O}}$.

$$D_{\text{P-O}} = \frac{\Delta H_{\text{atom}} - 3D_{\text{P-Cl}}}{\text{moles of bonds}} = \frac{(1473 - 970) \text{ kJ}}{1 \text{ mol}} = 503 \text{ kJ mol}^{-1}$$

Example 3.13

Use the bond energies in Table 3.3 and the fact that the heat of vaporization of water at 298 K is 44.0 kJ mol$^{-1}$ to estimate the heat of combustion of C$_4$H$_{10}$ at 298 K:

First write the balance equation for the combustion reaction at 298 K.

$$\text{C}_4\text{H}_{10}(g) + \frac{13}{2}\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 5\text{H}_2\text{O}(l)$$

Bond energies are valid only for gases, so their use will result in the value of $\Delta H$ for the reaction in which the water forms as a gas rather than a liquid.

$$\text{C}_4\text{H}_{10}(g) + \frac{13}{2}\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 5\text{H}_2\text{O}(g)$$

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Drawing Lewis structures for all substances shows that three C-C bonds, ten C-H bonds, and 6.5 O=O bonds must be broken, while eight C=O bonds and ten O-H bonds are formed. Consequently, the enthalpy of the reaction can be estimated as

$$\Delta H = 3D_{C-C} + 10D_{C-H} + 6.5D_{O=O} - 8D_{C=O} - 10D_{O-H}$$

$$\Delta H = 3(347) + 10(413) + 6.5(495) - 8(799) - 10(463) = -2634 \text{ kJ}$$

The above $\Delta H$ is for the reaction producing water gas, so we now use the heat of vaporization and Hess’ law of heat summation to obtain the desired enthalpy. We need to convert five moles of gaseous water into liquid water, so we multiply the heat of vaporization by 5, change its sign, and add it to the above reaction.

$$C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g) \quad \Delta H = -2634 \text{ kJ}$$

$$5H_2O(g) \rightarrow 5H_2O(l) \quad \Delta H = -5(44.0) = -220 \text{ kJ}$$

Summing these two reactions produces the desired result,

$$C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l) \quad \Delta H = -2634 - 220 = -2854 \text{ kJ}$$

which is within 1% of the actual heat of combustion.

### 3.9 CALORIMETRY

**Calorimetry** is the measurement of the heat flow of a process, and a schematic of a simple calorimeter is shown in Figure 3.6. The calorimeter consists of a thermally insulated container, a thermometer, and a carefully measured amount of water. The thermal insulation can range from Styrofoam™ as found in insulated cups to evacuated jackets as found in Thermos® bottles. A heat source or sink, which is often a reaction, is then placed in the calorimeter, and the temperature change of the calorimeter is measured. The entire system (reaction + calorimeter) is thermally insulated, so $q = q_{rxn} + q_{cal} = 0$, which can be rewritten as

$$q_{rxn} = -q_{cal} \quad \text{Eq. 3.13}$$

In other words, no heat enters or leaves the system; it simply flows between the reaction and the calorimeter. Because the calorimeter experiences only a temperature change, we can apply Equation 3.1 to $q_{cal}$ and obtain

$$q_{rxn} = -C_{cal}\Delta T_{cal} \quad \text{Eq. 3.14}$$

$C_{cal}$ is the heat capacity of the calorimeter, and $\Delta T_{cal}$ is the temperature change experienced by the calorimeter. However, most of the heat absorbed by the calorimeter is absorbed by the water, so it is often assumed that the calorimeter is simply the water. In this approximation, the heat capacity of the calorimeter is equal to the heat capacity of the water.
water, which is related to the specific heat and mass of the water by the following (see Equation 3.2):

$$C_{cal} \sim m_{water} s_{water}$$

Substitution of the above into Equation 3.14 yields the common approximation of the calorimetry equation.

$$q_{rxn} = -m_{water} s_{water} \Delta T_{water} \quad \text{Eq. 3.15}$$

The nature of $q_{rxn}$ depends on how the measurement is made. Remember that $\Delta E$ is the heat absorbed at constant volume ($\Delta E = q_V$) while $\Delta H$ is the heat absorbed at constant pressure ($\Delta H = q_P$). Thus, if the reaction is carried out in an open flask (at constant pressure), $q_{rxn} = q_P = \Delta H$; but, if the reaction is carried out in a bomb (at constant volume), $q_{rxn} = q_V = \Delta E$.

**Example 3.14**

9.0 g of Al at 100.0 °C are placed in 20.0 mL of water at 20.0 °C contained in a Styrofoam® cup. At thermal equilibrium, the temperature of the water/aluminum mixture is 27.1 °C. What is the specific heat of aluminum?

The process occurs in an insulated cup, so Equation 3.13 can be used. But a hot piece of aluminum, rather than a reaction, is the heat source, so we may write

$$q_{Al} = -q_{cal}$$

The heat flowing out of the aluminum flows into the calorimeter. Because both the calorimeter (water) and the aluminum involve only temperature changes, we write

$$m_{Al} s_{Al} \Delta T_{Al} = -m_{H_2O} s_{H_2O} \Delta T_{H_2O}$$

Consequently, we may express the specific heat of the aluminum as:

$$s_{Al} = -\frac{m_{H_2O} s_{H_2O} \Delta T_{H_2O}}{m_{Al} \Delta T_{Al}}$$

The aluminum experiences a temperature change of $\Delta T_{Al} = 27.1 - 100.0 = -72.9$ °C while the water undergoes a temperature change of $\Delta T_{H_2O} = 27.1 - 20.0 = +7.1$ °C. Substitution of these temperature changes, the known masses, and the specific heat of water yields the answer.

$$s_{Al} = -\frac{(20.0 \text{ g}) (4.18 \text{ J.g}^{-1}\cdot\text{oC}^{-1})(7.1 \text{ °C})}{(9.0 \text{ g})(-72.9 \text{ °C})} = 0.90 \text{ J.g}^{-1}\cdot\text{oC}^{-1}$$
Example 3.15

Combustion of 1.00 g of sucrose (C_{12}H_{22}O_{11}) causes the temperature in a bomb calorimeter with a heat capacity of 4.90 kJ·°C^{-1} to rise from 24.92 to 28.33° C.

a) What is the standard heat of combustion of sucrose?

We are given the heat capacity of the calorimeter and the temperature change, so we use Equation 3.13 to obtain \( q_{\text{rxn}} \)

\[
q_{\text{rxn}} = -C_{\text{cal}}\Delta T_{\text{cal}} = -(4.90 \text{ kJ·°C}^{-1})(28.33 - 24.92) = -16.7 \text{ kJ}
\]

This is typical of the combustion of carbohydrates, which average 17 kJ·g^{-1}. We will consider this further in the next section on foods and fuels.

The reaction is carried out in a bomb, so it is at constant volume, which means that \( q_{\text{rxn}} = \Delta E \). We next divide \( q_{\text{rxn}} \) by the number of moles of sucrose to get the molar energy change.

\[
n = \frac{1.00 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{342 \text{ g C}_{12}\text{H}_{22}\text{O}_{11}} = 0.00292 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}
\]

\[
\Delta E = \frac{-16.7 \text{ kJ}}{0.00292 \text{ mol}} = -5.71 \times 10^3 \text{ kJ·mol}^{-1}
\]

The balanced equation to which this \( \Delta E \) applies is for the combustion of one mole of sucrose or

\[
\text{C}_{12}\text{H}_{22}\text{O}_{11}(s) + 12 \text{ O}_2(g) \rightarrow 12 \text{ CO}_2(g) + 11 \text{ H}_2\text{O}(l)
\]

\( \Delta E^\circ = -5.71 \times 10^3 \text{ kJ} \)

\( \Delta n_g \) for the above reaction is \( \Delta n_g = 12 - 12 = 0 \). Therefore, \( \Delta H^\circ = \Delta E^\circ \)

The standard heat of combustion of sucrose is \( \Delta H^\circ_{\text{comb}} = -5.71 \times 10^3 \text{ kJ·mol}^{-1} \)

b) What is the standard heat of formation of sucrose?

The standard enthalpy of combustion can be expressed in terms of the standard heats of formation of the reactants and products as

\[
\Delta H^\circ = 12\Delta H^\circ_2[\text{CO}_2(g)] + 11\Delta H^\circ_2[\text{H}_2\text{O}(l)] - 1\Delta H^\circ_1[\text{C}_{12}\text{H}_{22}\text{O}_{11}(s)] - 12\Delta H^\circ_2[\text{O}_2(g)]
\]

Solving for the heat of formation of sucrose and substituting tabulated values, we obtain

\[
1\Delta H^\circ_1[\text{C}_{12}\text{H}_{22}\text{O}_{11}(s)] = -\Delta H^\circ + 12\Delta H^\circ_2[\text{CO}_2(g)] + 11\Delta H^\circ_2[\text{H}_2\text{O}(l)] - 12\Delta H^\circ_2[\text{O}_2(g)]
\]

\[
1\Delta H^\circ_1[\text{C}_{12}\text{H}_{22}\text{O}_{11}(s)] = 5.71 \times 10^3 + 12(-393.5) + 11(-285.8) -12(0) = -2.16 \times 10^3 \text{ kJ}
\]

Divide by the one mole (coefficient) to determine that the standard heat of formation of sucrose is -2.16 \times 10^3 \text{ kJ·mol}^{-1}.

PRACTICE EXAMPLE 3.12

Combustion of 6.346 mmol of liquid toluene (C_{7}H_{8}) in a bomb calorimeter with a heat capacity of 8.651 kJ·°C^{-1} resulted in a temperature rise of 2.864 °C in the calorimeter.

a) What is the heat of combustion of toluene?

Combustion Reaction:

\[
q_{\text{rxn}} = \\
\Delta E_{\text{comb}} = \\
\Delta n_g = \\
\Delta n_gRT = \\
\Delta H_{\text{comb}} = \\
\]

b) What is the heat of formation of toluene?

heat of combustion in terms of heats of formation of reactants and products:

\[
\Delta H_f = \text{___________} \text{ kJ·mol}^{-1}
\]

Solve the above for \( \Delta H_f(C_7H_8) \)
3.10 **COMBUSTION: FOOD AS FUEL**

The metabolism of carbohydrates and fats in the body also produces CO$_2$ and H$_2$O, and the energy that is derived from their metabolism is essentially the same as would be produced by their combustion in a calorimeter. As indicated in Example 3.15, a typical carbohydrate delivers about 17 kJ·g$^{-1}$ in a calorimeter. A *dietary calorie* (Cal, upper case ‘C’) is actually a kcal of energy and 1 kcal = 4.184 kJ. Thus, the combustion of a gram of carbohydrate delivers about 4 Cal. The combustion of fats produces about 38 kJ·g$^{-1}$ or 9 Cal·g$^{-1}$. The metabolism of proteins, like carbohydrates, averages about 17 kJ·g$^{-1}$ or 4 Cal·g$^{-1}$. For example, consider the following information for one serving that appears on the nutrition label of a can of soup:

<table>
<thead>
<tr>
<th>Calories</th>
<th>160</th>
<th>Calories from fat</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Fat</td>
<td>1g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Carbohydrates</td>
<td>31 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Protein</td>
<td>7 g</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Using our average energies of combustion, we would predict that a total fat of 1g would produce ~9 dietary calories, which is consistent with the 10 calories from fat listed on the can. The mass of the carbohydrates and protein is 31 + 7 = 38 g, so the energy derived from their combustion is (38 g)(4 Cal·g$^{-1}$) ~ 150 Cal. The total dietary calorie content is the sum of the 150 Cal from the protein and carbohydrates and the 10 Cal from the fat.

3.11 **CHAPTER SUMMARY AND OBJECTIVES**

The first law of thermodynamics states that energy is conserved for all processes, $\Delta E_{\text{univ}} = 0$. This means that no process can be devised that will create or destroy energy. Energy, however, can be transferred between the system and the surroundings, $\Delta E = -\Delta E_{\text{sur}}$. This is usually accomplished by a combination of heat ($q$) and work ($w$), or $\Delta E = q + w$, the energy change of the system equals the heat absorbed by it plus the work done on it. Thus, heat and work are two ways in which energy can be transferred. Heat is that form of energy that is transferred as the result of a temperature difference only. The amount of heat absorbed by a substance undergoing a temperature change only is $q = C\Delta T = ms\Delta T$ where $C$ is the system’s heat capacity, $m$ is its mass and $s$ is its specific heat.

In chemical reactions carried out at constant pressure, some of the energy change may be associated with the production or consumption of gases. However, that part of the energy is not of interest to us; it is the heat we must provide or that we can extract from the
reaction that is relevant. Thus, the enthalpy of reaction, ΔH, is defined as the heat absorbed by a reaction carried out at constant pressure. The enthalpy change of a reaction is related to the energy change of the reaction by the expression ΔE = ΔH - ΔngRT, where Δng is the change in the number of moles of gas during the reaction and ΔngRT is the work done by those gases.

The enthalpy of a reaction can be determined with the use of Hess’ law of heat summation if the thermochemical equations that sum to the desired reaction are available. The thermochemical equations most often used are those corresponding to the standard heats of formation. The standard heat of formation of a substance is the heat absorbed when one mole of the substance is formed from its elements in their standard states. The standard enthalpy of a reaction can be determined from the standard enthalpies of formation (ΔH°f) of the products and reactants as

\[ \Delta H = \sum_{\text{products}} c[\text{product}] \times \Delta H_f^\circ[\text{product}] - \sum_{\text{reactants}} c[\text{reactant}] \times \Delta H_f^\circ[\text{reactant}] \]

where \( c[\text{product}] \) is the coefficient in the chemical equation of the product that has a heat of formation of \( \Delta H_f^\circ[\text{product}] \).

Bond energies can be determined from atomization energies and used to estimate the enthalpies of gas-phase reactions by subtracting the energy that is released when the product bonds form from the energy required to break the reactant bonds.

Calorimetry is the measurement of heat flow. Since no heat enters or leaves the calorimeter, the heat of a reaction is simply transferred to or from the calorimeter, \( q_{\text{rxn}} = -q_{\text{cal}} \). Since most of the heat capacity of the calorimeter is due to the water, the calorimetry equation is often expressed as \( q_{\text{rxn}} = -m_w S_w \Delta T_w \), where "w" signifies water. If the reaction is carried out in an open container (constant pressure), \( q_{\text{rxn}} = \Delta H \), but if the reaction is carried out in a bomb calorimeter (constant volume), \( q_{\text{rxn}} = \Delta E \).

**ANSWERS TO PRACTICE EXAMPLES**

3.1 a) \( w_{\text{person}} = -1.4 \text{ kJ} \) \( w_{\text{mass}} = +1.4 \text{ kJ} \)
   b) \( q_{\text{metal}} = +120 \text{ J} \) \( q_{\text{water}} = -120 \text{ J} \)
   c) work is done by the person on the mass
   d) heat is absorbed by the metal and given off by the water

3.2 a) \( \Delta n_g = -3.5 \text{ mol} \) \( b) \Delta n_g = -0.3011 \text{ mol} \)

3.3 746 J done on gas

3.4 \( \Delta E_{\text{comb}} = -2847 \text{ kJ mol}^{-1} \) \( \Delta H_{\text{comb}} = -2856 \text{ kJ mol}^{-1} \)

3.5 a) \( \Delta H = +5712 \text{ kJ} \) \( b) \Delta H = -1229 \text{ kJ} \)

3.6 \( \Delta H_a = +2586 \text{ kJ}; \Delta H_b = -1576 \text{ kJ}; \Delta H_C = -1430 \text{ kJ} \)
   \( \Delta H_D = -150 \text{ kJ} \)

3.7 a) \( 12\text{C(s)} + 11\text{H}_2(g) + \frac{11}{2}\text{O}_2(g) \rightarrow \text{C}_12\text{H}_{22}\text{O}_{11}(s) \)
   b) \( 2\text{Na(s)} + \frac{1}{2}\text{O}_2(g) \rightarrow \text{Na}_2\text{O}(s) \)
   c) \( \frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{H}_2(g) \rightarrow \text{NH}_3(g) \)

3.8 \( \Delta H_{\text{comb}} = -2219.9 \text{ kJ mol}^{-1} \)

3.9 \( \Delta H_i = -147 \text{ kJ mol}^{-1} \)

3.10 \( D_{\text{C-H}} = 412 \text{ kJ mol}^{-1} \)

3.11 \( \Delta H_i = +8 \text{ kJ mol}^{-1} \)

3.12 \( \text{C}_7\text{H}_8(l) + 9\text{O}_2(g) \rightarrow 7\text{CO}_2(g) + 4\text{H}_2\text{O}(l) \)
   \( \Delta E_{\text{comb}} = -3905 \text{ kJ mol}^{-1} \) \( \Delta n_gRT = -4.96 \text{ kJ} \)
   \( \Delta H_{\text{comb}} = -3910 \text{ kJ mol}^{-1} \) \( \Delta H_i = 12.3 \text{ kJ mol}^{-1} \)

3.13 D C-H = 412 kJ mol\(^{-1}\)
3.14 \( \Delta H_f = 12.3 \text{ kJ mol}^{-1} \)
3.15 D C-H = 412 kJ mol\(^{-1}\)
3.16 \( \Delta H_f = 12.3 \text{ kJ mol}^{-1} \)
3.17 D C-H = 412 kJ mol\(^{-1}\)
3.18 \( \Delta H_f = 12.3 \text{ kJ mol}^{-1} \)
After studying the material presented in this chapter, you should be able to:

1. distinguish between a system, its surroundings, and the universe for a thermodynamic process (Section 3.1);
2. calculate the heat absorbed by a system given its heat capacity and temperature change (Section 3.2);
3. distinguish between heat capacity and specific heat (Section 3.2);
4. state the difference between the effects of work done on and work done by a system (Section 3.2);
5. use the expression, $\Delta E = q + w$, to determine how much of an energy flow is in the form of heat and how much is in the form of work (Section 3.3);
6. define a state function (Section 3.3);
7. calculate the amount of work associated with a change in the number of moles of gas in a reaction carried out at constant temperature and pressure (Section 3.3);
8. define the enthalpy of reaction and distinguish between it and the energy change of a reaction in terms of the heat absorbed at constant pressure or volume (Section 3.4);
9. calculate the enthalpy of reaction from the energy change of the reaction and vice versa (Section 3.4);
10. identify the standard state of a substance (Section 3.5);
11. apply Hess’ law of heat summation to determine the enthalpy of reaction (Section 3.6);
12. determine the enthalpy of reaction given the heats of formation of the reactants and products (Section 3.7);
13. determine the enthalpy of formation of one of the reactants or products of a reaction given the $\Delta H$ of the reaction and the heats of formation of all other participants in the reaction (Section 3.7);
14. determine the enthalpy of atomization of a molecule and the average bond energy of its bonds when all of the bonds are between the same pair of atoms (Section 3.8);
15. use bond energies to estimate enthalpies of gas-phase reactions (Section 3.8); and
16. calculate the heat of a reaction from the temperature change it causes in a calorimeter with known heat capacity, and decide whether the heat is an enthalpy change or a change in the energy of the system (Section 3.9).
3.12 EXERCISES

THE FIRST LAW OF THERMODYNAMICS

1. What state functions correspond to the heat absorbed at constant pressure and the heat absorbed at constant volume?

2. Many devices are constructed to convert one type of energy to another. Give an example for each of the following energy conversions:
   a) thermal → mechanical
   b) mechanical → thermal
   c) electrical → light
   d) chemical → electrical
   e) electrical → thermal
   f) chemical → thermal

3. Classify each of the following processes as endothermic or exothermic:
   a) melting a solid
   b) combustion of butane
   c) condensing a liquid
   d) photosynthesis
   e) a battery reaction

4. Can all of the potential energy of the object described in Figure 3.3 be transferred to the mechanical surroundings by its fall? Explain.

5. What is the energy change of the system if the system:
   a) absorbs 50 J of heat and does 50 J of work?
   b) releases 20 J of heat and has 415 J of work done on it?

6. What is the energy change of the system if the system:
   a) absorbs no heat and does 125 J of work?
   b) releases 180 J of heat and has 825 J of work done on it?

7. What are ΔE, ΔE_{surr} and ΔE_{univ} for a gas that gives off 312 J of heat while being compressed 862 ml by a pressure of 1.64 atm?

8. How much heat is required to heat 1.0 x 10^3 kg of aluminum from room temperature (25 °C) to its melting point (660. °C)? S_{Al} = 0.90 J·g^{-1}·°C^{-1}

9. Determine the mass of octane (C_{8}H_{18}, ΔH_{comb} = -5500. kJ·mol^{-1}) must be combusted to yield the amount of energy equivalent to:
   a) 3.1 kJ, the kinetic energy of a 220. lb linebacker running at a speed of 40. yd in 4.7 seconds.
   b) 17 J, the potential energy of a 5 lb bag of sugar on top of a 30. inch high counter.
   c) 320 kJ, the amount of heat required to raise the temperature of 1 quart of water from 25 °C to its boiling point.

10. How many joules of work must be done to inflate a balloon to a volume of 2.0 L if atmospheric pressure is 0.98 atm?

11. ΔH_{vap} = 26.7 kJ·mol^{-1} for CS_{2} at its normal boiling point (46 °C). What is ΔH for the condensation 41.2 g of CS_{2} gas to liquid at 46 °C.

12. How much heat must be supplied to 35 g of ice at -26 °C to convert it to steam at 148 °C? Specific heats: ice = 2.0 J·g^{-1}·°C^{-1}; water = 4.2 J·g^{-1}·°C^{-1}; steam = 2.0 J·g^{-1}·°C^{-1}. The molar heat of fusion of water at 273 K is ΔH_{273} = 6.01 kJ·mol^{-1}, and the molar heat of vaporization of water at 373 K is ΔH_{373} = 40.7 kJ·mol^{-1}.

13. Use the information in the preceding exercise to answer the following:
   a) What mass of ice can be melted at 0 °C by 35.0 kJ of heat?
   b) What mass of water can be vaporized at 100 °C by 35.0 kJ of heat?

14. Mercury has the following physical properties: melting point = -39 °C, boiling point = 357 °C, heat of fusion = 2.33 kJ·mol^{-1}, heat of vaporization = 284 J·g^{-1}, specific heat of liquid = 0.139 J·g^{-1}·°C^{-1}. Calculate ΔH for the conversion of 100. g of solid mercury at its freezing point to mercury vapor at its boiling point.

15. Determine ΔH, q, w, and ΔE for the evaporation of 0.10 mol CCl_{4} at 298 K and 1 atm pressure?

16. Determine ΔH, q, w, and ΔE at 298 K and 1 atm pressure for the reaction of 9.184 g of NH_{3}(g) with excess HCl(g) to produce NH_{4}Cl(s).

17. Indicate ΔH > ΔE, ΔH ~ ΔE, or ΔH < ΔE for each of the following processes:
   a) condensing steam
   b) melting ice
   c) heating a gas at constant pressure
   d) a solid decomposes into two gases at constant volume

18. The combustion of one cubic foot of natural gas produces 1000 kJ of heat. Assume 60% efficiency for the heat transfer and determine how many cubic feet of natural gas must be burned to raise the temperature of 40 gallons of water from 20.0 °C to 90.0 °C. Note: 1 gal = 3.79 L = 4 qt.
19. How much work is done on (or by) the gases in each of the following at 298 K and 1 atm? Indicate whether the work is done on or by the gas.
   a) evaporation of 0.80 g of CH₃OH
   b) decomposition of 3.2 g of CaCO₃(s) to CaO(s) and CO₂(g)
   c) reaction of 4.0 g of H₂(g) with excess N₂(g) to produce NH₄(g)
   d) reaction of 12 g of NH₃(g) with excess HCl(g) to produce NH₄Cl(s)

20. How much work is done on (or by) the gases in each of the following at 298 K and 1 atm? Indicate whether the work is done on or by the gas.
   a) the condensation of 16.0 g of water
   b) the reaction of 7.5 g Na(s) and 12.0 g Cl₂(g) to produce NaCl(s)
   c) the decomposition of 12.6 g KClO₃ into KCl(s) and O₂(g)
   d) 6.0 g of H₂(g) reacts with 4.0 g of CO₂(g) to form H₂O(g) and CO(g).

ENTHALPY AND ENTHALPIES OF FORMATION

21. Determine the enthalpy change for each of the processes in Exercise 19.
22. Determine the enthalpy change for each of the processes in Exercise 20.

23. Write the chemical equation for the reaction corresponding to the standard enthalpy of formation of N₂O₅ (g), and determine its value from the following thermochemical data:
   \[ \text{2 NO}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g) \quad \Delta H° = -114.1 \text{ kJ} \]
   \[ \text{4 NO}_2(g) + \text{O}_2(g) \rightarrow 2\text{N}_2\text{O}_3(g) \quad \Delta H° = -110.2 \text{ kJ} \]
   \[ \text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g) \quad \Delta H° = +180.5 \text{ kJ} \]

24. Given the following thermodynamic data:
   \[ \text{2 Fe(s) + } \frac{3}{2}\text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(s) \quad \Delta H° = -823 \text{ kJ} \]
   \[ \text{3 Fe(s) + 2 O}_2(g) \rightarrow \text{Fe}_3\text{O}_4(s) \quad \Delta H° = -1120. \text{ kJ} \]
Calculate the \( \Delta H° \) for: \[ 3\text{Fe}_2\text{O}_3(s) \rightarrow 2\text{Fe}_3\text{O}_4(s) + \frac{1}{2}\text{O}_2(g) \]

25. How are the heat of combustion of scandium and the heat of formation of Sc₂O₃ related?

26. Write the reaction formation for each of the following substances at 298 K. Refer to Appendix B to determine the standard states.
   a) NH₄NO₃(s)  b) CH₃I(g)  c) FeO(s)  d) Hg₂Cl₂(s)

27. Write the reaction formation for each of the following substances at 298 K. Refer to Appendix B to determine the standard states.
   a) B₂H₆(g)  b) SO₂(g)  c) PF₅(g)  d) NaCl(s)

28. Magnesium burns with a brilliant white light. How much heat is released when a 0.75 g magnesium ribbon is burned?

29. How much heat is liberated when a 1.00x10³ kg of aluminum reacts with oxygen at 25 °C and 1 atm?

30. The heat of combustion of toluene, C₇H₈(l), is -3910.3 kJ·mol⁻¹. What is the enthalpy of formation of toluene?

31. The heat of formation of OF₂(g) is 24.7 kJ/mol, that of Cl₂O(g) is 80.3 kJ/mol, and that of ClF₃(l) is -189.5 kJ·mol⁻¹.
   a) Determine the enthalpy of formation of ClF(g) given the following thermochemical equation:
   \[ 2\text{ClF}(g) + \text{O}_2(g) \rightarrow \text{Cl}_2\text{O}(g) + \text{OF}_2(g) \quad \Delta H° = 206 \text{ kJ} \]
   b) Determine the standard enthalpy change for the following reaction.
   \[ 2\text{ClIF}(l) + 2\text{O}_2(g) \rightarrow \text{Cl}_2\text{O}(g) + 3\text{OF}_2(g) \]

32. Use the data in Appendix B and the following thermochemical equation to determine the enthalpy of formation of MgCO₃(s).
   \[ \text{MgCO}_3(s) + 2\text{HCl}(g) \rightarrow \text{MgCl}_2(s) + \text{CO}_2(g) + \text{H}_2\text{O}(l) \quad \Delta H° = -24 \text{ kJ} \]

33. The reaction of quicklime (CaO) with water produces slaked lime [Ca(OH)_2]. The reaction of quicklime with water is highly exothermic:
   \[ \text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca(OH)}_2(s) \quad \Delta H = -350. \text{ kJ} \]
   a) What is the heat of reaction per gram of CaO?
   b) How much heat is released when 25.0 kg of slaked lime is produced?

34. C₂H₆ is ethane, a component of natural gas. All of the heat from the complete combustion of 8.506 mmol C₂H₆ gas at 298 K is transferred to 1.000 kg of water that is initially at 25.00 °C. Determine the final temperature of the water if the combustion is carried out at
   a) constant pressure  b) constant volume.

35. Use the data in Appendix B to determine \( \Delta H° \) of the following reactions.
   a) Pb²⁺(aq) + 2Br⁻(aq) → PbBr₂(s)
   b) NaCl(s) → Na⁺(aq) + Cl⁻(aq)
   c) CaCO₃(s) → CaO(s) + CO₂(g)
   d) NH₄Cl(s) → NH₃(g) + HCl(g)
   e) C₂H₅OH(l) + 2O₂(g) → 2CO₂(g) + 3H₂O(l)
36. Use the data in Appendix B to determine \( \Delta H^\circ \) for each of the following reactions:
   a) \( \text{Ag}_2\text{O}(s) + \text{H}_2(g) \rightarrow 2\text{Ag}(s) + \text{H}_2\text{O}(l) \)
   b) \( \text{Fe}_2\text{O}_3(s) + 3\text{CO}(g) \rightarrow 2\text{Fe}(s) + 3\text{CO}_2(g) \)
   c) \( 2\text{Ag}^{+}(aq) + \text{Pb}(s) \rightarrow 2\text{Ag}(s) + \text{Pb}^{2+}(aq) \)
   d) \( 4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(g) \)
   e) \( \text{CH}_3\text{COOH}(l) + 2\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(l) \)

37. Determine the heat liberated in the reaction of 5.0 g of Al and 20.0 g of \( \text{Fe}_2\text{O}_3 \) at 25 °C to produce Fe and \( \text{Al}_2\text{O}_3 \). The reaction, which is known as the thermite reaction, is so exothermic that it was used to weld railroad ties because the iron is produced in the molten state.

BOND ENERGIES

Use the data in Appendix B in Exercises 38-44.

38. Determine the P-H and Si-H bond energies.

39. Determine the Ti-Cl and Na-Cl bond energies.

40. What is the average O-O bond energy in \( \text{O}_2 \)? How does it compare to the O-O and O=O bond energies in Table 3.3?

41. What is the O-O bond energy in \( \text{H}_2\text{O}_2 \). What can you conclude about the O-O bond order in \( \text{H}_2\text{O}_2 \) based on its bond energy?

42. Determine N-O bond energy in \( \text{NOCl} \) (O is central atom). Based on your answer and the tabulated bond energies in Table 3.2, what is the bond order of the N-O bond in \( \text{NOCl} \)?

43. What is the N-N bond energy in \( \text{N}_2\text{O}_4 \), which is two \( \text{NO}_2 \) units bound through the N-N bond?

44. What is the C-H bond energy in \( \text{HCN} \)?

45. Use the data in Appendix B and the C-H bond energy in Table 3.3 to determine the average C-C bond energy in benzene (structure given below). How does this value compare to the average of a single bond and a double bond, the result expected from the Lewis structure? The difference is due to the fact that the pi system is delocalized that makes it more stable.

46. Use the bond energies given in Table 3.3 to estimate the enthalpy of combustion at 298 K for each of the following organic compounds. Remember that water is a liquid at 298 K.
   a) \( \text{H}_2\text{C}^{-}\text{CH}_3(g) \)
   b) \( \text{H}_2\text{C}^{-}\text{CH}_2(g) \)
   c) \( \text{HC}^{-}\text{CH}(g) \)

47. Use the data in Appendix B and the information given in Exercise 31 to determine values for the O-Cl and O-F bond energies.

48. Use bond energies to estimate the enthalpy change of each of the following gas-phase reactions:
   a) \( \text{H}_2\text{C}^{-}\text{CH}_2(g) + \text{HC}^{-}\text{N}(g) \rightarrow \text{H}_3\text{C}^{-}\text{CH}_2\text{-C}^{-}\text{N}(g) \)
   b) \( 2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g) \)
   c) \( \text{CH}_3\text{F}(g) + \text{HCl}(g) \rightarrow \text{CH}_3\text{Cl}(g) + \text{HF}(g) \)

49. Use bond energies and the data in Appendix B to estimate the enthalpies of formation of the following substances:
   a) \( \text{NF}_3(g) \)
   b) \( \text{H}_2\text{N-NH}_2(g) \)

50. Use bond energies and the data in Appendix B to estimate the enthalpies of formation of the following substances. Note that the standard state of C is graphite not a gas.
   a) \( \text{F}_2\text{C}^{-}\text{CH}_2(g) \)
   b) \( \text{CH}_3\text{Cl}(g) \)

CALORIMETRY

51. What is the final temperature of a mixture prepared by adding 12.4 g of Fe at 89.4 °C to 25.6 mL of water in an insulated container at 18.6 °C? The density of water is 1.00 g/mL and \( s_{\text{Fe}} = 0.44 \) J·g\(^{-1}\)·C\(^{-1}\).

52. What is the specific heat of tin if a mixture of 100.0 g of Cu at 10.0 °C and 200.0 g of Sn at 120.0 °C reach thermal equilibrium at a temperature of 69.0 °C? The specific heat of copper is 0.38 J·g\(^{-1}\)·oC\(^{-1}\).

53. At what temperature would thermal equilibrium be reached in a mixture prepared by adding 1.00 g of \( \text{N}_2 \) at 0 °C to 1.00 g of \( \text{Kr} \) at 200 °C in an insulated container? See Table 3.1 for specific heats.

54. A 14.6-g sample of beryllium at 96.7 °C is placed into 35.0 mL of water at 20.2 °C in an insulated container. The temperature of the water at thermal equilibrium is 32.0 °C. What is the specific heat of beryllium? Assume a density of 1.00 g·mL\(^{-1}\) for water.
55. A 35.4-g metal bar at 97.6 °C is placed into an insulated flask containing 75.0 g of ice at 0 °C. What is the specific heat of the metal if cooling the bar to 0 °C melted 2.36 g of the ice? The heat of fusion of water at 0 °C is 6.01 kJ·mol⁻¹.

56. A 0.186-mole sample of NaX is dissolved in 275 mL of water in an insulated container at 23.7 °C. After the solid dissolves, the temperature of the water is 19.2 °C. What is the heat of solution of NaX? The solution process is NaX(s) → NaX(aq).

57. 25.0 mL of 0.12 M HX(aq) at 22.0 °C and 25.0 mL of 0.12 M NaOH(aq) at 22.0 °C are mixed. After reaction, the temperature of the mixture is 27.6 °C. What is the heat of neutralization; HX(aq) + NaOH(aq) → H₂O(l) + NaX(aq)? Assume a specific heat of 4.18 J·g⁻¹·°C⁻¹ and a density of 1.00 g·mL⁻¹ for all solutions.

58. What is the heat of combustion of the sugar D-sorbose (C₆H₁₂O₆) at 298 K if combustion of 0.0187 moles of the solid caused a 6.56 °C rise in temperature in a bomb calorimeter with a heat capacity of 7.97 kJ·°C⁻¹?

59. The combustion of 0.3268 g of oleic acid, C₁₉H₃₂O₂(l), resulted in a temperature rise of 3.462 °C in a constant pressure calorimeter with a heat capacity of 3.715 kJ·°C⁻¹.
   a) What is the standard enthalpy of combustion of oleic acid at 298 K?
   b) What is the standard heat of formation of oleic acid at 298 K?

60. What is the heat capacity of a bomb calorimeter if the combustion of 2.360 mmol of salicylic acid (C₇H₆O₃(s), ΔH_{comb} = -3022 kJ·mol⁻¹) increases the temperature of the calorimeter by 2.612 °C?

61. Burning 117.7 mg of naphthalene, C₁₀H₈(s), the active ingredient in mothballs, results in a temperature rise of 3.275 °C in a bomb calorimeter with a heat capacity of 1.444 kJ·°C⁻¹.
   a) Write the balanced equation for the combustion at 25 °C.
   b) What is ΔE_{comb} of C₁₀H₈(s) in kJ·mol⁻¹?
   c) What is ΔH_{comb} of C₁₀H₈(s) at 298 K?
   d) What is ΔH_f of C₁₀H₈(s) at 298 K?

62. When 1.020 g of ethanol was burned in oxygen in a bomb calorimeter containing 2400 g of water, the temperature of the water rose from 22.46 °C to 25.52 °C. What is the enthalpy change, ΔH, for the combustion of 1 mol of ethanol? C₂H₅OH(l) + 3O₂(g) → 2CO₂(g) + 3H₂O(l)

63. Combustion of 2.000 g of propane (C₃H₈) in a bomb calorimeter produces 105.0 kJ of heat at 25 °C. What is the heat of combustion of propane?

64. ΔE_{comb} = -8942.6 kJ·mol⁻¹ for chrysene, C₁₈H₁₂(s), at 25 °C. When any hydrocarbon (such as chrysene) is burned completely, the products are CO₂ and H₂O.
   a) Write and balance a chemical equation for the combustion of chrysene and determine the value of Δn for the combustion reaction.
   b) Determine the value of ΔH per mole for the combustion of chrysene at 298 K.
   c) When 1.1492 g of chrysene, C₁₈H₁₂(s) (Mₙ = 228.29 g·mol⁻¹), was burned in a bomb calorimeter, the temperature of the water rose from 23.00 °C to 27.72 °C. What is the heat capacity of this calorimeter.

65. When 0.8681 g of cetyl palmitate (C₃₂H₆₄O(s), (Mₙ = 464.86 g·mol⁻¹) was burned in a calorimeter having a heat capacity of 9.535 kJ·°C⁻¹, the temperature rose by 3.99 °C. Calculate the standard enthalpy change per mole, ΔH° at 298 K for the combustion of cetyl palmitate.

66. The serving size listed on a bag of tortilla chips is 1 oz (28 g or ~ 6 chips), which contains 6 g or fat, 19 g of carbohydrates and 2 g of protein. What are the total number of dietary calories in one serving of chips?

67. A package of cookies from the vending machine has the following dietary information for a serving size of 6 cookies: 10 g of fat, 25 g of carbohydrates, and 6 g of protein. What are the total number of dietary calories in a serving?

68. The nutrition label on a jar of maple syrup indicates that a serving (60 mL) contains 200 Calories. Assume that all of the calories come from sugars (carbohydrates) and determine the number of grams of sugar that are in one serving of maple syrup.
MISCELLANEOUS PROBLEMS

69. Use Hess’ law of heat summation and the heats of combustion given below to determine the heat of hydrogenation of 1,3-butadiene (C_4H_6)?

\[ C_4H_6(g) + 2H_2(g) \rightarrow C_4H_{10} \quad \Delta H = ? \]

\[ \Delta H_{\text{comb}} = -2543.5 \text{ kJ mol}^{-1} \]

70. What are \( \Delta E \), \( q \), \( w \) and \( \Delta H \) for the evaporation of 10.0 g of Br_2(l) at 298 K and 1 atm?

71. Bicycle riding at 13 mph consumes 2800 kJ per hour for a 150 lb. person. How many miles must this person ride to lose 1 lb. of body fat? Hint: body fat contains 39 kJ g\(^{-1}\) of stored energy?

72. Kerosene is a mixture of organic compounds that has a density of 0.749 g/mL and a heat of combustion of -88 kJ g\(^{-1}\). Note that 1 gal = 3.79 L = 4 qt.

a) How much heat is liberated when 0.75 gal of kerosene is burned?

b) Assume that all of the heat of the combustion is transferred to the water and determine how many quarts of kerosene must be burned to take 1.0 gal of water from 25 °C to its boiling point. Give two reasons why the actual amount of heat required on a stove is much higher than the calculated value.

73. Use the following thermochemical equations:

i) \( \text{MnO}_2(s) + \text{CO(g)} \rightarrow \text{MnO(s)} + \text{CO}_2(g) \quad \Delta H^\circ = -151 \text{ kJ} \)

ii) \( \text{Mn}_3\text{O}_4(s) + \text{CO(g)} \rightarrow 3\text{MnO(s)} + \text{CO}_2(g) \quad \Delta H^\circ = -54 \text{ kJ} \)

iii) \( 3\text{Mn}_2\text{O}_3(s) + \text{CO(g)} \rightarrow 2\text{Mn}_3\text{O}_4(s) + \text{CO}_2(g) \quad \Delta H^\circ = -142 \text{ kJ} \)

To determine \( \Delta H^\circ \) for each of the following reactions:

a) \( 2\text{MnO}_2(s) + \text{CO(g)} \rightarrow 2\text{MnO}_3(s) + \text{CO}_2(g) \)

b) \( \text{Mn}_2\text{O}_4(s) + \text{CO(g)} \rightarrow 2\text{MnO(s)} + \text{CO}_2(g) \)

c) \( \text{MnO(s)} + \text{MnO}_2(s) \rightarrow \text{Mn}_2\text{O}_3(s) \)

d) \( \text{Mn}_3\text{O}_4(s) + \text{MnO(s)} \rightarrow 2\text{Mn}_2\text{O}_3(s) \)

74. Dissolving 8.65 g NH_4NO_3 in 50.0 mL water in an insulated container resulted in a temperature drop of 13.3 °C. What is the heat of solution of ammonium nitrate?

75. Ammonium nitrate is a common ingredient in fertilizers that can also be used to make explosives because it decomposes as follows:

\[ 2\text{NH}_4\text{NO}_3(s) \rightarrow 2\text{N}_2(g) + \text{O}_2(g) + 4\text{H}_2\text{O}(g) \quad \Delta H = -236 \text{ kJ} \]

The following questions deal with the decomposition of 12.0 g of NH_4NO_3.

a) How much heat is liberated under standard conditions?

b) How much work would be done by the gases at 300. °C?

c) What volume of gas would be produced at 1.00 atm and 300. °C?

76. Benzoic acid (HC_7H_5O_2, \( \Delta E_{\text{comb}} = -26.38 \text{ kJ g}^{-1} \)) is a common standard used to determine the heat capacities of bomb calorimeters. The following combustion data were collected in an experiment.

1. Combustion of 1.066 g of solid benzoic acid resulted in a rise of 2.860 °C in a bomb calorimeter.

2. Combustion of 0.7832 g of liquid toluene (C_7H_8) caused the temperature of the same bomb calorimeter to rise by 3.376 °C. Use the above data and 25 °C as the temperature of the experiment to determine the heat of formation of liquid toluene at 298 K.