**Thermodynamics** is the science of heat and temperature and, in particular, of the laws governing the conversion of thermal energy into mechanical, electrical, or other forms of energy. It is a central branch of science that has important applications in chemistry, physics, biology, and engineering. What makes thermodynamics such a powerful tool? It is a completely logical discipline and can be applied without any sophisticated mathematical techniques. The immense practical value of thermodynamics lies in the fact that it systematizes the information obtained from experiments performed on systems and enables us to draw conclusions, without further experimentation, about other aspects of the same systems and about similar aspects of other systems. It allows us to predict whether a certain reaction will proceed and what the maximum yield might be.

Thermodynamics is a macroscopic science concerning such properties as pressure, temperature, and volume. Unlike quantum mechanics, thermodynamics is not based on a specific molecular model, and therefore it is unaffected by our changing concepts of atoms and molecules. Indeed, the major foundations of thermodynamics were laid long before detailed atomic theories became available. This fact is one of its major strengths. On the negative side, equations derived from laws of thermodynamics do not provide us with a molecular interpretation of complex phenomena. Furthermore, although thermodynamics helps us predict the direction and extent of chemical reactions, it tells us nothing about the rate of a process; that issue is addressed by chemical kinetics, the topic of Chapter 9.

This chapter introduces the first law of thermodynamics and discusses some examples of thermochemistry.

### 3.1 Work and Heat

In this section, we shall study two concepts that form the basis of the first law of thermodynamics: work and heat.

**Work**

In classical mechanics, *work* is defined as force times distance. In thermodynamics, work becomes a more subtle concept; it encompasses a broader range of processes, including surface work, electrical work, work of magnetization, and so on. Let us consider a particularly useful example of a system doing work—the expansion of a gas. A sample of a gas is placed in a cylinder fitted with a weightless and frictionless piston. We assume the temperature of the system is kept constant at \( T \). The gas is
allowed to expand from its initial state—$P_1, V_1, T$—to $P_2, V_2, T$ as shown in Figure 3.1. We assume no atmospheric pressure is present, so the gas is expanding only against the weight of an object of mass $m$ placed on the piston. The work done ($w$) in lifting the mass from the initial height, $h_1$, to the final height, $h_2$, is given by

$$w = -\text{force} \times \text{distance}$$

$$= -\text{mass} \times \text{acceleration} \times \text{distance}$$

$$= -mg(h_2 - h_1)$$

$$= -mg\Delta h$$

where $g$ is the acceleration (9.81 m s$^{-2}$) due to gravity and $\Delta h = h_2 - h_1$. Because $m$ is in kilograms (kg) and $h$ in meters (m), we see that $w$ has the unit of energy (J). The minus sign in Equation 3.1 has the following meaning: in an expansion process, $h_2 > h_1$ and $w$ is negative. This notation follows the convention that when a system does work on its surroundings, the work performed is a negative quantity. In a compression process, $h_2 < h_1$, so work is done on the system, and $w$ is positive.

The external, opposing pressure, $P_{ex}$, acting on the gas is equal to force/area, so that

$$P_{ex} = \frac{mg}{A}$$

or

$$w = -P_{ex}A\Delta h = -P_{ex}(V_2 - V_1)$$

$$= -P_{ex}\Delta V$$

(3.2)

where $A$ is the area of the piston, and the product $A\Delta h$ gives the change in volume. Equation 3.2 shows that the amount of work done during expansion depends on the value of $P_{ex}$. Depending on experimental conditions, the amount of work performed by a gas during expansion from $V_1$ to $V_2$ at $T$ can vary considerably from one case to another. In one extreme, the gas is expanding against a vacuum (for example, if the mass $m$ is removed from the piston). Because $P_{ex} = 0$, the work done, $-P_{ex}\Delta V$, is also zero. A more common arrangement is to have some mass resting on the piston so that the gas is expanding against a constant external pressure. As we saw earlier, the amount of work performed by the gas in this case is $-P_{ex}\Delta V$, where $P_{ex} \neq 0$. Note that as the gas expands, the pressure of the gas, $P_{in}$, decreases constantly. For the gas to expand, however, we must have $P_{in} > P_{ex}$ at every stage of expansion. For example, if initially $P_{in} = 5 \text{ atm}$ and the gas is expanding against a constant external pressure of 1 atm ($P_{ex} = 1 \text{ atm}$) at constant temperature $T$, then the piston will finally come to a halt when $P_{in}$ decreases to exactly 1 atm.
Is it possible to have the gas perform a greater amount of work for the same increase in volume? Suppose we have an infinite number of identical weights exerting a total pressure of 5 atm on the piston. Because \( P_{in} = P_{ex} \), the system is at mechanical equilibrium. Removing one weight will decrease the external pressure by an infinitesimal amount so that \( P_{in} > P_{ex} \) and the gas will very slightly expand until \( P_{in} \) is again equal to \( P_{ex} \). When the second weight is removed, the gas expands a bit further and so on until enough weights have been lifted from the piston to decrease the external pressure to 1 atm. At this point, we have completed the expansion process as before. How do we calculate the amount of work done in this case? At every stage of expansion (that is, each time one weight is lifted), the infinitesimal amount of work done is given by \(-P_{ex} \, dV\), where \( dV \) is the infinitesimal increase in volume. The total work done in expanding from \( V_1 \) to \( V_2 \) is therefore

\[
 w = -\int_{V_1}^{V_2} P_{ex} \, dV
\]  

(3.3)

Because \( P_{ex} \) is no longer a constant value, the integral cannot be evaluated in this form. We note, however, that at every instant, \( P_{in} \) is only infinitesimally greater than \( P_{ex} \), that is,

\[
P_{in} - P_{ex} = dP
\]

so that we can rewrite Equation 3.3 as

\[
 w = -\int_{V_1}^{V_2} (P_{in} - dP) \, dV
\]

Realizing that \( dP \, dV \) is a product of two infinitesimal quantities, we have \( dP \, dV \approx 0 \), and we can write

\[
 w = -\int_{V_1}^{V_2} P_{in} \, dV
\]  

(3.4)

Equation 3.4 is a more manageable form, because \( P_{in} \) is the pressure of the system (that is, the gas), and we can express it in terms of a particular equation of state. For an ideal gas,

\[
P_{in} = \frac{nRT}{V}
\]

so that

\[
 w = -\int_{V_1}^{V_2} \frac{nRT}{V} \, dV
\]

\[
 w = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2}
\]  

(3.5)

because \( P_1 V_1 = P_2 V_2 \) (at constant \( n \) and \( T \)).

Equation 3.5 looks quite different from our earlier expression for work done \((-P_{ex} \, dV\), and in fact it represents the maximum amount of work of expansion from \( V_1 \) to \( V_2 \). The reason for this result is not difficult to see. Because work in expansion is performed against external pressure, we can maximize the work done by adjusting
the external pressure so that it is only infinitesimally smaller than the internal pressure at every stage, as described above. Under these conditions, expansion is a reversible process. By reversible, we mean that if we increase the external pressure by an infinitesimal amount, \( dP \), we can bring the expansion to a stop. A further increase in \( P_{\text{ex}} \) by \( dP \) would actually result in compression. Thus, a reversible process is one in which the system is always infinitesimally close to equilibrium.

A truly reversible process would take an infinite amount of time to complete, and therefore it can never really be done. We could set up a system so that the gas does expand very slowly and try to approach reversibility, but actually attaining it is impossible. In the laboratory, we must work with real processes that are always irreversible. The reason we are interested in a reversible process is that it enables us to calculate the maximum amount of work that could possibly be extracted from a process. This quantity is important in estimating the efficiency of chemical and biological processes, as we shall see in Chapter 4.

**Example 3.1**

A quantity of 0.850 mole of an ideal gas initially at a pressure of 15.0 atm and 300 K is allowed to expand isothermally until its final pressure is 1.00 atm. Calculate the value of the work done if the expansion is carried out (a) against a vacuum, (b) against a constant external pressure of 1.00 atm, and (c) reversibly.

**Answer**

(a) Because \( P_{\text{ex}} = 0 \), \( -P_{\text{ex}} \Delta V = 0 \), so that no work is performed in this case.

(b) Here the external, opposing pressure is 1.00 atm, so work will be done in expansion. The initial and final volumes can be obtained from the ideal gas equation:

\[
V_1 = \frac{nRT}{P_1}, \quad V_2 = \frac{nRT}{P_2}
\]

Furthermore, the final pressure of the gas is equal to the external pressure, so \( P_{\text{ex}} = P_2 \).

From Equation 3.2, we write

\[
w = -P_2(V_2 - V_1)
\]

\[
= -nRTP_2 \left( \frac{1}{P_2} - \frac{1}{P_1} \right)
\]

\[
= -19.5 \text{ L atm} = -1.98 \times 10^3 \text{ J}
\]

(c) For an isothermal, reversible process, the work done is given by Equation 3.5:

\[
w = -nRT \ln \frac{V_2}{V_1}
\]

\[
= -nRT \ln \frac{P_1}{P_2}
\]

\[
= -(0.850 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K}) \ln \frac{15}{1}
\]

\[
= -5.74 \times 10^3 \text{ J}
\]
As we can see, the reversible process produces the most work. Figure 3.2 shows graphically the work done for cases (b) and (c) in Example 3.1. In an irreversible process (Figure 3.2a), the amount of work done is given by \( P_2 \left( \frac{V_2}{V_1} \right) \), which is the area under the curve. For a reversible process, the amount of work is also given by the area under the curve (Figure 3.2b); because the external pressure is no longer held constant, however, the area is considerably greater.

From the foregoing discussion, we can draw several conclusions about work. First, work should be thought of as a mode of energy transfer. Gas expands because there is a pressure difference. When the internal and external pressure are equalized, the word *work* is no longer applicable. Second, the amount of work done depends on how the process is carried out—that is, the path (for example, reversible versus irreversible)—even though the initial and final states are the same in each case. Thus, work is not a *state function*, a property that is determined by the state of the system, and we cannot say that a system has, within itself, so much work or work content.

An important property of state functions is that when the state of a system is altered, a change in any state function depends only on the initial and final states of the system, not on how the change is accomplished. Let us assume that the change involves the expansion of a gas from an initial volume \( V_1 \) (2 L) to a final volume \( V_2 \) (4 L) at constant temperature. The change or the increase in volume is given by

\[
\Delta V = V_2 - V_1
\]

\[
= 4 \text{ L} - 2 \text{ L} = 2 \text{ L}
\]

The change can be brought about in many ways. We can let the gas expand directly from 2 L to 4 L as described above, or first allow it to expand to 6 L and then compress the volume down to 4 L, and so on. No matter how we carry out the process, the change in volume is always 2 L. Similarly, we can show that pressure and temperature, like volume, are state functions.

**Heat**

*Heat* is the transfer of energy between two bodies that are at different temperatures. Like work, heat appears only at the boundary of the system and is defined by a process. Energy is transferred from a hotter object to a colder one because there is a

Although *heat* already implies energy transfer, it is customary to speak of heat flow, heat absorbed, and heat released.
temperature difference. When the temperatures of the two objects are equal, the word heat is no longer applicable. Heat is not a property of a system and is not a state function. It is therefore path dependent. Suppose that we raise the temperature of 100.0 g of water initially at 20.0°C and 1 atm to 30.0°C and 1 atm. What is the heat transfer for this process? We do not know the answer because the process is not specified. One way to raise the temperature is to heat the water using a Bunsen burner or electrically using an immersion heater. The heat change, \( q \) (transferred from the surroundings to the system), is given by

\[
q = ms\Delta T
\]

\[
= (100.0 \text{ g})(4.184 \text{ J g}^{-1} \text{ K}^{-1})(10.0 \text{ K})
\]

\[
= 4184 \text{ J}
\]

where \( s \) is the specific heat of water. Alternatively, we can bring about the temperature increase by doing mechanical work on the system; for example, by stirring the water with a magnetic stirring bar until the desired temperature is reached as a result of friction. The heat transfer in this case is zero. Or, we could first raise the temperature of water from 20.0°C to 25.0°C by direct heating and then stir the bar to bring it up to 30.0°C. In this case, \( q \) is somewhere between zero and 4184 J. Clearly, then, an infinite number of ways are available to increase the temperature of the system by the same amount, but the heat change always depends on the path of the process.

In conclusion, work and heat are not functions of state. They are measures of energy transfer, and changes in these quantities are path dependent. The conversion factor between the thermochemical calorie and the joule, which is the mechanical equivalent of heat, is 1 cal = 4.184 J.

### 3.2 The First Law of Thermodynamics

The first law of thermodynamics states that energy can be converted from one form to another but cannot be created or destroyed. Put another way, this law says that the total energy of the universe is a constant. In general, we can divide the energy of the universe into two parts:

\[
E_{\text{univ}} = E_{\text{sys}} + E_{\text{surr}}
\]

where the subscripts denote the universe, system, and surroundings, respectively. For any given process, the changes in energies are

\[
\Delta E_{\text{univ}} = \Delta E_{\text{sys}} + \Delta E_{\text{surr}} = 0
\]

or

\[
\Delta E_{\text{sys}} = -\Delta E_{\text{surr}}
\]

Thus, if one system undergoes an energy change, \( \Delta E_{\text{sys}} \), the rest of the universe, or the surroundings, must undergo a change in energy that is equal in magnitude but opposite in sign; energy gained in one place must have been lost somewhere else. Furthermore, because energy can be changed from one form to another, the energy lost by one system can be gained by another system in a different form. For example, the energy lost by burning oil in a power plant may ultimately turn up in our homes as electrical energy, heat, light, and so on.

In chemistry, we are normally interested in the energy changes associated with
the system, not with the surroundings. We have seen that because heat and work are not state functions, it is meaningless to ask how much heat or work a system possesses. On the other hand, the internal energy of a system is a state function, because it depends only on the thermodynamic parameters of the state, such as temperature, pressure, and composition. Note that the adjective internal implies that other kinds of energy may be associated with the system. For example, the whole system may be in motion and therefore possess kinetic energy (KE). The system may also possess potential energy (PE). Thus, the total energy of the system, $E_{\text{total}}$, is given by

$$E_{\text{total}} = \text{KE} + \text{PE} + U$$

where $U$ denotes internal energy. This internal energy consists of translational, rotational, vibrational, electronic, and nuclear energies of the molecules, as well as intermolecular interactions. In most cases we shall consider, the system will be at rest, and external fields (for example, electric or magnetic fields) will not be present. Thus, both KE and PE are zero and $E_{\text{total}} = U$. As mentioned earlier, thermodynamics is not based on a particular model; therefore, we have no need to know the exact nature of $U$. In fact, we normally have no way to calculate this quantity accurately. All we are interested in, as you will see below, are methods for measuring the change in $U$ for a process. For simplicity, we shall frequently refer to internal energy simply as energy and write its change, $\Delta U$, as

$$\Delta U = U_2 - U_1$$

where $U_2$ and $U_1$ are the internal energies of the system in the final and initial states, respectively.

Energy differs from both heat and work in that it always changes by the same amount in going from one state to another, regardless of the nature of the path. Mathematically, the first law of thermodynamics can be expressed as

$$\Delta U = q + w$$

or, for an infinitesimal change,

$$dU = dq + dw$$

Equations 3.6 and 3.7 tell us that the change in the internal energy of a system in a given process is the sum of the heat exchange, $q$, between the system and its surroundings and the work done, $w$, on (or by) the system. The sign conventions for $q$ and $w$ are summarized in Table 3.1. Note that we have deliberately omitted the $\Delta$

<table>
<thead>
<tr>
<th>Table 3.1</th>
<th>Sign Conventions for Work and Heat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process</td>
<td>Sign</td>
</tr>
<tr>
<td>Work done by the system on the surroundings</td>
<td>$-$</td>
</tr>
<tr>
<td>Work done on the system by the surroundings</td>
<td>$+$</td>
</tr>
<tr>
<td>Heat absorbed by the system from the surroundings (endothermic process)</td>
<td>$+$</td>
</tr>
<tr>
<td>Heat absorbed by the surroundings from the system (exothermic process)</td>
<td>$-$</td>
</tr>
</tbody>
</table>
sign for \( q \) and \( w \), because this notation represents the difference between the final and initial states and is therefore not applicable to heat and work, which are not state functions. Similarly, although \( dU \) is an exact differential (see Appendix 1), that is, an integral of the type \( \int_{1}^{2} dU \) is independent of the path, the \( \delta \) notation reminds us that \( \delta q \) and \( \delta w \) are inexact differentials and therefore are path dependent. In this text, we shall use capital letters for thermodynamic quantities (such as \( U \), \( P \), \( T \), and \( V \)) that are state functions, and lowercase letters for thermodynamic quantities (such as \( q \) and \( w \)) that are not.

As a simple illustration of Equation 3.6, consider the heating of a gas in a closed container. Because the volume of the gas is constant, no expansion work can be done so that \( w = 0 \) and we can write

\[
\Delta U = q_V + w = q_V
\]

where the subscript \( V \) denotes that this is a constant-volume process. Thus, the increase in the energy of the gas equals the heat absorbed by the gas from the surroundings. Equation 3.8 may seem strange at first: \( \Delta U \) is equated to the heat absorbed, but heat, as we said earlier, is not a state function. However, we have restricted ourselves to a particular process or path—that is, one that takes place at constant volume; hence, \( q_V \) can have only one value under the given conditions.

**Enthalpy**

In the laboratory, most chemical and physical processes are carried out under constant pressure (that is, atmospheric pressure) rather than constant volume conditions. Consider a gas undergoing an irreversible expansion against a constant external pressure \( P \), so that \( w = -P\Delta V \). Equation 3.6 becomes

\[
\Delta U = q + w = q_P - P\Delta V
\]

or

\[
U_2 - U_1 = q_P - P(V_2 - V_1)
\]

where the subscript \( P \) reminds us that this is a constant-pressure process. Rearrangement of the equation above gives

\[
q_P = (U_2 + PV_2) - (U_1 + PV_1)
\]

We define a function, called enthalpy \( (H) \), as follows

\[
H = U + PV
\]

where \( U \), \( P \), and \( V \) are the energy, pressure, and volume of the system. All the terms in Equation 3.10 are functions of state; \( H \) has the units of energy. From Equation 3.10, we can write the change in \( H \) as

\[
\Delta H = H_2 - H_1 = (U_2 + P_2 V_2) - (U_1 + P_1 V_1)
\]

Setting \( P_2 = P_1 = P \) for a constant-pressure process, we obtain, by comparison with
Again, we have restricted the change to a specific path—this time at constant pressure—so that the heat change, \( q_P \), can be equated directly to the change in the state function, \( H \).

In general, when a system undergoes a change from state 1 to state 2, the change in enthalpy is given by

\[
\Delta H = \Delta U + \Delta (PV) = \Delta U + P \Delta V + V \Delta P + \Delta P \Delta V
\]  

(3.11)

This equation applies if neither pressure nor volume is kept constant. The last term, \( \Delta P \Delta V \), is not negligible.* Recall that both \( P \) and \( V \) in Equation 3.11 refer to the system. If the change is carried out, say, at constant pressure, and if the pressure exerted by the system on the surroundings (\( P_{\text{in}} \)) is equal to the pressure exerted by the surroundings on the system (\( P_{\text{ext}} \))—that is,

\[
P_{\text{in}} = P_{\text{ext}} = P
\]

then we have \( \Delta P = 0 \), and Equation 3.11 now becomes

\[
\Delta H = \Delta U + P \Delta V
\]  

(3.12)

Similarly, for an infinitesimal change

\[
dH = dU + P \, dV
\]  

(3.13)

A Comparison of \( \Delta U \) with \( \Delta H \)

What is the difference between \( \Delta U \) and \( \Delta H \)? Both terms represent the change in energy, but their values differ because the conditions are not the same. Consider the following situation. The heat evolved when 2 moles of sodium react with water,

\[
2\text{Na}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{NaOH}(aq) + \text{H}_2(g)
\]

is 367.5 kJ. Because the reaction takes place at constant pressure, \( q_P = \Delta H = -367.5 \text{ kJ} \). To calculate the change in internal energy, from Equation 3.12, we write

\[
\Delta U = \Delta H - P \Delta V
\]

If we assume the temperature to be 25°C and ignore the small change in the volume of solution, we can show that the volume of 1 mole of \( \text{H}_2 \) generated at 1 atm is 24.5 L, so that \( -P \Delta V = -24.5 \text{ L atm or } -2.5 \text{ kJ} \). Finally,

\[
\Delta U = -367.5 \text{ kJ} - 2.5 \text{ kJ} = -370.0 \text{ kJ}
\]

* Note that \( \Delta (PV) \), which represents the change in \( PV \) from state 1 to state 2, can be written as

\[
\Delta (PV) = [(P + \Delta P)(V + \Delta V) - PV] = P \Delta V + V \Delta P + \Delta P \Delta V.
\]

For an infinitesimal change, we would write

\[
dH = dU + P \, dV + V \, dP + dP \, dV.
\]

Because \( dP \)\( dV \) is the product of two infinitesimal quantities, we would ignore it and have

\[
dH = dU + P \, dV + V \, dP.
\]
This calculation shows that $\Delta U$ and $\Delta H$ are slightly different. The reason $\Delta H$ is smaller than $\Delta U$ in this case is that some of the internal energy released is used to do gas expansion work (the H$_2$ generated has to push the air back), so less heat is evolved. In general, the difference between $\Delta H$ and $\Delta U$ in reactions involving gases is $\Delta(PV)$ or $\Delta(nRT) = RT\Delta n$ (if $T$ is constant), where $\Delta n$ is the change in the number of moles of gases, that is,

$$\Delta n = n_{\text{products}} - n_{\text{reactants}}$$

At constant temperature we have $\Delta H = \Delta U + RT\Delta n$. For the above reaction, $\Delta n = 1$ mol. Thus, at $T = 298$ K, $RT\Delta n$ is approximately 2.5 kJ, which is a small but not negligible quantity in accurate work. On the other hand, for chemical reactions occurring in the condensed phases (liquids and solids), $\Delta V$ is usually a small number ($\leq 0.1$ L per mole of reactant converted to product) so that $P\Delta V = 0.1$ L atm, or 10 J, which can be neglected in comparison with $\Delta U$ and $\Delta H$. Thus, changes in enthalpy and energy in reactions not involving gases or in cases for which $\Delta n = 0$ are one and the same for all practical purposes.

**Example 3.2**

Compare the difference between $\Delta H$ and $\Delta U$ for the following physical changes: (a) 1 mol ice $\rightarrow$ 1 mol water at 273 K and 1 atm and (b) 1 mol water $\rightarrow$ 1 mol steam at 373 K and 1 atm. The molar volumes of ice and water at 273 K are 0.0196 L mol$^{-1}$ and 0.0180 L mol$^{-1}$, respectively, and the molar volumes of water and steam at 373 K are 0.0188 L mol$^{-1}$ and 30.61 L mol$^{-1}$, respectively.

**Answer**

Both cases are constant-pressure processes:

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + P\Delta V$$

or

$$\Delta H - \Delta U = P\Delta V$$

(a) The change in molar volume when ice melts is

$$\Delta V = V(l) - V(s)$$

$$= (0.0180 - 0.0196) \text{ L mol}^{-1}$$

$$= -0.0016 \text{ L mol}^{-1}$$

Hence,

$$P\Delta V = (1 \text{ atm})(-0.0016 \text{ L mol}^{-1})$$

$$= -0.0016 \text{ atm mol}^{-1}$$

$$= -0.16 \text{ J mol}^{-1}$$

(b) The change in molar volume when water boils is

$$\Delta V = V(g) - V(l)$$

$$= (30.61 - 0.0188) \text{ L mol}^{-1}$$

$$= 30.59 \text{ L mol}^{-1}$$
Hence,

\[ P \Delta V = (1 \text{ atm})(30.59 \text{ L mol}^{-1}) \]
\[ = 30.59 \text{ L atm mol}^{-1} \]
\[ = 3100 \text{ J mol}^{-1} \]

**COMMENT**

This example clearly shows that \((\Delta H - \Delta U)\) is negligibly small for condensed phases but can be quite appreciable if the process involves gases. Further, in (a), \(\Delta U > \Delta H\); that is, the increase in the internal energy of the system is greater than the heat absorbed by the system because when ice melts, there is a decrease in volume. Consequently, work is done on the system by the surroundings. The opposite situation holds for (b) because in this case, steam is doing work on the surroundings.

### 3.3 Heat Capacities

In this section we shall study a thermodynamic quantity, called heat capacity, that enables us to measure energy changes (\(\Delta U\) and \(\Delta H\)) of a system as a result of changes in its temperature.

When heat is added to a substance, its temperature will rise. This fact we know well. But just how much the temperature will rise depends on (1) the amount of heat delivered \((q)\), (2) the amount of the substance present \((m)\), (3) the specific heat \((s)\), which is determined by the chemical nature and physical state of the substance, and (4) the conditions under which heat is added to the substance. The temperature rise \((\Delta T)\) for a given amount of a substance is related to heat added by the equation

\[ q = ms\Delta T \]
\[ = C\Delta T \]

or

\[ C = \frac{q}{\Delta T} \]

where \(C\), a proportionality constant, is called the heat capacity. (The specific heat of a substance is the energy required to raise the temperature of 1 g of the substance by 1°C or 1 K. It has the units of J g\(^{-1}\) K\(^{-1}\). Here we have \(C = ms\), where \(m\) is in grams and hence \(C\) has the units of J K\(^{-1}\).)

Because the increase in temperature depends on the amount of substance present, it is often convenient to speak of the heat capacity of 1 mole of a substance or molar heat capacity \(\bar{C}\), where

\[ \bar{C} = \frac{C}{n} = \frac{q}{n\Delta T} \]

(3.15)

where \(n\) is the number of moles of the substance present and \(\bar{C}\) has the units of J K\(^{-1}\) mol\(^{-1}\). Note that \(C\) is an extensive property but \(\bar{C}\), like all molar quantities, is intensive.
Constant-Volume and Constant-Pressure Heat Capacities

Heat capacity is a directly measurable quantity. Knowing the amount of the substance present, the heat added, and the temperature rise, we can readily calculate $C$ using Equation 3.15. However, it turns out that the value we calculate also depends on how the heating process is carried out. Although many different conditions can be realized in practice, we shall consider only two important cases here: constant volume and constant pressure. We have already seen in Section 3.2 that for a constant-volume process, the heat absorbed by the system equals the increase in internal energy; that is, $\Delta U = q_V$. Hence the heat capacity at constant volume, $C_V$, of a given amount of substance is given by

$$C_V = \frac{q_V}{\Delta T} = \frac{\Delta U}{\Delta T}$$

or, expressed in partial derivatives (see Appendix 1)

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V$$

so that

$$dU = C_V dT$$

We have seen that for a constant-pressure process we have $\Delta H = q_P$, so that the heat capacity at constant pressure is

$$C_P = \frac{q_P}{\Delta T} = \frac{\Delta H}{\Delta T}$$

or, expressed in partial derivatives

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P$$

so that

$$dH = C_P dT$$

From the definitions of $C_V$ and $C_P$ we can calculate $\Delta U$ and $\Delta H$ for processes carried out under constant-volume or constant-pressure conditions. Integrating Equations 3.17 and 3.19 between temperatures $T_1$ and $T_2$, we obtain

$$\Delta U = \int_{T_1}^{T_2} C_V dT = C_V(T_2 - T_1) = C_V\Delta T = nC_V\Delta T$$

(3.20)

$$\Delta H = \int_{T_1}^{T_2} C_P dT = C_P(T_2 - T_1) = C_P\Delta T = nC_P\Delta T$$

(3.21)

where $n$ is the number of moles of the substance present and $C_V = nC_V$ and $C_P = nC_P$. We have assumed that both $C_V$ and $C_P$ are independent of temperature. This is not true, however. Studies of the temperature dependence of constant-pressure heat
capacity for many substances, for example, show that it can be represented by an equation $C_P = a + bT$, where $a$ and $b$ are constants for a given substance over a particular temperature range. Such an expression must be used in Equation 3.21 in accurate work. A similar equation applies to $C_V$. However, if the temperature change in a process is small, say 50 K or less, we can often treat $C_V$ and $C_P$ as if they were temperature independent.

**Molecular Interpretation of Heat Capacity**

Let us for now focus on gases, assuming ideal behavior. In Section 2.5 we saw that the translational kinetic energy of 1 mole of a gas is $\frac{1}{2}RT$; therefore, the molar heat capacity $\bar{C}_V$ is given by

$$\bar{C}_V = \left(\frac{\partial U}{\partial T}\right)_V = \left[\frac{\partial (\frac{1}{2}RT)}{\partial T}\right]_V = \frac{3}{2}R = 12.47 \text{ J K}^{-1} \text{ mol}^{-1}$$

Table 3.2 shows the measured molar heat capacities for several gases. The agreement is excellent for monatomic gases (that is, the noble gases), but considerable discrepancies are found for molecules. To see why the heat capacities are larger than 12.47 J K$^{-1}$ mol$^{-1}$ for molecules, we need to use quantum mechanics. Molecules, unlike atoms, can have rotational and vibrational motions in addition to translational motion—that is, motion through space of the whole molecule (Figure 3.3).

![Figure 3.3](image)

(a) Translational, (b) rotational, and (c) vibrational motion of a diatomic molecule, such as HCl.

According to quantum mechanics, the electronic, vibrational, and rotational energies of a molecule are quantized (further discussed in Chapters 11 and 14). That is, different molecular energy levels are associated with each type of motion, as shown in Figure 3.4. Note that the spacing between successive electronic energy levels is much

![Figure 3.4](image)

Energy levels associated with translational, rotational, vibrational, and electronic motions.
larger than that between the vibrational energy levels, which in turn is much larger than that between the rotational energy levels. The spacing between successive translational energy levels is so small that the levels practically merge into a continuum of energy. In fact, for most practical purposes, they can be treated as a continuum. Translational motion, then, is treated as a classical rather than a quantum mechanical phenomenon because its energy can vary continuously.

What do these energy levels have to do with heat capacities? When a gas sample absorbs heat from the surroundings, the energy is used to promote various kinds of motion. In this sense, the term heat capacity really means energy capacity because its value tells us the capacity of the system to store energy. Energy may be stored partly in rotational motion—the molecules may be promoted to a higher rotational energy level (that is, they will rotate faster), or it may be stored partly in vibrational motion. In each case, the molecules are promoted to higher energy levels.

Figure 3.4 suggests that it is much easier to excite a molecule to a higher rotational energy level than to a higher vibrational or electronic energy level, and this is indeed the case. Quantitatively, the ratio of the populations in any two energy levels $E_2$ and $E_1$ at temperature $T$ is given by the Boltzmann distribution law:

$$\frac{N_2}{N_1} = e^{\frac{-\Delta E}{k_B T}}$$

where $N_2$ and $N_1$ are the number of molecules in $E_2$ and $E_1$, respectively, $\Delta E = E_2 - E_1$, and $k_B$ is the Boltzmann constant ($1.381 \times 10^{-23}$ J K$^{-1}$). Equation 3.22 tells us that for a system at thermal equilibrium at a finite temperature, $N_2/N_1 < 1$, which means that the number of molecules in the upper level is always less than that in the lower level (Figure 3.5).

We can make some simple estimates using Equation 3.22. For translational motion, the spacing between adjacent energy levels $\Delta E$ is about $10^{-37}$ J, so that $\Delta E/k_B T$ at 298 K is

$$\frac{10^{-37} \text{ J}}{(1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})} = 2.4 \times 10^{-17}$$

This number is so small that the exponential term on the right-hand side of Equation 3.22 is essentially unity. Thus, the number of molecules in a higher energy level is the same as in the one below it. The physical meaning of this result is that the kinetic energy is not quantized and a molecule can absorb any arbitrary amount of energy to increase its kinetic motion.

![Figure 3.5](image-url) Qualitative illustration of the Boltzmann distribution law at some finite temperature $T$ for three different types of energy levels. Note that if the energy spacing is large compared to $k_B T$, the molecules will crowd into the lowest energy level.
With rotational motion we find that $\Delta E$ is also small compared to the $k_B T$ term; therefore, the ratio $N_2/N_1$ is close to (although smaller than) unity. This means that the molecules are distributed fairly evenly among the rotational energy levels. The difference between rotational and translational motions is that only the energies of the former are quantized.

The situation is quite different when we consider vibrational motion. Here the spacing between levels is quite large (that is, $\Delta E \gg k_B T$), so that the ratio $N_2/N_1$ is much smaller than 1. Thus, at 298 K, most of the molecules are in the lowest vibrational energy level and only a small fraction of them are in the higher levels. Finally, because the spacing between electronic energy levels is very large, almost all the molecules are found in the lowest electronic energy level at room temperature.

From this discussion, we see that at room temperature both the translational and rotational motions contribute to the heat capacity of molecules and hence the $C_V$ values are greater than 12.47 J K$^{-1}$ mol$^{-1}$. As temperature increases, vibrational motions also begin to contribute to $C_V$. Therefore, heat capacity increases with temperature. (In most cases we can ignore electronic motion’s contribution to heat capacity except at very high temperatures.)

**A Comparison of $C_V$ with $C_P$**

In general, $C_V$ and $C_P$ for a given substance are not equal to each other. The reason is that work has to be done on the surroundings in a constant-pressure process, so that more heat is required to raise the temperature by a definite amount in a constant-pressure process than in a constant-volume process. It follows, therefore, that $C_P > C_V$. This is true mainly for gases. The volume of a liquid or solid does not change appreciably with temperature, so the work done as it expands is quite small. For most purposes, therefore, $C_V$ and $C_P$ are practically the same for condensed phases.

Our next step is to see how $C_P$ differs from $C_V$ for an ideal gas. We start by writing

$$H = U + PV = U + nRT$$

For an infinitesimal change in temperature, $dT$, the change in enthalpy for a given amount of an ideal gas is

$$dH = dU + d(nRT)$$

$$= dU + nRdT$$

Substituting $dH = C_P dT$ and $dU = C_V dT$ into the above equation, we get

$$C_P dT = C_V dT + nR dT$$

$$C_P = C_V + nR$$

or

$$\bar{C}_P - \bar{C}_V = R$$

Thus, for an ideal gas, the molar constant-pressure heat capacity is greater than the molar constant-volume heat capacity by $R$, the gas constant. Appendix 2 lists the $\bar{C}_P$ values of many substances.
Example 3.3

Calculate the values of $\Delta U$ and $\Delta H$ for the heating of 55.40 g of xenon from 300 K to 400 K. Assume ideal-gas behavior and that the heat capacities at constant volume and constant pressure are independent of temperature.

**ANSWER**

Xenon is a monatomic gas. Earlier we saw that $C_V = \frac{3}{2} R = 12.47 \text{ J K}^{-1} \text{ mol}^{-1}$. Thus, from Equation 3.24, we have $C_P = \frac{5}{2} R + R = \frac{7}{2} R = 20.79 \text{ J K}^{-1} \text{ mol}^{-1}$. The quantity 55.40 g of Xe corresponds to 0.4219 mole. From Equations 3.21 and 3.22,

$$\Delta U = n C_V \Delta T = (0.4219 \text{ mol})(12.47 \text{ J K}^{-1} \text{ mol}^{-1})(400 - 300) \text{ K} = 526 \text{ J}$$

$$\Delta H = n C_P \Delta T = (0.4219 \text{ mol})(20.79 \text{ J K}^{-1} \text{ mol}^{-1})(400 - 300) \text{ K} = 877 \text{ J}$$

Example 3.4

The molar heat capacity of oxygen at constant pressure is given by $(25.7 + 0.0130T)$ J K$^{-1}$ mol$^{-1}$. Calculate the enthalpy change when 1.46 moles of O$_2$ are heated from 298 K to 367 K.

**ANSWER**

From Equation 3.21

$$\Delta H = \int_{T_1}^{T_2} n C_P dT = \int_{298 \text{ K}}^{367 \text{ K}} (1.46 \text{ mol})(25.7 + 0.0130T) \text{ J K}^{-1} \text{ mol}^{-1} dT$$

$$= (1.46 \text{ mol}) \left( 25.7T + \frac{0.0130T^2}{2} \right)_{298 \text{ K}}^{367 \text{ K}} \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 3.02 \times 10^3 \text{ J}$$

Heat Capacity and Hypothermia

Hypothermia describes the condition when the body mechanisms for producing and conserving heat are exceeded by exposure to severe cold. As warm-blooded animals, our body temperature is maintained at around 37°C. The human body is about 70 percent water by mass, and the high heat capacity of water ensures that normally there is only a slight fluctuation in body temperature. An ambient temperature of 25°C (often described as room temperature) feels warm to us because air has a small specific heat (about 1 J g$^{-1}$ °C$^{-1}$) and a low density. Consequently, little heat is lost from the body to the surrounding air. The situation is drastically different if one’s body is immersed in water at the same temperature. A rough estimate shows that for the same increase in temperature of the surrounding fluid (air or water), the heat lost by the body is nearly 3,000 times greater in the case of water. A mild case of hypo-
thermia occurs when the body temperature is reduced to 35°C, and in severe cases the body temperature may be as low as 28°C. Victims of hypothermia from mild to severe cases exhibit symptoms ranging from shivering (a way to generate heat), muscle rigidity, abnormal heart rhythms, and eventually, to death. Once the body temperature has been significantly lowered, the metabolic rate is slowed to the point that the body cannot recover without an external heat source.

The above discussion shows that hypothermia occurs much more quickly when a person falls into a frozen lake than when exposed to cold air temperature. Sometimes a child survives the trauma of hypothermia caused by immersion in ice water even after breathing has stopped for as long as 30 minutes. When the icy water is inhaled, it enters the lungs and spreads quickly through the relatively short blood stream. The chilled blood cools the brain and reduces the cells’ need for oxygen.

3.4 Gas Expansions

The expansion of a gas is a simple process to which we can apply what we have learned so far about the first law of thermodynamics. Although gas expansion does not have much chemical significance, it enables us to use some of the equations derived in previous sections to calculate changes in thermodynamic quantities. We shall assume ideal behavior and consider two special cases: isothermal expansion and adiabatic expansion.

Isothermal Expansions

An isothermal process is one in which the temperature is held constant. The work done in isothermal reversible and irreversible expansions was discussed in some detail in Section 3.1 and will not be repeated here. Instead we shall look at changes in heat, internal energy, and enthalpy during such a process.

Because temperature does not change in an isothermal process, the change in energy is zero; that is, \( \Delta U = 0 \). This follows from the fact that ideal gas molecules neither attract nor repel each other. Consequently, their total energy is independent of the distance of separation between them and therefore the volume. Mathematically, this relationship is expressed as

\[
\left( \frac{\partial U}{\partial V} \right)_T = 0
\]

This partial derivative tells us that the change in internal energy of the system with respect to volume is zero at constant temperature. For an isothermal process, then, Equation 3.6 becomes

\[ \Delta U = q + w = 0 \]

or

\[ q = -w \]

In an isothermal expansion, the heat absorbed by the gas equals the work done by the ideal gas on its surroundings. Referring to Example 3.1, we see that the heat absorbed by an ideal gas when it expands from a pressure of 15 atm to 1 atm at 300 K is zero in (a), 1980 J in (b), and 5740 J in (c). Because maximum work is performed in a reversible process, it is not surprising that the heat absorbed is greatest for (c).
Finally, we also wish to calculate the enthalpy change for such an isothermal process. Starting from
\[ \Delta H = \Delta U + \Delta(PV) \]
we have \( \Delta U = 0 \), as mentioned above, and because \( PV \) is constant at constant \( T \) and \( n \) (Boyle’s law), \( \Delta(PV) = 0 \), so that \( \Delta H = 0 \). Alternatively, we could write \( \Delta(PV) = \Delta(nRT) \). Because the temperature is unchanged and no chemical reaction occurs, both \( n \) and \( T \) are constant and \( \Delta(nRT) = 0 \); hence \( \Delta H = 0 \).

**Adiabatic Expansions**

Referring to Figure 3.1, suppose we now isolate the cylinder thermally from its surroundings so there is no heat exchange during the expansion. This means that \( q = 0 \) and the process is *adiabatic*. (The word adiabatic means no heat exchange with the surroundings.) Consequently, there will be a temperature drop and \( T \) will no longer be a constant. We consider two cases here.

**Reversible Adiabatic Expansion.** Let us first suppose that the expansion is reversible. The two questions we ask are: What is the \( P-V \) relationship for the initial and final states, and how much work is done in the expansion?

For an infinitesimal adiabatic expansion, the first law takes the form
\[
dU = dq + dw = -P \, dV = \frac{nRT}{V} dV
\]
or
\[
\frac{dU}{nT} = -R \frac{dV}{V}
\]
Note that \( dq = 0 \) and we have replaced the external, opposing pressure with the internal pressure of the gas, because it is a reversible process. Substituting \( dU = C_V \, dT \) into the above equation, we obtain
\[
\frac{C_V}{nT} dT = \bar{C}_V \frac{dT}{T} = -R \frac{dV}{V} \quad (3.25)
\]
Integration of Equation 3.25 between the initial and final states gives
\[
\int_{T_1}^{T_2} \bar{C}_V \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}
\]
\[
\bar{C}_V \ln \frac{T_2}{T_1} = R \ln \frac{V_1}{V_2}
\]
(We assume \( \bar{C}_V \) to be temperature independent.) Because \( \bar{C}_P - \bar{C}_V = R \) for an ideal gas, we write
\[
\bar{C}_V \ln \frac{T_2}{T_1} = (\bar{C}_P - \bar{C}_V) \ln \frac{V_1}{V_2}
\]
Dividing by \( \bar{C}_V \) on both sides, we get
\[
\frac{\ln T_2}{T_1} = \left( \frac{\bar{C}_p}{\bar{C}_v} - 1 \right) \ln \frac{V_1}{V_2} \\
= (\gamma - 1) \ln \frac{V_1}{V_2} = \ln \left( \frac{V_1}{V_2} \right)^{\gamma - 1}
\]

where \( \gamma \) is called the heat capacity ratio, given by

\[
\gamma = \frac{\bar{C}_p}{\bar{C}_v}
\]

For a monatomic gas, \( \bar{C}_v = \frac{3}{2} R \) and \( \bar{C}_p = \frac{5}{2} R \), so that \( \gamma = \frac{5}{3} \) or 1.67. Finally, we arrive at the following useful results:

\[
\left( \frac{V_1}{V_2} \right)^{\gamma - 1} = \frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1} \quad \left( \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \right)
\]

or

\[
\left( \frac{V_1}{V_2} \right)^{\gamma} = \frac{P_2}{P_1}
\]

Thus, for an adiabatic process, the \( P-V \) relationship becomes

\[
P_1V_1^\gamma = P_2V_2^\gamma
\]

(3.27)

It is useful to keep in mind the conditions under which this equation was derived: (1) It applies to an ideal gas, and (2) it applies to a reversible adiabatic change. Equation 3.27 differs from Boyle’s law \( (P_1V_1 = P_2V_2) \) in the exponent \( \gamma \), because temperature is not kept constant in an adiabatic expansion.

The work done in an adiabatic process is given by

\[
w = \int_{T_1}^{T_2} dU = \Delta U = \int_{T_1}^{T_2} C_v \, dT \\
= C_v(T_2 - T_1)
\]

\[
w = n\bar{C}_v(T_2 - T_1)
\]

(3.28)

where \( T_2 < T_1 \). Because the gas expands, the internal energy of the system decreases.

Appearance of the quantity \( C_v \) in Equation 3.28 may seem strange because the volume is not held constant. However, adiabatic expansion (from \( P_1, V_1, T_1 \) to \( P_2, V_2, T_2 \)) can be thought of as a two-step process, as shown in Figure 3.6. First, the

**Figure 3.6**

Because \( U \) is a state function, \( \Delta U \) is the same whether the change of a gas from \( P_1, V_1, T_1 \) to \( P_2, V_2, T_2 \) occurs directly or indirectly.
gas is isothermally expanded from $P_1 V_1$ to $P'_2 V_2$ at $T_1$. Because the temperature is constant, $\Delta U = 0$. Next the gas is cooled at constant volume from $T_1$ to $T_2$ and its pressure drops from $P'_2$ to $P_2$. In this case, $\Delta U = nC_v(T_2 - T_1)$, which is Equation 3.28. The fact that $U$ is a state function enables us to analyze the process by employing a different path.

<table>
<thead>
<tr>
<th>Example 3.5</th>
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A quantity of 0.850 mole of a monatomic ideal gas initially at a pressure of 15.0 atm and 300 K is allowed to expand until its final pressure is 1.00 atm (see Example 3.1). Calculate the work done if the expansion is carried out adiabatically and reversibly.

**ANSWER**

Our first task is to calculate the final temperature, $T_2$. This is done in three steps. First, we need to evaluate $V_1$, given by $V_1 = nRT_1/P_1$.

$$V_1 = \frac{(0.850 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{15.0 \text{ atm}} = 1.40 \text{ L}$$

Next, we calculate the value of $V_2$ using the following relation:

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$V_2 = \left(\frac{P_1}{P_2}\right)^{\gamma/\gamma} V_1 = \left(\frac{15.0}{1.00}\right)^{\gamma/\gamma} (1.40 \text{ L}) = 7.1 \text{ L}$$

Finally, we have $P_2 V_2 = nRT_2$, or

$$T_2 = \frac{P_2 V_2}{nR} = \frac{(1.00 \text{ atm})(7.1 \text{ L})}{(0.850 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})} = 102 \text{ K}$$

Hence,

$$\Delta U = w = nC_v(T_2 - T_1) = (0.850 \text{ mol})(12.47 \text{ J K}^{-1} \text{ mol}^{-1})(102 - 300) \text{ K} = -2.1 \times 10^3 \text{ J}$$

This comparison shows that not all reversible processes do the same amount of work.

Examples 3.1 and 3.5 show that less work is performed in a reversible adiabatic expansion than in a reversible isothermal expansion. In the latter case, heat is absorbed from the surroundings to make up for the work done by the gas, but this does not occur in an adiabatic process so that the temperature drops. Plots of reversible isothermal and adiabatic expansions are shown in Figure 3.7.

**Irreversible Adiabatic Expansion.** Finally, consider what happens in an irreversible adiabatic expansion. Suppose we start with an ideal gas at $P_1$, $V_1$, and $T_1$, and $P_2$ is the constant external pressure. The final volume and temperature of the gas are $V_2$ and $T_2$. Again, $q = 0$ so that

$$\Delta U = nC_v(T_2 - T_1) = w = -P_2(V_2 - V_1) \quad (3.29)$$
Furthermore, from the ideal gas equation we write

\[ V_1 = \frac{nRT_1}{P_1} \quad \text{and} \quad V_2 = \frac{nRT_2}{P_2} \]

Substituting the expressions for \( V_1 \) and \( V_2 \) in Equation 3.29, we obtain

\[
nC_v(T_2 - T_1) = -P_2 \left( \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right) \tag{3.30}
\]

Thus, knowing the initial conditions and \( P_2 \), we can solve for \( T_2 \) and hence the work done (see Problem 3.35).

The decrease in temperature, or the cooling effect that occurs in an adiabatic expansion, has some interesting practical consequences. A familiar example is the formation of fog when the caps of soft drinks or corks of champagne bottles are removed. Initially, the bottles are pressurized with carbon dioxide and air, and the space above the liquid is saturated with water vapor. When the cap is removed, the gases inside rush out. The process takes place so rapidly that the expansion of the gases can be compared to adiabatic expansion. As a result, the temperature drops and water vapor condenses to form the observed fog.

Liquefaction of gases is based on the same principle. Normally, the steps are: (1) compress a gas isothermally, (2) let the compressed gas expand adiabatically, (3) recompress the cooled gas isothermally, and so on, until the gas condenses to liquid.

### 3.5 Calorimetry

Calorimetry is the measurement of heat changes. In the laboratory, heat changes in physical and chemical processes are measured with a calorimeter, an apparatus designed specifically for this purpose. There are many types of calorimeters, depending on the purpose of the experiment. We shall consider three types in this section.

#### Constant-Volume Calorimetry

Heat of combustion is usually measured in a constant-volume adiabatic bomb calorimeter (Figure 3.8). It is a tightly sealed, heavy-walled, stainless steel container, which, together with the water, are thermally isolated from the surroundings. The substance under investigation is placed inside the container, which is filled with oxygen at about 30 atm. The combustion is started by an electrical discharge through a

Adiabatic means no heat exchange between the calorimeter and the surroundings and bomb denotes the explosive nature of the reaction (on a small scale).
A pair of wires that are in contact with the substance. The heat released by the reaction can be measured by registering the rise in the temperature of the water filling the inner jacket of the calorimeter. To determine the heat of combustion, we need to know the heat capacity of the calorimeter. The combined heat capacities of the water and the bomb are first determined by burning a compound of accurately known heat of combustion. As shown earlier, in a constant-volume process the heat produced is equal to the change in internal energy of the system:

\[ \Delta U = q_V + w = q_V - P \Delta V = q_V \]

**Example 3.6**

When a 0.5122-g sample of naphthalene (C<sub>10</sub>H<sub>8</sub>) was burned in a constant-volume bomb calorimeter, the temperature of the water in the inner jacket (see Figure 3.8) rose from 20.17°C to 24.08°C. If the effective heat capacity \( C_V \) of the bomb calorimeter plus water is 5267.8 J K<sup>-1</sup>, calculate \( \Delta U \) and \( \Delta H \) for the combustion of naphthalene in kJ mol<sup>-1</sup>.

**Answer**

The reaction is

\[ \text{C}_{10}\text{H}_8(s) + 12\text{O}_2(g) \rightarrow 10\text{CO}_2(g) + 4\text{H}_2\text{O}(l) \]
The amount of heat evolved is given by

$$C_V \Delta T = (5267.8 \text{ J K}^{-1} \text{K}) = 20.60 \text{ kJ}$$

From the molar mass of naphthalene (128.2 g), we write

$$q_V = \Delta U = -\frac{(20.60 \text{ kJ})(128.2 \text{ g mol}^{-1})}{0.5122 \text{ g}} = -5156 \text{ kJ mol}^{-1}$$

The negative sign indicates that the reaction is exothermic.

To calculate $\Delta H$, we start with $\Delta H = \Delta U + \Delta(PV)$. When all reactants and products are in condensed phases, $\Delta(PV)$ is negligible in comparison with $\Delta H$ and $\Delta U$. When gases are involved, $\Delta(PV)$ cannot be ignored. Assuming ideal gas behavior, we have $\Delta(PV) = \Delta(nRT) = RT\Delta n$, where $\Delta n$ is the change in the number of moles of gas in the reaction. Note that $T$ refers to the initial temperature here because we are comparing reactants and products under the same conditions. For our reaction, $\Delta n = (10 - 12) \text{ mol} = -2 \text{ mol}$ so that

$$\Delta H = \Delta U + RT\Delta n$$

$$= -5156 \text{ kJ mol}^{-1} + \frac{(8.314 \text{ J K}^{-1} \text{mol}^{-1})(293.32 \text{ K})(-2)}{1000 \text{ J/kJ}}$$

$$= -5161 \text{ kJ mol}^{-1}$$

**COMMENT**

(1) The difference between $\Delta U$ and $\Delta H$ is quite small for this reaction. The reason is that $\Delta(PV)$ (which in this case is equal to $RT\Delta n$) is small compared to $\Delta U$ or $\Delta H$. Because we assumed ideal gas behavior (we ignored the volume change of condensed phases), $\Delta U$ has the same value ($-5156 \text{ kJ mol}^{-1}$) whether the process occurs at constant $V$ or at constant $P$ because the internal energy is independent of pressure or volume. Similarly, $\Delta H = -5161 \text{ kJ mol}^{-1}$ whether the process is carried out at constant $V$ or at constant $P$. The heat change $q$, however, is $-5156 \text{ kJ mol}^{-1}$ at constant $V$ and $-5161 \text{ kJ mol}^{-1}$ at constant $P$, because it is path dependent. (2) In our calculation we ignored the heat capacities of the products (water and carbon dioxide) because the amounts of these substances are small compared to the bomb calorimeter itself. This omission does not introduce serious errors.

**Constant-Pressure Calorimetry**

For many physical processes (such as phase transitions and dissolutions and dilutions) and chemical reactions (for example, acid–base neutralization), which take place under atmospheric conditions, the heat change is equal to the enthalpy change; that is, $q_p = \Delta H$. Figure 3.9 shows a crude constant-pressure calorimeter, made of two Styrofoam coffee cups. To determine $\Delta H$, we need to know the heat capacity of the calorimeter ($C_p$) and the temperature change. A more refined calorimeter employs a Dewar flask and a thermocouple to monitor the temperature. As in the case of constant-volume calorimeter, no heat exchange is assumed to take place between the calorimeter and the surroundings during the experiment.

Suppose we wish to measure the heat of hydrolysis ($\Delta H$) of adenosine 5′-triphosphate (ATP) to give adenosine 5′-diphosphate (ADP), a key reaction in many biological processes:

$$\text{ATP} + \text{H}_2\text{O} \rightarrow \text{ADP} + \text{P}_i$$
where $P_i$ denotes the inorganic phosphate group. We start by placing a solution of known concentration of ATP in the calorimeter. The reaction is then initiated by adding a small amount of the enzyme adenosine triphosphatase (ATPase), which catalyzes the hydrolysis reaction. From the rise in temperature, $D_T$, we have

$$D_H = CP D_T$$

In reality, $D_H$ depends on many factors such as pH and the nature of counter ions. A typical value is $D_H \approx -30$ kJ per mole of ATP hydrolyzed to ADP.

**Differential Scanning Calorimetry**

Differential scanning calorimetry (DSC) is a powerful technique that enables us to study the energetics of biopolymers (for example, proteins and nucleic acids). Suppose we are interested in the thermodynamics of protein denaturation. In its physiologically functioning state, a protein molecule has a unique three-dimensional structure held together by various intra- and intermolecular forces. But this delicately balanced structure can be disrupted by various chemical reagents (called denaturants), changes in pH, and temperature, which cause the protein to unfold. When this happens, the protein has lost its biological function and is said to be denatured. Most proteins denature at elevated temperatures, sometimes only a few degrees higher than those at which they function.

To measure the enthalpy change of protein denaturation ($\Delta H_d$), we use a differential scanning calorimeter (shown schematically in Figure 3.10). The sample cell containing a protein in a buffer solution and a reference cell containing only the buffer solution are slowly heated electrically and the temperature rise in both cells is kept the same. Because the protein solution has a greater heat capacity, additional electric current is required to maintain its temperature rise. Figure 3.11a shows a plot of specific heat capacity, which is the difference between the heat capacity of the protein solution and the reference solution, versus temperature. Initially the curve rises slowly. As the protein begins to denature, there is a large absorption of heat because the process is highly endothermic. The temperature corresponding to the peak is called the
melting temperature \( (T_m) \). When unfolding is complete, the specific heat capacity again rises slowly, although at an elevated level because the denatured protein has a greater heat capacity than the native one. The shaded area gives the enthalpy of denaturation; that is,

\[
\Delta H_d = \int_{T_1}^{T_2} C_P \, dT
\]

The mechanism of protein denaturation for many small proteins (molar mass \( \leq 40,000 \) g) is that of a two-state model. That is, we can describe the process as the
transition between the native protein (N) and denatured protein (D) as follows Figure 3.12:

$$N \rightleftharpoons D$$

Near the denaturation temperature, when one non-covalent bond breaks, all such bonds break simultaneously in an all-or-none fashion. The more cooperative the process, the narrower the peak. (A familiar example of a two-state cooperative transition is that between ice and water at 0°C.) The melting temperature $T_m$ is defined as the temperature at which $[N] = [D]$, or that the protein is half denatured (Figure 3.11b). Studies show that the enthalpy of denaturation, $\Delta H_d$, falls between 200 kJ mol$^{-1}$ and 800 kJ mol$^{-1}$ for most proteins. As a general rule, the more stable the protein, the greater are the $T_m$ and $\Delta H_d$ values. Note that in such a calorimetric measurement, we do not need to know the molecular structure or composition of the protein in determining $\Delta H_d$. By the same token, when we say that one protein is more stable than another because it has a higher $T_m$ and a larger $\Delta H_d$ value, we have no idea why this is so in the absence of X-ray diffraction and spectroscopic data.

### 3.6 Thermochemistry

In this section we shall apply the first law of thermodynamics to thermochemistry, the study of energy changes in chemical reactions. Calorimetry provides us with the experimental approach; here we shall derive the necessary equations for dealing with such processes.

#### Standard Enthalpy of Formation

Chemical reactions almost always involve changes in heat. The *heat of reaction* can be defined as the heat change in the transformation of reactants at some temperature and pressure to products at the same temperature and pressure. For a constant-pressure process, the heat of reaction, $q_p$, is equal to the enthalpy change of the reaction, $\Delta_r H$, where the subscript $r$ denotes reaction. An *exothermic reaction* is a process that gives off heat to its surroundings and for which $\Delta_r H$ is negative; for an *endothermic reaction*, $\Delta_r H$ is positive because the process absorbs heat from the surroundings.

Consider the following reaction:

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

When 1 mole of graphite is burned in an excess of oxygen at 1 bar and 298 K to form 1 mole of carbon dioxide at the same temperature and pressure, 393.5 kJ of heat is given off.* The enthalpy change for this process is called the *standard enthalpy of reaction*, denoted $\Delta_r H^\circ$. It has the units of kJ (mol reaction)$^{-1}$. One mole of reaction is when the appropriate numbers of moles of substances (as specified by the stoichiometric coefficients) on the left side are converted to the substances on the right side of the equation. We express $\Delta_r H^\circ$ for the combustion of graphite as $\Delta_r H^\circ = -393.5$ kJ mol$^{-1}$, which is defined as the enthalpy change when the reactants in their standard states are converted to the product in its standard state. The standard state is defined as follows: For a pure solid or liquid, it is the state at a pressure $P = 1$ bar (see Section

---

* The temperature during combustion is much higher than 298 K, but we are measuring the total heat change from reactants at 1 bar and 298 K to product at 1 bar and 298 K. Therefore, the heat given off when the product cools to 298 K is part of the enthalpy of reaction.
1.2) and some temperature $T$. For a pure gas, the standard state refers to the hypothetical ideal gas at a pressure of 1 bar and some temperature of interest. The symbol for a standard state is a zero superscript.

In general, the standard enthalpy change of a chemical reaction can be thought of as the total enthalpy of the products minus the total enthalpy of the reactants:

$$
\Delta_r H^\circ = \sum v \overline{H}^\circ(\text{products}) - \sum v \overline{H}^\circ(\text{reactants})
$$

where $\overline{H}^\circ$ is the standard molar enthalpy and $v$ is the stoichiometric coefficient. The units of $\overline{H}^\circ$ are kJ mol$^{-1}$, and $v$ is a number without units. For the hypothetical reaction

$$aA + bB \rightarrow cC + dD$$

the standard enthalpy of reaction is given by

$$\Delta_r H^\circ = c\overline{H}^\circ(C) + d\overline{H}^\circ(D) - a\overline{H}^\circ(A) - b\overline{H}^\circ(B)$$

We cannot measure the absolute values of molar enthalpy of any substance, however. To circumvent this dilemma, we use standard molar enthalpy of formation ($\Delta_f H^\circ$) of reactants and products, where the subscript $f$ denotes formation. The standard molar enthalpy of formation is an intensive quantity. It is the enthalpy change when 1 mole of a compound is formed from its constituent elements at 1 bar and 298 K. The standard enthalpy change for the above reaction can now be written as

$$\Delta_f H^\circ = c\overline{H}^\circ(C) + d\overline{H}^\circ(D) - a\overline{H}^\circ(A) - b\overline{H}^\circ(B) \quad (3.31)$$

In general, we write

$$\Delta_f H^\circ = \sum v \Delta_f \overline{H}^\circ(\text{products}) - \sum v \Delta_f \overline{H}^\circ(\text{reactants}) \quad (3.32)$$

For the formation of CO$_2$ shown above, we express the standard enthalpy of reaction as

$$\Delta_f H^\circ = \Delta_f \overline{H}^\circ(\text{CO}_2) - \Delta_f \overline{H}^\circ(\text{graphite}) - \Delta_f \overline{H}^\circ(\text{O}_2)$$

$$= -393.5 \text{ kJ mol}^{-1}$$

By convention, we arbitrarily assign a value of zero to $\Delta_f \overline{H}^\circ$ for elements in their most stable allotropic forms at a particular temperature. If we choose 298 K, then

$$\Delta_f \overline{H}^\circ(\text{O}_2) = 0$$

$$\Delta_f \overline{H}^\circ(\text{graphite}) = 0$$

because O$_2$ and graphite are the stable allotropic forms of oxygen and carbon at this temperature. Now neither ozone nor diamond is the more stable allotropic form at 1 bar and 298 K, and so we have

$$\Delta_f \overline{H}^\circ(\text{O}_3) \neq 0 \quad \text{and} \quad \Delta_f \overline{H}^\circ(\text{diamond}) \neq 0$$

For the combustion of graphite, the standard enthalpy for the combustion of graphite can now be written as

$$\Delta_f H^\circ = \Delta_f \overline{H}^\circ(\text{CO}_2) = -393.5 \text{ kJ mol}^{-1}$$

Allotropes are two or more forms of the same element that differ in physical and chemical properties.
Thus, the standard molar enthalpy of formation for CO₂ is equal to the standard enthalpy of reaction.

There is no mystery in the assignment of a zero value to \( \Delta_f H^\circ \) for the elements. As mentioned above, we cannot determine the absolute value of the enthalpy of a substance. Only values relative to an arbitrary reference can be given. In thermodynamics, we are primarily interested in the changes of \( H \). Although any arbitrarily assigned value of \( \Delta_f H^\circ \) for an element would work, zero makes calculations simpler.

The importance of the standard molar enthalpies of formation is that once we know their values, we can calculate the standard enthalpies of reaction. The \( \Delta_f H^\circ \) values are obtained by either the direct method or the indirect method, described below.

**The Direct Method.** This method of measuring \( \Delta_f H^\circ \) works for compounds that can be readily synthesized from their elements. The formation of CO₂ from graphite and O₂ is such an example. Other compounds that can be directly synthesized from their elements are SF₆, P₄O₁₀, and CS₂. The equations representing their syntheses are

\[
\begin{align*}
S(\text{rhombic}) + 3F_2(g) & \rightarrow SF_6(g) \quad \Delta_f H^\circ = -1209 \text{ kJ mol}^{-1} \\
4P(\text{white}) + 5O_2(g) & \rightarrow P_4O_{10}(s) \quad \Delta_f H^\circ = -2984.0 \text{ kJ mol}^{-1} \\
C(\text{graphite}) + 2S(\text{rhombic}) & \rightarrow CS_2(l) \quad \Delta_f H^\circ = 89.7 \text{ kJ mol}^{-1}
\end{align*}
\]

Note that S(rhombic) and P(white) are the most stable allotropes of sulfur and phosphorus, respectively, at 1 bar and 298 K, so their \( \Delta_f H^\circ \) values are zero. As for CO₂, the standard enthalpy of reaction (\( \Delta_f H^\circ \)) for the three reactions shown is equal to \( \Delta_f H^\circ \) for the compound in each case.

**The Indirect Method.** Most compounds cannot be synthesized directly from their elements. In some cases, the reaction proceeds too slowly or not at all, or side reactions produce compounds other than the desired product. In these cases, the value of \( \Delta_f H^\circ \) can be determined by an indirect approach, which is based on Hess’s law. Hess’s law (after the Swiss chemist Germain Henri Hess, 1802–1850) can be stated as follows: When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps. In other words, if we can break down a reaction into a series of reactions for which the value of \( \Delta_r H^\circ \) can be measured, we can calculate the \( \Delta_f H^\circ \) value for the overall reaction.

The logic of Hess’s law is that because enthalpy is a state function, its change is path independent.

A simple analogy for Hess’s law is as follows. Suppose you go from the first floor to the sixth floor of a building by elevator. The gain in your gravitational potential energy (which corresponds to the enthalpy change for the overall process) is the same whether you go directly there or stop at each floor on your way up (breaking the reaction into a series of steps).

Let us apply Hess’s law to find the value of \( \Delta_f H^\circ \) for carbon monoxide. We might represent the synthesis of CO from its elements as

\[
C(\text{graphite}) + \frac{1}{2}O_2(g) \rightarrow CO(g)
\]

We cannot burn graphite in oxygen without also forming some CO₂, however, so this approach will not work. To circumvent this difficulty, we can carry out the following two separate reactions, which do go to completion:
First, we reverse equation 2 to get

\[(3) \quad \text{CO}_2(g) \rightarrow \text{CO}(g) + \frac{1}{2} \text{O}_2(g) \quad \Delta_r H^\circ = +283.0 \text{ kJ mol}^{-1}\]

Because chemical equations can be added and subtracted just like algebraic equations, we carry out the operation \((1) + (3)\) and obtain

\[(4) \quad \text{C(graphite)} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{CO}(g) \quad \Delta_r H^\circ = -110.5 \text{ kJ mol}^{-1}\]

Thus, \(\Delta_r H^\circ(\text{CO}) = -110.5 \text{ kJ mol}^{-1}\). Looking back, we see that the overall reaction is the formation of \(\text{CO}_2\) (reaction 1), which can be broken down into two parts (reactions 2 and 4). Figure 3.13 shows the overall scheme of our procedure.

The general rule in applying Hess’s law is that we should arrange a series of chemical equations (corresponding to a series of steps) in such a way that, when added together, all species cancel except for the reactants and product that appear in the overall reaction. This means that we want the elements on the left and the compound of interest on the right of the arrow. To achieve this goal, we often need to multiply some or all of the equations representing the individual steps by the appropriate coefficients.

Table 3.3 lists the \(\Delta_r H^\circ\) values for a number of common elements and inorganic and organic compounds. (A more extensive listing is given in Appendix 2.) Note that compounds differ not only in the magnitude of \(\Delta_r H^\circ\) but in the sign as well. Water and other compounds that have negative \(\Delta_r H^\circ\) values lie “downhill” on the enthalpy scale relative to their constituent elements (Figure 3.14). These compounds tend to be more stable than those that have positive \(\Delta_r H^\circ\) values. The reason is that energy has to be supplied to the former to decompose them into the elements, while the latter decompose with the evolution of heat.
Dependence of Enthalpy of Reaction on Temperature

Suppose you have measured the standard enthalpy of a reaction at a certain temperature, say 298 K, and want to know its value at 350 K. One way to find out is to repeat the measurement at the higher temperature. Fortunately, we also can obtain the desired quantity from tabulated thermodynamic data without doing another experiment. For any reaction, the change in enthalpy at a particular temperature is

\[ \Delta_r H = \Delta_r H^0 \]

To see how the enthalpy of reaction (\( \Delta_r H \)) itself changes with temperature, we differentiate this equation with respect to temperature at constant pressure as follows:

\[ \Delta_r H = \sum H(\text{products}) - \sum H(\text{reactants}) \]

Table 3.3
Standard Molar Enthalpies of Formation at 298 K and 1 Bar for Some Inorganic and Organic Substances

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta_r H^0 )/kJ \cdot mol(^{-1} )</th>
<th>Substance</th>
<th>( \Delta_r H^0 )/kJ \cdot mol(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(graphite)</td>
<td>0</td>
<td>CH(_4)(g)</td>
<td>−74.85</td>
</tr>
<tr>
<td>C(diamond)</td>
<td>1.90</td>
<td>C(_2)H(_6)(g)</td>
<td>−84.7</td>
</tr>
<tr>
<td>CO(g)</td>
<td>−110.5</td>
<td>C(_2)H(_2)(g)</td>
<td>−103.8</td>
</tr>
<tr>
<td>CO(_2)(g)</td>
<td>−393.5</td>
<td>C(_2)H(_4)(g)</td>
<td>226.6</td>
</tr>
<tr>
<td>HF(g)</td>
<td>−268.6</td>
<td>C(_2)H(_4)(g)</td>
<td>52.3</td>
</tr>
<tr>
<td>HCl(g)</td>
<td>−92.3</td>
<td>C(_2)H(_6)(l)</td>
<td>49.04</td>
</tr>
<tr>
<td>HBr(g)</td>
<td>−36.4</td>
<td>CH(_3)OH(l)</td>
<td>−238.7</td>
</tr>
<tr>
<td>HI(g)</td>
<td>26.48</td>
<td>C(_2)H(_4)OH(l)</td>
<td>−277.0</td>
</tr>
<tr>
<td>H(_2)O(g)</td>
<td>−241.8</td>
<td>CH(_3)CHO(l)</td>
<td>−192.3</td>
</tr>
<tr>
<td>H(_2)O(l)</td>
<td>−285.8</td>
<td>HCOOH(l)</td>
<td>−424.7</td>
</tr>
<tr>
<td>NH(_3)(g)</td>
<td>−46.3</td>
<td>CH(_3)COOH(l)</td>
<td>−484.2</td>
</tr>
<tr>
<td>NO(g)</td>
<td>90.4</td>
<td>C(_4)H(_8)O(_8)(s)</td>
<td>−1274.5</td>
</tr>
<tr>
<td>NO(_2)(g)</td>
<td>33.9</td>
<td>C(_12)H(_22)O(_11)(s)</td>
<td>−2221.7</td>
</tr>
<tr>
<td>N(_2)O(_4)(g)</td>
<td>9.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(_2)O(g)</td>
<td>81.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(_3)(g)</td>
<td>142.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO(_2)(g)</td>
<td>−296.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO(_3)(g)</td>
<td>−395.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.14
Two representative compounds with negative and positive \( \Delta_r H^0 \) values.

Dependence of Enthalpy of Reaction on Temperature

Suppose you have measured the standard enthalpy of a reaction at a certain temperature, say 298 K, and want to know its value at 350 K. One way to find out is to repeat the measurement at the higher temperature. Fortunately, we also can obtain the desired quantity from tabulated thermodynamic data without doing another experiment. For any reaction, the change in enthalpy at a particular temperature is

\[ \Delta_r H = \Sigma H(\text{products}) - \Sigma H(\text{reactants}) \]

To see how the enthalpy of reaction (\( \Delta_r H \)) itself changes with temperature, we differentiate this equation with respect to temperature at constant pressure as follows
\[
\left( \frac{\partial \Delta_r H}{\partial T} \right)_p = \left[ \frac{\partial \Sigma H(\text{products})}{\partial T} \right]_p - \left[ \frac{\partial \Sigma H(\text{reactants})}{\partial T} \right]_p \\
= \Sigma C_p(\text{products}) - \Sigma C_p(\text{reactants}) \\
= \Delta C_p \tag{3.33}
\]

because \((\partial H/\partial T)_p = C_p\). Integration of Equation 3.33 gives

\[
\int_{T_1}^{T_2} d\Delta_r H = \Delta_r H_2 - \Delta_r H_1 = \int_{T_1}^{T_2} \Delta C_p \, dT = \Delta C_p(T_2 - T_1) \tag{3.34}
\]

where \(\Delta_r H_1\) and \(\Delta_r H_2\) are the enthalpies of reaction at \(T_1\) and \(T_2\), respectively. Equation 3.34 is known as Kirchhoff’s law (after the German physicist Gustav-Robert Kirchhoff, 1824–1887). This law says that the difference between the enthalpies of a reaction at two different temperatures is just the difference in the enthalpies of heating the products and reactants from \(T_1\) to \(T_2\) (Figure 3.15). Note that in deriving this equation, we have assumed the \(C_p\) values are all independent of temperature. Otherwise, they must be expressed as a function of \(T\) in the integration, as mentioned in Section 3.3.

**Example 3.7**

The standard enthalpy change for the reaction

\[3O_2(g) \rightarrow 2O_3(g)\]

is given by \(\Delta_r H^\circ = 285.4 \text{ kJ mol}^{-1}\) at 298 K and 1 bar. Calculate the value of \(\Delta_r H^\circ\) at 380 K. Assume that the \(C_p\) values are all independent of temperature.

**Answer**

In Appendix 2, we find the molar heat capacities at constant pressure for \(O_2\) and \(O_3\) to be 29.4 J K\(^{-1}\) mol\(^{-1}\) and 38.2 J K\(^{-1}\) mol\(^{-1}\), respectively. From Equation 3.34

\[
\Delta_r H^\circ_{380} - \Delta_r H^\circ_{298} = \left[ \frac{(2)38.2 - (3)29.4}{1000 \text{ J/kJ}} \right] \times (380 - 298) \text{ K} \\
= -0.97 \text{ kJ mol}^{-1} \\
\Delta_r H^\circ_{380} = (285.4 - 0.97) \text{ kJ mol}^{-1} \\
= 284.4 \text{ kJ mol}^{-1}
\]
Note that the value of $\Delta_r H^\circ_{140}$ is not appreciably different from that of $\Delta_r H^\circ_{298}$. For gas-phase reactions, the increase in enthalpy from $T_1$ to $T_2$ for products tends to cancel that for reactants.

### 3.7 Bond Energies and Bond Enthalpies

Because chemical reactions involve the breaking and making of chemical bonds in the reactant and product molecules, a proper understanding of the thermochemical nature of reactions clearly requires a detailed knowledge of bond energies. Bond energy is the energy required to break a bond between two atoms. Consider the dissociation of 1 mole of H$_2$ molecules at 298 K and 1 bar:

$$H_2(g) \rightarrow 2H(g) \quad \Delta_r H^\circ = 436.4 \text{ kJ mol}^{-1}$$

Assigning the energy of the H–H bond a value of 436.4 kJ mol$^{-1}$ might be tempting, but the situation is more complicated. What is measured is actually the bond enthalpy of H$_2$, not its bond energy. To understand the difference between these two quantities, consider first what we mean by bond energy.

Figure 3.16 shows the potential-energy curve of the H$_2$ molecule. Let us start by asking how the molecule is formed. At first, the two hydrogen atoms are far apart and exert no influence on each other. As the distance of separation is shortened, both Coulombic attraction (between electron and nucleus) and Coulombic repulsion (between electron and electron and nucleus and nucleus) begin to affect each atom. Because attraction outweighs repulsion, the potential energy of the system decreases with decreasing distance of separation. This process continues until the net attraction force reaches a maximum, leading to the formation of a hydrogen molecule. Further shortening of the distance increases the repulsion, and the potential rises steeply. The

![Potential-energy curve for a diatomic molecule. The short horizontal line represents the lowest vibrational energy level (the zero-point energy) of the molecule (for example, H$_2$). The intercepts of this line with the curve shows the maximum and minimum bond lengths during a vibration.](image)
reference state (zero potential energy) corresponds to the case of two infinitely separated H atoms. Potential energy is a negative quantity for the bound state (that is, H\textsubscript{2}), and energy in the form of heat is given off as a result of the bond formation.

The most important features in Figure 3.16 are the minimum point on the potential-energy curve for the bonding state, which represents the most stable state for the molecule, and the corresponding distance of separation, called the equilibrium distance. However, molecules are constantly executing vibrational motions that persist even at absolute zero. Furthermore, the energies associated with vibration, like the energies of an electron in an atom, are quantized. The lowest vibrational energy is not zero but equal to \( \frac{1}{2} \hbar v \), called the zero-point energy, where \( v \) is the frequency of vibration of H\textsubscript{2}. Consequently, the two hydrogen atoms cannot be held rigidly in the molecule, as is the case when a molecule is situated at the minimum point. Instead, the lowest vibrational state for H\textsubscript{2} is represented by the horizontal line. The intercepts between this line and the potential-energy curve represent the two extreme bond lengths during the course of a vibration. We can still speak of equilibrium distance in this case, although technically it is the average of the two extreme bond lengths. The bond energy of H\textsubscript{2} is the vertical distance from lowest vibrational energy level to the reference state of zero potential energy.

The measured enthalpy change (436.4 kJ mol\(^{-1}\)) should not be identified with the bond energy of H\textsubscript{2} for two reasons. First, upon dissociation, the number of moles of gas doubles, and hence gas-expansion work is done on the surroundings. The enthalpy change \( (\Delta H) \) is not equal to the internal energy change \( (\Delta U) \), which is the bond energy, but is related to it by the equation

\[
\Delta H = \Delta U + P\Delta V
\]

Second, the hydrogen molecules have vibrational, rotational, and translational energy before they dissociate, whereas the hydrogen atoms have only translational energy. Thus, the total kinetic energy of the reactant differs from that of the product. Although these kinetic energies are not relevant to the bond energy, their difference is unavoidably incorporated in the \( \Delta_r H^0 \) value. Thus, despite the fact that bond energy has a firmer theoretical basis, for practical reasons we shall use bond enthalpies to help us study energy changes of chemical reactions.

**Bond Enthalpy and Bond Dissociation Enthalpy**

With respect to diatomic molecules such as H\textsubscript{2} and the following examples,

\[
\begin{align*}
\text{N}_2(g) & \rightarrow 2\text{N}(g) & \Delta_r H^0 &= 941.4 \text{ kJ mol}^{-1} \\
\text{HCl}(g) & \rightarrow \text{H}(g) + \text{Cl}(g) & \Delta_r H^0 &= 430.9 \text{ kJ mol}^{-1}
\end{align*}
\]

bond enthalpy has a special significance because there is only one bond in each molecule, so that the enthalpy change can be assigned unequivocally to that bond. For this reason, we shall use the term bond dissociation enthalpy for diatomic molecules. Polyatomic molecules are not so straightforward. Measurements show that the energy needed to break the first O–H bond in H\textsubscript{2}O, for example, is different from that needed to break the second O–H bond:

\[
\begin{align*}
\text{H}_2\text{O}(g) & \rightarrow \text{H}(g) + \text{OH}(g) & \Delta_r H^0 &= 502 \text{ kJ mol}^{-1} \\
\text{OH}(g) & \rightarrow \text{H}(g) + \text{O}(g) & \Delta_r H^0 &= 427 \text{ kJ mol}^{-1}
\end{align*}
\]

In each case, an O–H bond is broken, but the first step is more endothermic than the second. The difference between the two \( \Delta_r H^0 \) values suggests that the second O–H
bond itself undergoes change, because the chemical environment has been altered. If we were to study the O–H breaking process in other compounds, such as H₂O₂, CH₃OH, and so on, we would find still other Δ_rH/C₁₄ values. Thus, for polyatomic molecules, we can speak only of the average bond enthalpy of a particular bond. For example, we can measure the bond enthalpy of the O–H bond in 10 different polyatomic molecules and obtain the average O–H bond enthalpy by dividing the sum of the bond enthalpies by 10. When we use the term bond enthalpy, then, it is understood that we are referring to an average quantity, whereas bond dissociation enthalpy means a precisely measured value. Table 3.4 lists the bond enthalpies of a number of common chemical bonds. As you can see, triple bonds are stronger than double bonds, which, in turn, are stronger than single bonds.

The usefulness of bond enthalpies is that they enable us to estimate Δ_rH/C₁₄ values when precise thermochemical data (that is, Δ_lH/C₁₄ values) are not available. Because energy is required to break chemical bonds and chemical bond formation is accompanied by a release of heat, we can estimate Δ_rH/C₁₄ values by counting the total number of bonds broken and formed in the reaction and recording all the corresponding energy changes. The enthalpy of reaction in the gas phase is given by

$$\Delta_rH = \Sigma \text{BE}\text{(reactants)} - \Sigma \text{BE}\text{(products)}$$

(3.35)

where BE stands for average bond enthalpy. As written, Equation 3.35 takes care of the sign convention for Δ_rH/C₁₄. If the total energy input is greater than the total energy

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Enthalpy</th>
<th>Bond</th>
<th>Bond Enthalpy</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–H</td>
<td>436.4</td>
<td>C–S</td>
<td>255</td>
</tr>
<tr>
<td>H–N</td>
<td>393</td>
<td>C–S</td>
<td>477</td>
</tr>
<tr>
<td>H–O</td>
<td>460</td>
<td>N–N</td>
<td>393</td>
</tr>
<tr>
<td>H–S</td>
<td>368</td>
<td>N=N</td>
<td>418</td>
</tr>
<tr>
<td>H–P</td>
<td>326</td>
<td>N=N</td>
<td>941.4</td>
</tr>
<tr>
<td>H–F</td>
<td>568.2</td>
<td>N–O</td>
<td>176</td>
</tr>
<tr>
<td>H–Cl</td>
<td>430.9</td>
<td>N–P</td>
<td>209</td>
</tr>
<tr>
<td>H–Br</td>
<td>366.1</td>
<td>O–O</td>
<td>142</td>
</tr>
<tr>
<td>H–I</td>
<td>298.3</td>
<td>O=O</td>
<td>498.8</td>
</tr>
<tr>
<td>C–H</td>
<td>414</td>
<td>O–P</td>
<td>502</td>
</tr>
<tr>
<td>C–C</td>
<td>347</td>
<td>O=S</td>
<td>469</td>
</tr>
<tr>
<td>C=C</td>
<td>619</td>
<td>P–P</td>
<td>197</td>
</tr>
<tr>
<td>C≡C</td>
<td>812</td>
<td>P–P</td>
<td>490</td>
</tr>
<tr>
<td>C≡N</td>
<td>276</td>
<td>S–S</td>
<td>268</td>
</tr>
<tr>
<td>C≡N</td>
<td>615</td>
<td>S–S</td>
<td>351</td>
</tr>
<tr>
<td>C≡N</td>
<td>891</td>
<td>F–F</td>
<td>150.6</td>
</tr>
<tr>
<td>C–O</td>
<td>351</td>
<td>Cl–Cl</td>
<td>242.7</td>
</tr>
<tr>
<td>C=O</td>
<td>724</td>
<td>Br–Br</td>
<td>192.5</td>
</tr>
<tr>
<td>C–P</td>
<td>264</td>
<td>I–I</td>
<td>151.0</td>
</tr>
</tbody>
</table>

* Bond enthalpies for diatomic molecules have more significant figures than those for polyatomic molecules because they are directly measurable quantities and are not averaged over many compounds as for polyatomic molecules.

* The C–O bond enthalpy in CO₂ is 799 kJ mol⁻¹.
released, the $\Delta_r H^\circ$ value is positive and the reaction is endothermic. Conversely, if more energy is released than absorbed, the $\Delta_r H^\circ$ value is negative and the reaction is exothermic (Figure 3.17). If reactants and products are all diatomic molecules, then Equation 3.35 will yield accurate results because the bond dissociation enthalpies of diatomic molecules are accurately known. If some or all of the reactants and products are polyatomic molecules, Equation 3.35 will yield only approximate results because the bond enthalpies for calculation will be average values.

**Example 3.8**

Estimate the enthalpy of combustion for methane

$$\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$$

at 298 K and 1 bar using the bond enthalpies in Table 3.4. Compare your result with that calculated from the enthalpies of formation of products and reactants.

**ANSWER**

The first step is to count the number of bonds broken and the number of bonds formed. This is best done by creating a table:

<table>
<thead>
<tr>
<th>Type of bonds broken</th>
<th>Number of bonds broken</th>
<th>Bond enthalpy (kJ mol$^{-1}$)</th>
<th>Enthalpy change (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H</td>
<td>4</td>
<td>414</td>
<td>1656</td>
</tr>
<tr>
<td>O–O</td>
<td>2</td>
<td>498.8</td>
<td>997.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type of bonds formed</th>
<th>Number of bonds formed</th>
<th>Bond enthalpy (kJ mol$^{-1}$)</th>
<th>Enthalpy change (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–O</td>
<td>2</td>
<td>799</td>
<td>1598</td>
</tr>
<tr>
<td>O–H</td>
<td>4</td>
<td>460</td>
<td>1840</td>
</tr>
</tbody>
</table>
From Equation 3.35,
\[
\Delta_r H^\circ = [(1656 \text{ kJ mol}^{-1} + 997.6 \text{ kJ mol}^{-1}) - (1598 \text{ kJ mol}^{-1} + 1840 \text{ kJ mol}^{-1})] \\
= -784.4 \text{ kJ mol}^{-1}
\]

To calculate the \( \Delta_r H^\circ \) value using Equation 3.32, we obtain the \( \Delta_f H^\circ \) values from Table 3.3 and write
\[
\Delta_r H^\circ = [\Delta_f H^\circ (\text{CO}_2) + 2 \Delta_f H^\circ (\text{H}_2\text{O})] - [\Delta_f H^\circ (\text{CH}_4) + 2 \Delta_f H^\circ (\text{O}_2)] \\
= [-393.5 \text{ kJ mol}^{-1} + 2(-241.8 \text{ kJ mol}^{-1})] - (-74.85 \text{ kJ mol}^{-1}) \\
= -802.3 \text{ kJ mol}^{-1}
\]

**COMMENT**
The agreement between the estimated \( \Delta_r H^\circ \) value using bond enthalpies and the actual \( \Delta_r H^\circ \) value is fairly good in this case. In general, the more exothermic (or endothermic) the reaction, the better the agreement. If the actual \( \Delta_r H^\circ \) value is a small positive or negative quantity, then the value obtained from bond enthalpies becomes unreliable. Such values may even give the wrong sign for the reaction.

**Suggestions for Further Reading**

**Books**

**Articles**
*Work and Heat*

*First Law of Thermodynamics*

*Heat Capacity*

*Thermochemistry*

*General*


Problems

**Work and Heat**

3.1 Explain the term *state function*. Which of the following are state functions? *P, V, T, w, q.*

3.2 What is heat? How does heat differ from thermal energy? Under what condition is heat transferred from one system to another?

3.3 Show that 1 L atm = 101.3 J.

3.4 A 7.24-g sample of ethane occupies 4.65 L at 294 K. (a) Calculate the work done when the gas expands isothermally against a constant external pressure of 0.500 atm until its volume is 6.87 L. (b) Calculate the work done if the same expansion occurs reversibly.

3.5 A 19.2-g quantity of dry ice (solid carbon dioxide) is allowed to sublime (evaporate) in an apparatus like the one shown in Figure 3.1. Calculate the expansion work done against a constant external pressure of 0.995 atm and at a constant temperature of 22°C. Assume that the initial volume of dry ice is negligible and that CO₂ behaves like an ideal gas.

3.6 Calculate the work done by the reaction

\[ \text{Zn}(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{ZnSO}_4(aq) + \text{H}_2(g) \]

when 1 mole of hydrogen gas is collected at 273 K and 1.0 atm. (Neglect volume changes other than the change in gas volume.)

**First Law of Thermodynamics**

3.7 A truck traveling 60 kilometers per hour is brought to a complete stop at a traffic light. Does this change in velocity violate the law of conservation of energy?

3.8 Some driver’s test manuals state that the stopping distance quadruples as the velocity doubles. Justify this statement by using mechanics and thermodynamic arguments.

3.9 Provide a first law analysis for each of the following cases: (a) When a bicycle tire is inflated with a hand pump, the temperature inside rises. You can feel the warming effect at the valve stem. (b) Artificial snow is made by quickly releasing a mixture of compressed air and water vapor at about 20 atm from a snow-making machine to the surroundings.

3.10 An ideal gas is compressed isothermally by a force of 85 newtons acting through 0.24 meter. Calculate the values of \( \Delta U \) and \( q \).

3.11 Calculate the internal energy of 2 moles of argon (assuming ideal behavior) at 298 K. Suggest two ways to increase its internal energy by 10 J.

3.12 A thermos bottle containing milk is shaken vigorously. Consider the milk as the system. (a) Will the temperature rise as a result of the shaking? (b) Has heat been added to the system? (c) Has work been done on the system? (d) Has the system’s internal energy changed?

3.13 A 1.00-mole sample of ammonia at 14.0 atm and 25°C in a cylinder fitted with a movable piston expands against a constant external pressure of 1.00 atm. At equilibrium, the pressure and volume of the gas are 1.00 atm and 23.5 L, respectively. (a) Calculate the final temperature of the sample. (b) Calculate the values of \( q, w, \) and \( \Delta U \) for the process.

3.14 An ideal gas is compressed isothermally from 2.0 atm and 2.0 L to 4.0 atm and 1.0 L. Calculate the values of \( \Delta U \) and \( \Delta H \) if the process is carried out (a) reversibly and (b) irreversibly.

3.15 Explain the energy changes at the molecular level when liquid acetone is converted to vapor at its boiling point.

3.16 A piece of potassium metal is added to water in a beaker. The reaction that takes place is

\[ 2\text{K}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{KOH}(aq) + \text{H}_2(g) \]

Predict the signs of \( q, \Delta U, \) and \( \Delta H \).

3.17 At 373.15 K and 1 atm, the molar volume of liquid water and steam are \( 1.88 \times 10^{-5} \) m³ and \( 3.06 \times 10^{-2} \) m³, respectively. Given that the heat of vaporization of water is 40.79 kJ mol⁻¹, calculate the values of \( \Delta H \) and \( \Delta U \) for 1 mole in the following process:

\[ \text{H}_2\text{O}(l, 373.15 \text{ K}, 1 \text{ atm}) \rightarrow \text{H}_2\text{O}(g, 373.15 \text{ K}, 1 \text{ atm}) \]
3.18 Consider a cyclic process involving a gas. If the pressure of the gas varies during the process but returns to the original value at the end, is it correct to write \( \Delta H = q_P \)?

3.19 Calculate the value of \( \Delta H \) when the temperature of 1 mole of a monatomic gas is increased from 25°C to 300°C.

3.20 One mole of an ideal gas undergoes an isothermal expansion at 300 K from 1.00 atm to a final pressure while performing 200 J of expansion work. Calculate the final pressure of the gas if the external pressure is 0.20 atm.

### Heat Capacities

3.21 A 6.22-kg piece of copper metal is heated from 20.5°C to 324.3°C. Given that the specific heat of Cu is 0.385 J g\(^{-1}\) °C\(^{-1}\), calculate the heat absorbed (in kJ) by the metal.

3.22 A 10.0-g sheet of gold with a temperature of 18.0°C is laid flat on a sheet of iron that weighs 20.0 g and has a temperature of 55.6°C. Given that the specific heats of Au and Fe are 0.129 J g\(^{-1}\) °C\(^{-1}\) and 0.444 J g\(^{-1}\) °C\(^{-1}\), respectively, what is the final temperature of the combined metals? Assume that no heat is lost to the surroundings. (Hint: The heat gained by the gold must be equal to the heat lost by the iron.)

3.23 It takes 330 joules of energy to raise the temperature of 24.6 g of benzene from 21.0°C to 28.7°C at constant pressure. What is the molar heat capacity of benzene at constant pressure?

3.24 The molar heat of vaporization for water is 44.01 kJ mol\(^{-1}\) at 298 K and 40.79 kJ mol\(^{-1}\) at 373 K. Give a qualitative explanation of the difference in these two values.

3.25 The constant-pressure molar heat capacity of nitrogen is given by the expression

\[
\overline{C}_P = (27.0 + 5.90 \times 10^{-3} T - 0.34 \times 10^{-6} T^2) \text{ J K}^{-1} \text{ mol}^{-1}
\]

Calculate the value of \( \Delta H \) for heating 1 mole of nitrogen from 25.0°C to 125°C.

3.26 The heat capacity ratio (\( \gamma \)) of an ideal gas is 1.38. What are its \( C_V \) and \( C_P \) values?

3.27 One way to measure the heat capacity ratio (\( \gamma \)) of a gas is to measure the speed of sound in the gas (\( c \)), which is given by

\[
c = \left( \frac{\gamma R T}{\mu} \right)^{1/2}
\]

where \( \mu \) is the molar mass of the gas. Calculate the speed of sound in helium at 25°C.

3.28 Which of the following gases has the largest \( \overline{C}_V \) value at 298 K? He, N\(_2\), CCl\(_4\), HCl.

3.29 (a) For most efficient use, refrigerator freezer compartments should be fully packed with food. What is the thermochemical basis for this recommendation? (b) Starting at the same temperature, tea and coffee remain hot longer in a thermal flask than soup. Explain.

3.30 In the nineteenth century, two scientists named Dulong and Petit noticed that the product of the molar mass of a solid element and its specific heat is approximately 25 J °C\(^{-1}\). This observation, now called Dulong and Petit’s law, was used to estimate the specific heat of metals. Verify the law for aluminum (0.900 J g\(^{-1}\) °C\(^{-1}\)), copper (0.385 J g\(^{-1}\) °C\(^{-1}\)), and iron (0.444 J g\(^{-1}\) °C\(^{-1}\)). The law does not apply to one of the metals. Which one is it? Why?

### Gas Expansion

3.31 The following diagram represents the \( P-V \) changes of a gas. Write an expression for the total work done.

3.32 The equation of state for a certain gas is given by

\[
P(V/n) = RT.
\]

Obtain an expression for the maximum work done by the gas in a reversible isothermal expansion from \( V_1 \) to \( V_2 \).

3.33 Calculate the values of \( q, w, \Delta U, \) and \( \Delta H \) for the reversible adiabatic expansion of 1 mole of a monatomic ideal gas from 5.00 m\(^3\) to 25.0 m\(^3\). The temperature of the gas is initially 298 K.

3.34 A quantity of 0.27 mole of neon is confined in a container at 2.50 atm and 298 K and then allowed to expand adiabatically under two different conditions: (a) reversibly to 1.00 atm and (b) against a constant pressure of 1.00 atm. Calculate the final temperature in each case.

3.35 One mole of an ideal monatomic gas initially at 300 K and a pressure of 15.0 atm expands to a final pressure of 1.00 atm. The expansion can occur via any one of four different paths: (a) isothermal and reversible, (b) isothermal and irreversible, (c) adiabatic and reversible, and (d) adiabatic and irreversible. In irreversible processes, the expansion occurs against an external pressure of 1.00 atm. For each case, calculate the values of \( q, w, \Delta U, \) and \( \Delta H \).
Calorimetry

3.36 A 0.1375-g sample of magnesium is burned in a constant-volume bomb calorimeter that has a heat capacity of 1769 J °C⁻¹. The calorimeter contains exactly 300 g of water, and the temperature increases by 1.126 °C. Calculate the heat given off by the burning magnesium, in kJ g⁻¹ and in kJ mol⁻¹.

3.37 The enthalpy of combustion of benzoic acid (C₆H₅COOH) is commonly used as the standard for calibrating constant-volume bomb calorimeters; its value has been accurately determined to be -3226.7 kJ mol⁻¹. (a) When 0.9862 g of benzoic acid was oxidized, the temperature rose from 21.84°C to 25.67°C. What is the heat capacity of the calorimeter? (b) In a separate experiment, 0.4654 g of naphthalene (C₁₀H₈) was oxidized in the same calorimeter, and the temperature rose from 21.22°C to 22.28°C. Calculate the enthalpy of combustion of glucose, the value of ΔₚU for the combustion, and the molar enthalpy of formation of glucose.

3.38 A quantity of 2.00 × 10⁻² mL of 0.862 M HCl is mixed with 2.00 × 10⁻² mL of 0.431 M Ba(OH)₂ in a constant-pressure calorimeter that has a heat capacity of 453 J °C⁻¹. The initial temperature of the HCl and Ba(OH)₂ solutions is the same at 20.48°C. For the process

\[ \text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l) \]

the heat of neutralization is -56.2 kJ mol⁻¹. What is the final temperature of the mixed solution?

3.39 When 1.034 g of naphthalene (C₁₀H₈) are completely burned in a constant-volume bomb calorimeter at 298 K, 41.56 kJ of heat is evolved. Calculate the values of ΔₚU and ΔₚH for the reaction.

Thermochemistry

3.40 Consider the following reaction:

\[ 2\text{CH}_3\text{OH}(l) + 3\text{O}_2(g) \rightarrow 4\text{H}_2\text{O}(l) + 2\text{CO}_2(g) \]

\[ \Delta_r H^\circ = -1452.8 \text{ kJ mol}^{-1} \]

What is the value of ΔₚH° if (a) the equation is multiplied throughout by 2, (b) the direction of the reaction is reversed so that the products become the reactants and vice versa, and (c) water vapor instead of liquid water is the product?

3.41 Which of the following standard enthalpy of formation values is not zero at 25°C? Na(s), Ne(g), CH₄(g), S₈(s), Hg(l), H(g).

3.42 The standard enthalpies of formation of ions in aqueous solution are obtained by arbitrarily assigning a value of zero to H⁺ ions; that is, ΔₚH°[H⁺(aq)] = 0. (a) For the following reaction,

\[ \text{HCl}(g) \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq) \]

\[ \Delta_r H^\circ = -74.9 \text{ kJ mol}^{-1} \]

calculate the value of ΔₚH° for the Cl⁻ ions. (b) The standard enthalpy of neutralization between a HCl solution and a NaOH solution is found to be -56.2 kJ mol⁻¹. Calculate the standard enthalpy of formation of the hydroxide ion at 25°C.

3.43 Determine the amount of heat (in kJ) given off when 1.26 × 10⁻⁴ g of ammonia is produced according to the equation

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \]

\[ \Delta_r H^\circ = -92.6 \text{ kJ mol}^{-1} \]

Assume the reaction takes place under standard-state conditions at 25°C.

3.44 When 2.00 g of hydrazine decomposed under constant-pressure conditions, 7.00 kJ of heat were transferred to the surroundings:

\[ 3\text{N}_2\text{H}_4(l) \rightarrow 4\text{NH}_3(g) + \text{N}_2(g) \]

What is the ΔₚH° value for the reaction?

3.45 Consider the reaction

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \]

\[ \Delta_r H^\circ = -92.6 \text{ kJ mol}^{-1} \]

If 2.0 moles of N₂ react with 6.0 moles of H₂ to form NH₃, calculate the work done (in joules) against a pressure of 1.0 atm at 25°C. What is the value of ΔₚU for this reaction? Assume the reaction goes to completion.

3.46 The standard enthalpies of combustion of fumaric acid and maleic acids (to form carbon dioxide and water) are -1336.0 kJ mol⁻¹ and -1359.2 kJ mol⁻¹, respectively. Calculate the enthalpy of the following isomerization process:

![Maleic acid to Fumaric acid](image)

3.47 From the reaction

\[ \text{C}_10\text{H}_8(s) + 12\text{O}_2(g) \rightarrow 10\text{CO}_2(g) + 4\text{H}_2\text{O}(l) \]

\[ \Delta_r H^\circ = -5153.0 \text{ kJ mol}^{-1} \]

and the enthalpies of formation of CO₂ and H₂O (see Appendix 2), calculate the enthalpy of formation of naphthalene (C₁₀H₈).

3.48 The standard molar enthalpy of formation of molecular oxygen at 298 K is zero. What is its value at 315 K? (Hint: Look up the Cᵥ value in Appendix 2.)

3.49 Which of the following substances has a nonzero ΔₚH° value at 25°C? Fe(s), I₂(l), H₂(g), Hg(l), O₂(g), C(graphite).
3.50 The hydrogenation for ethylene is

\[ \text{C}_2\text{H}_4(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g) \]

Calculate the change in the enthalpy of hydrogenation from 298 K to 398 K. The \( C_p \) values are: \( \text{C}_2\text{H}_4: 43.6 \text{ J K}^{-1} \text{ mol}^{-1} \) and \( \text{C}_2\text{H}_6: 52.7 \text{ J K}^{-1} \text{ mol}^{-1} \).

3.51 Use the data in Appendix 2 to calculate the value of \( \Delta_r H^\circ \) for the following reaction at 298 K:

\[ \text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g) \]

What is its value at 350 K? State any assumptions used in your calculation.

3.52 Calculate the standard enthalpy of formation for diamond, given that

\[ \text{C(graphite)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \]
\[ \Delta_r H^\circ = -393.5 \text{ kJ mol}^{-1} \]
\[ \text{C(diamond)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \]
\[ \Delta_r H^\circ = -395.4 \text{ kJ mol}^{-1} \]

3.53 Photosynthesis produces glucose, \( \text{C}_6\text{H}_{12}\text{O}_6 \), and oxygen from carbon dioxide and water:

\[ 6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \]

(a) How would you determine the \( \Delta_r H^\circ \) value for this reaction experimentally? (b) Solar radiation produces approximately \( 7.0 \times 10^{14} \text{ kg glucose a year on Earth.} \)

What is the corresponding change in the \( \Delta_r H^\circ \) value?

3.54 From the following heats of combustion,

\[ \text{CH}_3\text{OH}(l) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l) \]
\[ \Delta_r H^\circ = -726.4 \text{ kJ mol}^{-1} \]
\[ \text{C(graphite)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \]
\[ \Delta_r H^\circ = -393.5 \text{ kJ mol}^{-1} \]
\[ \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \]
\[ \Delta_r H^\circ = -285.8 \text{ kJ mol}^{-1} \]

calculate the enthalpy of formation of methanol (\( \text{CH}_3\text{OH} \)) from its elements:

\[ \text{C(graphite)} + 2\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CH}_3\text{OH}(l) \]

3.55 The standard enthalpy change for the following reaction is 436.4 kJ mol\(^{-1}\):

\[ \text{H}_2(g) \rightarrow \text{H}(g) + \text{H}(g) \]

Calculate the standard enthalpy of formation of atomic hydrogen (H).

3.56 Calculate the difference between the values of \( \Delta_r H^\circ \) and \( \Delta_r U^\circ \) for the oxidation of \( \alpha\)-d-glucose at 298 K:

\[ \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \]

3.57 Alcoholic fermentation is the process in which carbohydrates are broken down into ethanol and carbon dioxide. The reaction is very complex and involves a number of enzyme-catalyzed steps. The overall change is

\[ \text{C}_6\text{H}_{12}\text{O}_6(s) \rightarrow 2\text{C}_2\text{H}_5\text{OH}(l) + 2\text{CO}_2(g) \]

Calculate the standard enthalpy change for this reaction, assuming that the carbohydrate is \( \alpha\)-d-glucose.

**Bond Enthalpy**

3.58 (a) Explain why the bond enthalpy of a molecule is always defined in terms of a gas-phase reaction. (b) The bond dissociation enthalpy of \( \text{F}_2 \) is 150.6 kJ mol\(^{-1}\). Calculate the value of \( \Delta_r H^\circ \) for \( \text{F}_2(g) \). (c) From the molar enthalpy of vaporization of water at 373 K and the bond dissociation enthalpies of \( \text{H}_2 \) and \( \text{O}_2 \) (see Table 3.4), calculate the average O–H bond energy in water, given that

\[ \text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \]
\[ \Delta_r H^\circ = -285.8 \text{ kJ mol}^{-1} \]

3.60 Use the bond enthalpy values in Table 3.4 to calculate the enthalpy of combustion for ethanol,

\[ 2\text{C}_2\text{H}_6(g) + 7\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \]

Compare your result with that calculated from the enthalpy of formation values of the products and reactants listed in Appendix 2.

**Additional Problems**

3.61 A 2.10-mole sample of crystalline acetic acid, initially at 17.0°C, is allowed to melt at 17.0°C and is then heated to 118.1°C (its normal boiling point) at 1.00 atm. The sample is allowed to vaporize at 118.1°C and is then rapidly quenched to 17.0°C, so that it recrystallizes. Calculate the value of \( \Delta_r H^\circ \) for the total process as described.

3.62 Predict whether the values of \( q, w, \Delta U, \) and \( \Delta H \) are positive, zero, or negative for each of the following processes: (a) melting of ice at 1 atm and 273 K, (b) melting of solid cyclohexane at 1 atm and the normal melting point, (c) reversible isothermal expansion of an ideal gas, and (d) reversible adiabatic expansion of an ideal gas.

3.63 Einstein’s special relativity equation is \( E = mc^2 \), where \( E \) is energy, \( m \) is mass, and \( c \) is the velocity of light. Does this equation invalidate the law of conser-
vation of energy, and hence the first law of thermodynamics?

3.64 The convention of arbitrarily assigning a zero enthalpy value to all the (most stable) elements in the standard state and (usually) 298 K is a convenient way of dealing with the enthalpy changes of chemical processes. This convention does not apply to one kind of process, however. What process is it? Why?

3.65 Two moles of an ideal gas are compressed isothermally at 298 K from 1.00 atm to 200 atm. Calculate the values of $q$, $w$, $\Delta U$, and $\Delta H$ for the process if it is carried out reversibly.

3.66 The fuel value of hamburger is approximately 3.6 kcal g$^{-1}$. If a person eats 1 pound of hamburger for lunch and if none of the energy is stored in his body, estimate the amount of water that would have to be lost in perspiration to keep his body temperature constant. (1 lb = 454 g.)

3.67 A quantity of 4.50 g of CaC$_2$ is reacted with an excess of water at 298 K and atmospheric pressure:

$$\text{CaC}_2(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{Ca(OH)}_2(aq) + \text{C}_2\text{H}_2(g)$$

Calculate the work done in joules by the acetylene gas against the atmospheric pressure.

3.68 An oxyacetylene flame is often used in the welding of metals. Estimate the flame temperature produced by the reaction

$$2\text{C}_2\text{H}_2(g) + 5\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 2\text{H}_2\text{O}(g)$$

Assume the heat generated from this reaction is all used to heat the products. (Hint: First calculate the value of $\Delta_r H^\circ$ for the reaction. Next, look up the heat capacities of the products. Assume the heat capacities are temperature independent.)

3.69 The $\Delta_r H^\circ$ values listed in Appendix 2 all refer to 1 bar and 298 K. Suppose that a student wants to set up a new table of $\Delta_r H^\circ$ values at 1 bar and 273 K. Show how she should proceed on the conversion, using aceton as an example.

3.70 The enthalpies of hydrogenation of ethylene and benzene have been determined at 298 K:

$$\text{C}_2\text{H}_4(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g)$$

$$\Delta_r H^\circ = -132 \text{ kJ mol}^{-1}$$

$$\text{C}_6\text{H}_6(g) + 3\text{H}_2(g) \rightarrow \text{C}_6\text{H}_{12}(g)$$

$$\Delta_r H^\circ = -246 \text{ kJ mol}^{-1}$$

What would be the enthalpy of hydrogenation for benzene if it contained three isolated, unconjugated double bonds? How would you account for the difference between the calculated value based on this assumption and the measured value?

3.71 The molar enthalpies of fusion and vaporization of water are 6.01 kJ mol$^{-1}$ and 44.01 kJ mol$^{-1}$ (at 298 K), respectively. From these values, estimate the molar enthalpy of sublimation of ice.

3.72 The standard enthalpy of formation at 298 K of HF(aq) is $-320.1$ kJ mol$^{-1}$; OH$^-$ (aq), $-229.6$ kJ mol$^{-1}$; F$^-$ (aq), $-329.11$ kJ mol$^{-1}$; and H$_2$O(l), $-285.84$ kJ mol$^{-1}$. (a) Calculate the enthalpy of neutralization of HF(aq),

$$\text{HF}(aq) + \text{OH}^-(aq) \rightarrow \text{F}^-(aq) + \text{H}_2\text{O}(l)$$

(b) Using the value of $-55.83$ kJ mol$^{-1}$ as the enthalpy change from the reaction

$$\text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l)$$
calculate the enthalpy change for the dissociation

$$\text{HF}(aq) \rightarrow \text{H}^+(aq) + \text{F}^-(aq)$$

3.73 It was stated in the chapter that for reactions in condensed phases, the difference between the values of $\Delta_r H$ and $\Delta_r U$ is usually negligibly small. This statement holds for processes carried out under atmospheric conditions. For certain geochemical processes, however, the external pressures may be so great that $\Delta_r H$ and $\Delta_r U$ values can differ by a significant amount. A well-known example is the slow conversion of graphite to diamond under Earth’s surface. Calculate the value of the quantity $(\Delta_r H - \Delta_r U)$ for the conversion of 1 mole of graphite to 1 mole of diamond at a pressure of 50,000 atm. The densities of graphite and diamond are 2.25 g cm$^{-3}$ and 3.52 g cm$^{-3}$, respectively.

3.74 Metabolic activity in the human body releases approximately $1.0 \times 10^4$ kJ of heat per day. Assuming the body is 50 kg of water, how fast would the body temperature rise if it were an isolated system? How much water must the body eliminate as perspiration to maintain the normal body temperature (98.6°F)? Comment on your results. The heat of vaporization of water may be taken as 2.41 kJ g$^{-1}$.

3.75 An ideal gas in a cylinder fitted with a movable piston is adiabatically compressed from $V_1$ to $V_2$. As a result, the temperature of the gas rises. Explain what causes the temperature of the gas to rise.

3.76 Calculate the fraction of the enthalpy of vaporization of water used for the expansion of steam at its normal boiling point.

3.77 The combustion of what volume of ethane (C$_2$H$_6$), measured at 23.0°C and 752 mmHg, would be required to heat 855 g of water from 25.0°C to 98.0°C?

3.78 Calculate the internal energy of a Goodyear blimp filled with helium gas at 1.20 $\times$ 10$^3$ Pa (compared to the empty blimp). The volume of the inflated blimp is $5.5 \times 10^3$ m$^3$. If all the energy were used to heat 10.0
tons of copper at 21°C, calculate the final temperature of the metal. (Hint: 1 ton = 9.072 × 10^5 g.)

3.79 Without referring to the chapter, state the conditions for each of the following equations:
(a) ΔH = ΔU + PΔV, (b) C_P = C_V + nR, (c) γ = 5/3, (d) $P_1 V_1^2 = P_2 V_2^2$, (e) $w = nC_V(T_2 - T_1)$, (f) $w = -PΔV$, (g) $w = -nRT\ln(V_2/V_1)$, and (h) $dH = dq$.

3.80 An ideal gas is isothermally compressed from $P_1$, $V_1$ to $P_2$, $V_2$. Under what conditions would the work done be a minimum? A maximum? Write the expressions for minimum and maximum work done for this process. Explain your reasoning.

3.81 Construct a table with the headings $q$, $w$, $ΔU$, and $ΔH$. For each of the following processes, deduce whether each of the quantities listed is positive (+), negative (−), or zero (0). (a) Freezing of acetone at 1 atm and its normal melting point. (b) Irreversible isothermal expansion of an ideal gas. (c) Adiabatic compression of an ideal gas. (d) Reaction of sodium with water. (e) Boiling of liquid ammonia at its normal boiling point. (f) Irreversible adiabatic expansion of a gas against an external pressure. (g) Reversible isothermal compression of an ideal gas. (h) Heating of a gas at constant volume. (i) Freezing of water at 0°C.

3.82 State whether each of the following statements is true or false: (a) $ΔU \approx ΔH$ except for gases or high-pressure processes. (b) In gas compression, a reversible process does maximum work. (c) $ΔU$ is a state function. (d) $ΔU = q + w$ for an open system. (e) $C_V$ is temperature independent for gases. (f) The internal energy of a real gas depends only on temperature.

3.83 Show that $(δC_V/δV)_T = 0$ for an ideal gas.

3.84 Derive an expression for the work done during the isothermal, reversible expansion of a van der Waals gas. Account physically for the way in which the coefficients $a$ and $b$ appear in the final expression. [Hint: You need to apply the Taylor series expansion:
$$\ln(1 - x) = -x - \frac{x^2}{2} \cdots \text{ for } |x| < 1$$
to the expression $\ln(V - nb)$. Recall that the $a$ term represents attraction and the $b$ term repulsion.]

3.85 Show that for the adiabatic reversible expansion of an ideal gas,
$$T_1^{C_V/R} V_1^2 = T_2^{C_V/R} V_2^2$$

3.86 One mole of ammonia initially at 5°C is placed in contact with 3 moles of helium initially at 90°C. Given that $C_V$ for ammonia is 3$R$, if the process is carried out at constant total volume, what is the final temperature of the gases?

3.87 The typical energy differences between successive rotational, vibrational, and electronic energy levels are $5 \times 10^{-22}$ J, $0.50 \times 10^{-19}$ J, and $1.0 \times 10^{-17}$ J, respectively. Calculate the ratios of the numbers of molecules in the two adjacent energy levels (higher to lower) in each case at 298 K.

3.88 The first excited electronic energy level of the helium atom is $3.13 \times 10^{-19}$ J above the ground level. Estimate the temperature at which the electronic motion will begin to make a significant contribution to the heat capacity. That is, at what temperature will the ratio of the population of the first excited state to the ground state be 5.0%?

3.89 Calculate the total translational kinetic energy of the air molecules in a spherical balloon of radius 43.0 cm at 24°C and 1.2 atm. Is this enough energy to heat 200 mL of water from 20°C to 90°C for a cup of tea? The density of water is 1.0 g cm$^{-3}$, and its specific heat is 4.184 J g$^{-1}$ °C$^{-1}$.

3.90 From your knowledge of heat capacity, explain why hot, humid air is more uncomfortable than hot, dry air and cold, damp air is more uncomfortable than cold, dry air.

3.91 A hemoglobin molecule (molar mass = 65,000 g) can bind up to four oxygen molecules. In a certain experiment a 0.085-L solution containing 6.0 g of deoxygenated hemoglobin was reacted with an excess of oxygen in a calorimeter of negligible heat capacity. Calculate the enthalpy of reaction per mole of oxygen bound if the temperature rose by 0.044°C. Assume the solution is dilute so that the specific heat of the solution is equal to that of water.

3.92 Give an interpretation for the following DSC thermogram for the thermal denaturation of a protein.