II. Thermodynamics: The First Law

A. A thermodynamic system

Thermodynamics is the study of energy changes within a system and energy transfer between a system and its surroundings. The study of thermodynamics was prompted by the desire to design more productive ways to convert heat into work. In order to study energy changes, it was found useful from the beginning to identify a portion of the universe and refer to that portion as a system. The rest of the universe came to be called the surroundings.

The flow of energy between the system and the surroundings and the performance of work by the system on the surroundings or vice-versa is the essence of the study of thermodynamics. As a by-product, however, thermodynamic calculations are of immense usefulness in the study of chemical reactions and in the characterization of the reactivity of substances.

Thermodynamic systems are classified according to whether they can exchange energy and/or matter with the surroundings. Some definitions are as follows:

Isolated system: Neither matter nor energy may be exchanged with the surroundings.

Closed system: Matter cannot be exchanged with the surroundings, but energy may be exchanged.

Open system: Matter and energy may be exchanged with the surroundings

Adiabatic system: Energy in the form of heat may not be transferred between the system and its surroundings. The system is insulated.

For chemists, the most common systems are defined by the walls of the container in which a reaction is carried out: a beaker or reaction vessel on the laboratory bench; a sealed reaction container in a protective vessel; etc.

B. Heat and work

1. Introduction

Work is the transfer of energy accompanied by organized motion with or against an opposing force. Most often, we are concerned with the work done by a system on the surroundings, or vice-versa.

Heat is the transfer of energy that is a result of a temperature difference between two parts of a system or between a system and the surroundings. The source of the heat may be a chemical reaction within the system, in which case it is of especial interest to chemists.
From a molecular point of view, heat is associated with chaotic motion of molecules, while work is associated with a certain order in the motion of the molecules.

In thermodynamics we choose to classify all energy transfers as heat or work. Note that heat or work defines energy in transition, not energy content of a system or its surroundings.

2. Description of a simple process

Consider a container with a tight-fitting piston that is partially filled with liquid water at a temperature at which its equilibrium vapor pressure is equal to the outside pressure (i.e., it is at its boiling point). Imagine also a heat source under the container: a candle, a gas flame, or a hot plate. As the system is heated, liquid is evaporated to form additional gaseous water. The additional gas lifts the piston in order to maintain equal pressures inside and outside the container. Thus, the system does work on the surroundings (the moving piston could be harnessed to some useful process). The heat input to the system is transferred to work done by the system, although a portion of the energy input as heat may be retained by the system. How much work can be done by the input of a given amount of heat? That is a question for thermodynamics.

Although not required by thermodynamics, a molecular picture may be made of the process just described. This molecular picture goes as follows:

a. The energy released by the oxidation of the fuel in the candle or gas flame produces gaseous molecules with high kinetic energy. Collisions with these molecules increase the speeds of the surrounding molecules. Some of the molecules collide with the bottom of the container that holds the water. These collisions increase the energy of the atoms or molecules in the walls of the container, which in turn transfer their excess energy to the water molecules that come in contact with the bottom of the container. This increases the agitation of the water molecules, which in turn makes them more likely to escape the surface of the liquid.

b. More molecules in the gas phase in the same enclosed volume means more collisions per unit time per unit area on the face of the piston and therefore higher pressure. This causes the piston to move in the direction that increases the volume of the container so that the pressure can be brought back to the equilibrium vapor pressure. As the molecules collide with a piston that is moving away from them, they give up some of their energy and some of the molecules may actually condense back to liquid. Thus, not all of the energy transferred as heat increases the energy of the molecules; some of the energy is used to move the piston.

3. Measurement of work

a. Definition and units
By definition, work requires force to move an object and also requires that the object move some distance. The magnitude of the work done \( (w) \) is defined to be the magnitude of the force \( (f) \) multiplied by the distance \( (x_2 - x_1) \), or, if the force varies as the object moves, it is the integral of the force over the distance.

\[
w = f \times (x_2 - x_1) \quad \text{or} \quad w = \int_{x_1}^{x_2} f \, dx
\]

The unit used for work is the product of the unit of force times the unit of length. In SI units this is the newton-meter, N m, which is the joule (J). This is the same unit used for energy. Thus, performance of work requires expenditure of an equivalent amount of energy.

In chemical thermodynamics an important form of work is that called expansion work or pressure-volume work \( (pV \text{ work}) \). One reason why this is so important is that many chemical reactions are carried out in a system that is open to the atmosphere. In most cases in such systems, there is some pressure-volume work, which means that not all of the energy change appears as heat.

b. Simple System I

To see how the \( pV \) product relates to work done, consider the simple system described above. The work done is the force on the piston multiplied by the distance that the piston moves. We recall that pressure is force per unit area. Therefore, the force opposing the move is the external pressure multiplied by the area of the piston \( (pA) \). If the piston moves a distance \( d \), the work done \( (w) \) is

\[
w = pAd
\]

But, \( Ad = V_2 - V_1 \) is the volume swept out by the piston, as seen in the following diagram:

Therefore,

\[
w = p(V_2 - V_1) = p\Delta V
\]

If the pressure is in Pa (i.e., N m\(^{-2}\)) and the volume is in m\(^3\), the work is in J. Note that the result of this calculation is work done by the system on the surroundings. The work done by the
surroundings on the system is the negative of this result. Since we will consistently define \( w \) as the *work done by the surroundings on the system*, we will always write for \( pV \) work either,

\[
\Delta = -p\Delta V \quad \text{or} \quad dw = -pdV
\]

c. A second simple system

The calculation of work done is more complicated if the force varies during the process. In this case, it is necessary to calculate the integral of the force over the distance. To see how this works, consider another simple system. We again assume a cylinder with a tight-fitting piston. This time, however, the cylinder contains a gas that is at the same pressure as the external pressure. Now, we slowly decrease the external pressure. Then, the gas in the cylinder pushes up the piston and increases its volume. We imagine that this is done slowly enough that the inside and outside pressure never differ more than infinitesimally and the temperature remains constant. In this case, the work done by the surroundings on the system is

\[
w = \int_{V_1}^{V_2} p_{\text{ext}} \, dV = \int_{V_1}^{V_2} p_{\text{sys}} \, dV
\]

In this expression, \( V_1 \) is the volume of the system before the work is done and \( V_2 \) is the volume of the system after the work is done; \( p_{\text{ext}} \) is the external pressure and \( p_{\text{sys}} = p_{\text{ext}} = p \) is the system pressure. As the volume of the system increases, the pressure of the gas in the cylinder decreases. We assume an ideal gas (\( pV = nRT \)), so that

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

It is worth emphasizing again that the work just calculated was the work done by the surroundings on the system and would be negative for the process described (\( V_2 > V_1 \)). It should be recalled that the work done by the system on the surroundings is the negative of the work done by the surroundings on the system. In this case, the work done by the system on the surroundings is a positive number, but if the gas had been compressed rather than allowed to expand, the final volume would have been smaller than the original volume and the work done by the system on the surroundings would have been negative. It is of crucial importance in thermodynamic calculations to keep track of the sign of the energy changes.

If one wishes to convert heat into work by one of the simple systems just described, it would be of considerable interest to know the maximum amount of work that can be accomplished by the process of heating the system. Now, the useful work done by the system is the product of the external pressure times the change in volume of the system. Clearly, the system can not do work at all unless the system pressure exceeds the external pressure by at least an infinitesimal amount. Since the amount of work done is proportional to the external pressure, the largest amount of
work will be done when the external pressure is the largest, which is when it is just slightly smaller than the internal pressure. This turns out to be a general conclusion.

The maximum amount of $pV$ work is done when the internal and external pressures are the same (actually when one of the two pressures is infinitesimally larger, but essentially the same). This is the condition of mechanical equilibrium. It is also the condition under which the expansion process can be converted to a compression process by an infinitesimal change in the external pressure. That is, the process is reversible. In irreversible processes, some energy is necessarily converted to heat.

We conclude that maximum work results when system and surroundings are just slightly different from equilibrium, or, said another way, maximum work results from a reversible process.

It turns out that our conclusion is valid for other forms of work as well. For example, we will see that maximum electrical work results from an electrochemical cell (a battery) when the voltage supplied by the battery just equals the opposing voltage. That is, when the battery is operating reversibly.

C. First Law of Thermodynamics

The first law of thermodynamics can be stated in a number of ways that all turn out to be equivalent. In the Atkins text the statement is

"The internal energy of a system is constant unless it is changed by doing work or by heating"

We prefer a more pragmatic form, as follows:

The increase in the internal energy of a system is equal to the sum of the heat input to the system and the work done by the surroundings on the system.

$$U_2 - U_1 \equiv \Delta U = q + w$$

In this mathematical form of the First Law, $\Delta U$ is the increase in the internal energy of the system; it is the internal energy of the system after the conclusion of the process ($U_2$) minus the internal energy of the system before the start of the process ($U_1$). Also, $q$ is the heat input to the system from the surroundings and $w$ is the work done by the surroundings on the system.

It will sometimes be necessary to consider an infinitesimal process in which an infinitesimal amount of work is done and an infinitesimal amount of heat is input. In this case the First Law reads

$$dU = dq + dw$$
The original mathematical equation for the first law follows from this one by integration. We will see that we have to be careful when performing the integration.

One of the more difficult aspects of thermodynamics is understanding the sign conventions. If, for example, \( q = 40 \text{ J} \), then 40 J heat is input to the system. If, on the other hand, \( q = -50 \text{ J} \), then -50 J of heat is input to the system. Since the sign is negative, actually +50 J of heat is given off by the system to the surroundings, but we would still say that -50 J of heat is input to the system. Similarly, if \( w = -100 \text{ J} \), then -100 J of work is done by the surroundings on the system, which means that the system did +100 J of work on the surroundings. It is of crucial importance to keep the sign of the energy and the statement of the process consistent.

Finally, it is worth pointing out that because the heat input to a system and the work done by the system (in a steam engine, for example) are often the practical concern of thermodynamics, in some books, particularly older ones, the First Law is defined with a minus sign between the \( q \) and the \( w \). With such a definition, \( w \) has the opposite sense of the meaning that we use.

D. Calculations involving the First Law of Thermodynamics

1. Adiabatic and constant volume processes

An adiabatic process is one in which no heat is transferred from the system to the surroundings or vice-versa. In such a process, \( q = 0 \) and \( \Delta U = w \). Such a process can take place in a thermally-insulated container or it may take place so rapidly that there has been no chance for heat transfer to take place.

In a constant volume process there can be no \( pV \) work done because, as we saw earlier, \( pV \) work is \( w = -p \Delta V \). In such a process, \( \Delta U = q \). A constant volume system is sometimes referred to as a "bomb", because if one is not careful about heating such a system or carrying out a reaction in such a system, that is just what it becomes.

2. Calorimetry and heat capacity

The ability to change the temperature of a system by heating or cooling it is determined by the heat capacity of the system. The heat capacity of a system depends on the process used for the heating. In a constant volume process, all of the heating increases the internal energy of the system. We write

\[
\Delta U = C_V \Delta T \quad \text{or} \quad dU = C_V dT
\]

Therefore, for a constant volume process,

\[
q_V = C_V \Delta T \quad \text{or} \quad dq_V = C_V dT
\]

We use the subscript \( V \) on the \( q \) to indicate a constant volume heating. The \( C_V \) is called the heat capacity at constant volume. It has units J K\(^{-1}\). If the heat capacity is constant over the
temperature range of interest, the integrated forms of these equations given on the left may be used. If the heat capacity varies over the temperature range of interest, the differential forms on the right must be integrated over the temperature.

3. **The enthalpy**

We have just described the relationship between the heat capacity at constant volume and the temperature change in constant volume processes. But most processes are carried out in containers that are open to the atmosphere and are therefore more nearly constant pressure processes. The first of the two simple processes described above, in which water was heated in a closed container with a movable piston with constant applied pressure, is close to a process in an open container. The work done by the system on the surroundings would be the same if the piston were removed, because the external atmosphere would have to be moved to make room for the water vapor produced. For such processes, it is convenient to define a quantity called the *enthalpy*, which is related to, but not quite the same as, the energy. We will first define the enthalpy and then show why it is useful for constant pressure processes. We use \( H \) as the symbol for the enthalpy and define it as follows:

\[
H = U + pV
\]

Here, \( U \) is the internal energy, \( p \) is the pressure of the system, and \( V \) is the volume of the system. There is no requirement here for an ideal gas, or even for a gas at all.

For any process,

\[
H_2 - H_1 \equiv \Delta H = (U_2 + p_2V_2) - (U_1 + p_1V_1) = \Delta U + \Delta(pV)
\]

For a constant pressure process, \( p_2 = p_1 \), so

\[
\Delta H = \Delta U + p\Delta V \quad \text{(constant pressure process)}
\]

where \( p = p_1 = p_2 \). We showed earlier for the reversible constant pressure evaporation of water that

\[
w = -p\Delta V
\]

so

\[
\Delta U = q + w = q_p - p\Delta V
\]

where \( q_p \) is the heat input for a constant pressure process. If we put this expression for \( \Delta U \) into the expression for \( \Delta H \) for a constant pressure process, the \( p\Delta V \) terms cancel and we find

\[
\Delta H = q_p
\]

That is, the change in enthalpy for a constant pressure process is the heat input to the system for the process. There is an important limitation on this expression. The \( p \) that appears in the
definition of \( H \) is the system pressure whereas the \( p \) that appears in the expression for the work done is the external pressure. If the system and the surroundings are in mechanical equilibrium, then the two pressures are the same and our equation relating the enthalpy change to the heat input at constant pressure is valid. This turns out to be the case for the most common use of this equation -- namely, for a reaction in a vessel that is open to the atmosphere.

4. **State functions**

There is an important practical and mathematical difference between the functions \( U \) and \( H \) on the one hand and the energy transfer quantities \( q \) and \( w \) on the other hand. The functions \( U \) and \( H \) are called *state functions*. By this we mean that they are properties of the system for the given conditions. State functions depend on a limited number of variables such as the pressure, temperature, volume, and numbers of moles per unit volume of the components of the system. The number of such state variables (usually called the number of *degrees of freedom* and symbolized \( F \)) is determined by the *Gibbs phase rule*, which relates \( F \) to the number of *components* \( (C) \) and the number of *physical phases* \( (P) \). We will discuss the meanings of these quantities in more detail later, but for now, we will just state that a gaseous system is a one-phase system, whereas a system that has some liquid in equilibrium with gas is a two-phase system. The Gibbs phase rule is

\[
F = C - P + 2
\]

If \( C = 1 \) and \( P = 1 \), then \( F = 2 \). We already pointed out that the state of a gaseous system is determined by just two of three variables: pressure, volume, and temperature. The internal energy of a single-component gaseous system depends only on two of these three variables. The internal energy of a two-component gas depends on three variables, etc. The important point is that any two identical systems with the same values of the \( F \) variables has the same internal energy. It does not matter how the systems were prepared in their states; the internal energies are the same. That is what is meant by a state function; it depends only on the state and not on the *path*, by which we mean how the state was prepared.

By contrast, the heat transferred and the work done normally depend on the particular process by which heat is transferred and work is done (i.e., they depend on the path). It is possible to convert a system from one state to another by more than one path. The change in internal energy does not depend on the path, but the amount of heat transferred and the amount of work done normally do depend on the path. Interestingly enough, \( q + w \) does not depend on the path even though \( q \) and \( w \), by themselves, normally do.

Since \( H \) depends only on the values of \( U, p, \) and \( V \) for the system, and these are all state functions, then \( H \) is a state function also.

5. **Examples**

a. Assume a system with 2 moles of an ideal gas at 2 atm pressure and a temperature of 300 K. The state of the system is changed to 5 atm and 400 K by two reversible paths: (1) a constant
temperature compression followed by a constant pressure heating; and (2) a constant pressure heating followed by a constant temperature compression. Calculate $\Delta U$, $\Delta H$, $q$ and $w$ for the two paths. Assume that the heat capacity, $C_p = 21 \text{ J K}^{-1} \text{ mol}^{-1}$ (the bar over the symbol $C_p$ means heat capacity per mole).

(1) The first path is as follows:

$$2 \text{ atm, } 300 \text{ K } \rightarrow 5 \text{ atm, } 300 \text{ K } \rightarrow 5 \text{ atm, } 400 \text{ K}$$

For the first step in this path, $\Delta U = 0$, because there is no temperature change (for an ideal gas, $U$ depends on the temperature only). The work done for this compression was worked out above and found to be

$$w = -nRT \ln \frac{V_2}{V_1}$$

For constant temperature, $\frac{V_2}{V_1} = \frac{p_1}{p_2}$, so

$$w = -nRT \ln \frac{p_1}{p_2}$$

Therefore,

$$w = -(2 \text{ mol})(8.315 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K}) \ln \frac{2 \text{ atm}}{5 \text{ atm}} = 4571 \text{ J}$$

Since, $q = \Delta U - w$, $q = 0 - (4571 \text{ J}) = -4571 \text{ J}$.

Because the temperature is constant, $U$ and $pV$ are both constant. Therefore, $\Delta U = \Delta(pV) = 0$, so $\Delta H = 0$. (Recall that $H = U + pV$, so $\Delta H = \Delta U + \Delta(pV)$.)

For the second step in this path, the pressure is constant, but the temperature increases from 300 K to 400 K. For this step,

$$q = q_p = nC_p\Delta T$$

and

$$w = -p\Delta V$$

To obtain $w$, we write

$$w = -p\Delta V = -(pV_2 - pV_1) = -nR(T_2 - T_1)$$

Put in the numbers:
\[ w = -(2 \text{ mol})(8.315 \text{ J} \text{ K}^{-1} \text{ mol}^{-1})(400 \text{ K} - 300 \text{ K}) = -1,663 \text{ J} \]

To obtain \( q \), we put in the numbers

\[ q = (2 \text{ mol})(21 \text{ J} \text{ mol}^{-1} \text{ K}^{-1})(400 \text{ K} - 300 \text{ K}) = 4,200 \text{ J} \]

Then, for this step, \( \Delta U = 4,200 \text{ J} + (-1,663 \text{ J}) = 2,537 \text{ J} \)

Also, because this is a constant pressure step, \( \Delta H = q = 4,200 \text{ J} \).

The totals for the two steps in the first path are

\[ w = 4,571 - 1,663 = 2,908 \text{ J} \]
\[ q = -4,571 + 4,200 = -371 \text{ J} \]
\[ \Delta U = 0 + 2,537 = 2,537 \text{ J} \]
\[ \Delta H = 0 + 4,200 = 4,200 \text{ J} \]

(2) The second path is as follows:

\[ 2 \text{ atm}, 300 \text{ K} \rightarrow 2 \text{ atm}, 400 \text{ K} \rightarrow 5 \text{ atm}, 400 \text{ K} \]

The first step in this path is a constant pressure heating, for which

\[ q = nC_p(T_2 - T_1) = (2 \text{ mol})(21 \text{ J} \text{ K}^{-1} \text{ mol}^{-1})(400 \text{ K} - 300 \text{ K}) = 4,200 \text{ J} \]
\[ w = -p\Delta V = -p(V_2 - V_1) = -nRT_2(T_2 - T_1) \]
\[ = -(2 \text{ mol})(8.315 \text{ J} \text{ K}^{-1} \text{ mol}^{-1})(400 \text{ K} - 300 \text{ K}) = -1,663 \text{ J} \]
\[ \Delta U = q + w = 4,200 \text{ J} + (-1,663 \text{ J}) = 2,537 \text{ J} \]
\[ \Delta H = q = 4,200 \text{ J} \]

The second step in this path is a constant temperature compression at 400 K, for which

\[ \Delta U = 0 \text{ .} \]

Also

\[ w = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{p_1}{p_2} \]
\[ = -(2 \text{ mol})(8.315 \text{ J} \text{ K}^{-1} \text{ mol}^{-1})(400 \text{ K}) \ln \left( \frac{2 \text{ atm}}{5 \text{ atm}} \right) = 6,095 \text{ J} , \]
so that \( q = \Delta U - w = 0 - w = -6,095 \text{ J} \).

Finally,
\[
\Delta H = \Delta U + \Delta(pV) = \Delta U + p_2 V_2 - p_1 V_1 = \Delta U + nR(T_2 - T_1) = 0 ,
\]
because \( T_2 = T_1 \) for constant temperature.

The totals for path (2) are as follows:
\[
w = -1,663 + 6,095 = 4,432 \text{ J} \\
q = 4,200 - 6,095 = -1895 \text{ J} \\
\Delta U = 2,537 + 0 = 2,537 \text{ J} \\
\Delta H = 4,200 + 0 = 4,200 \text{ J}
\]

Comparison of the totals for paths (1) and (2) shows that \( \Delta U \) and \( \Delta H \) are the same, as expected for the state functions \( U \) and \( H \). However, \( q \) and \( w \) are different, showing their dependence on path. Nevertheless, \( \Delta U = q + w \) for both paths, as expected from the First Law.

6. Thermochemistry

a. Enthalpy of reaction: introduction and definitions

We want to develop a procedure for computation of the heat absorbed or emitted when a chemical reaction occurs. If the reaction occurs at constant pressure, we have seen that the quantity desired is the enthalpy change for the process. If the reaction occurs at constant volume, it is the internal energy change that we seek. For reactions that do not follow these ideal conditions, we will have to use some combination of these quantities.

We want a procedure that makes use of the properties of elements and compounds, not properties of reactions. This is because there are many more reactions than elements or compounds.

We will begin with an idealized calculation, because it is simplest. Effects of complications can be added if necessary.

The enthalpy or internal energy change for a chemical reaction depends proportionally on how much reactant is consumed and how much product is produced. Therefore, we will calculate the enthalpy or internal energy change for a reaction by assuming that the amounts of reactants and products are given by the stoichiometric coefficients in the accompanying balanced chemical equation with the coefficients assumed to represent moles. Thus, every time we write a number for \( \Delta H \) or \( \Delta U \) for a chemical reaction, there must be some agreed-upon balanced chemical equation.
For example, consider the balanced chemical equation for the combustion of carbon monoxide to produce carbon dioxide:

\[ 2 \text{CO}(g) + \text{O}_2(g) = 2 \text{CO}_2(g) \]

We read this equation as follows: Two moles of carbon monoxide gas react with one mole of oxygen gas to form two moles of carbon dioxide gas. The 2's and the 1 are read to mean moles. The g's in parentheses are added in order to identify the physical states of the constituents in the reaction, because the amount of energy consumed or produced depends on the physical states of the substances.

We refer to the substances on the left of the equals sign as the reactants and the substances on the right of the equals sign as products. We know, however, that sometimes we will get the reaction backwards; that in fact the substances on the right are reacting whereas the substances on the left are forming. Furthermore, in many cases, the reaction goes both ways. Nevertheless, for consistency and clarity, we call the substances on the left reactants and the substances on the right products.

In the reaction as written, two moles of CO(g) and one mole of O\(_2\)(g) disappear and two moles of CO\(_2\)(g) appear. Therefore, the enthalpy change for the process at 298 K is

\[ \Delta H_{298} = 2H_{298}(\text{CO}_2(g)) - H_{298}(\text{O}_2(g)) - 2H_{298}(\text{CO}(g)) \]

In this equation, \( \Delta H_{298} \) is the enthalpy change at 298 K (normally in thermodynamics 298 K really means 298.15 K) for the reaction as written and \( H_{298}(i) \) is the enthalpy per mole at 298 K of the substance \( i \).

The enthalpy per mole in the equation just written must be the enthalpy per mole of the substance as it occurs in the reaction mixture, which may be different from the enthalpy per mole of the substance when it is pure. In fact, because a system changes as a substance is added or deleted, we have to be careful about the definition of the enthalpy per mole. The enthalpy per mole is sometimes called the partial molar enthalpy and is defined as follows:

\[ H_{298}(\text{CO}_2(g)) = \left( \frac{\partial H_{\text{total}}}{\partial m(\text{CO}_2(g))} \right)_{p,T,m'} \]

In this equation, \( m(\text{CO}_2(g)) \) is the number of moles of CO\(_2\) in the reaction vessel.

There are two equivalent interpretations of the right-hand side of this equation:
(i) \( \overline{H}_{298}^{\text{CO}_2(g)} \) is the increase in the total enthalpy of the system when one mole of \( \text{CO}_2(g) \) is added to a very large system at constant temperature \( T \), constant pressure \( p \), and constant numbers of moles per unit volume of all of the other substances in the system.

(ii) \( \overline{H}_{298}^{\text{CO}_2(g)} \) is the ratio of the increase in the total enthalpy of the system to the number of moles of \( \text{CO}_2(g) \) added when a very small amount of \( \text{CO}_2(g) \) is added at constant temperature \( T \), constant pressure \( p \), and constant numbers of moles per unit volume of all of the other substances in the system.

It looks as though we could proceed by simply measuring the enthalpy per mole of all of the chemicals that we are interested in. We recall, however, that the enthalpy is the internal energy + \( pV \), and then we remember that there is a problem with the zero of energy. We normally are able only to measure energy differences, not absolute values of the energy. For this reason, no one has been able to devise a scheme for reporting absolute enthalpies per mole of elements and compounds. Fortunately, there exists an alternative way of proceeding.

An important point to remember is that almost no chemical system is composed of only the reactants and products of a chemical reaction, and even the reactants themselves are seldom present in stoichiometric amounts. It turns out that the total enthalpy of a reaction mixture is a sum of the partial molar enthalpies of all of the substances in the mixture each multiplied by the number of moles of the substance in the mixture.

\[
H_{\text{total}} = m_1 \overline{H}(1) + m_2 \overline{H}(2) + m_3 \overline{H}(3) + \cdots
\]

Here, the \( m_i \) are the numbers of moles of the substances in the reaction mixture; they are not the stoichiometric coefficients in any chemical equation. The equation for \( \Delta H_{\text{total}} \) that we wrote above is the equation for the change in \( H_{\text{total}} \) as a result of a reaction.

b. \( \textbf{Enthalpy of reaction: Hess's Law} \)

Consider the two-step process:

\[
\begin{align*}
\text{C}(s) \; + \; \frac{1}{2} \text{O}_2(g) & \; = \; \text{CO}(g) \\
\text{CO}(g) \; + \; \frac{1}{2} \text{O}_2(g) & \; = \; \text{CO}_2(g)
\end{align*}
\]

(We are allowed to use \( \frac{1}{2} \) for a stoichiometric coefficient, because we are interpreting the coefficients as numbers of moles.)

If we add the reactants of the two equations, add the products of the two equations, and cancel the \( \text{CO}(g) \) occurring on both sides of the result, we obtain
C(s) + O_2(g) = CO_2(g)

Hess's law says that the energy or enthalpy change of the overall reaction is exactly the sum of the energy or enthalpy changes of the two constituent reactions. That is, the overall energy or enthalpy change is the same whether a reaction is carried out all at once or whether it is carried out in steps. Of course, because \( U \) and \( H \) are state functions, their changes do not depend on the path; so Hess's Law is obvious. Also, if the two methods of carrying out a reaction were different, it would be possible to create or destroy energy by carrying out one of the processes in reverse. The First Law and all of our experience says that this is impossible. Indeed, our understanding of atoms and molecules also says that this is impossible, but the First Law is silent on this point.

c. **Enthalpy of reaction: definition and use of enthalpies of formation**

Chemists know that atoms are neither created nor destroyed in chemical reactions (we ignore nuclear reactions, for which what we are about to say still works after slight modification). To use this fact to set up a system for calculation of the enthalpy of reaction, we begin by making three definitions:

i) The **standard state of a substance** is a defined physical state of the pure substance at 1 bar pressure and the temperature of interest. Normally, the defined state of the substance is the state in which the substance is found at the specified temperature: i.e., liquid for water at 298 K, gas for nitrogen at 298 K, etc.

ii) The **formation reaction for a substance** is the reaction in which one mole of the substance in the state of interest is formed at the temperature of interest from its elements in their **standard reference states**. The **standard reference states** of the elements are the standard states of agreed-upon reference forms of the elements.

For example,

\[ \text{C(s, graphite)} + \text{O}_2(g) = \text{CO}_2(g) \]

is the formation reaction for \( \text{CO}_2(g) \). First, we note that one mole of \( \text{CO}_2(g) \) is produced in the reaction, as required by the definition of a formation reaction. The reason for the specification of the elemental carbon as graphite is that graphite has been selected to be the reference form of solid carbon. Other forms of solid carbon (e.g., diamond) have slightly different partial molar enthalpies. The reference form for \( \text{O}_2 \) is the common standard state for the gas - the gas at 1 bar pressure (actually, it is a hypothetical state in which the gas is behaving ideally; more about this later). A more complicated example is the formation reaction for calcium sulfate, which is

\[ \text{Ca(s)} + \text{S(s, rhombic)} + 2 \text{O}_2(g) = \text{CaSO}_4(s) \]

Here, we assume that the rhombic crystalline modification of \( \text{S} \) is the reference form.
An important point about the formation reaction is that it need not be necessary for the formation reaction to be a practical method of preparation, or even that it be a feasible reaction. Carbon dioxide can be formed by burning graphite, but it is probably very difficult to prepare calcium sulfate from its elements.

iii) The enthalpy of formation of a substance in a particular state is defined to be the enthalpy change for the formation reaction for the substance in the state of interest. We will write the enthalpy of formation of a substance as $\Delta H_f$. The standard enthalpy of formation of a substance is the enthalpy change for the formation reaction in which the substance is formed in its standard state; it is written $\Delta H_f^0$. The unit for enthalpy of formation is kJ mol$^{-1}$ because one mole of substance is formed in every formation reaction.

Before proceeding, we point out that the formation reaction for an element in its standard reference state is a null reaction; for example,

$$\text{N}_2(\text{g}) = \text{N}_2(\text{g})$$

is the formation reaction for nitrogen gas. Since this is no reaction at all, it is apparent that the standard enthalpy of formation of nitrogen gas is zero. Similarly, the standard enthalpy of formation of every elemental substance in its standard reference state is zero. Note that the enthalpies of formation of O(g) and O$_3$(g) are not zero, because these are not the reference forms of oxygen. Thus, a convenient way to determine the reference form for an elemental substance is to look for the form that has $\Delta H_f^0 = 0$ in a table of enthalpies of formation.

Now, we make the statement that every reaction can be considered to be a sequence of reversed formation reactions for the reactants followed by formation reactions for the products. Nothing will be left over, because of the rule about conservation of atoms in a balanced chemical equation. It follows from this statement and from Hess’s Law that the enthalpy change for a reaction is the sum of the enthalpies of formation for the products minus the sum of the enthalpies of formation for the reactants.

$$\Delta H = \sum_p \Delta H_f(p) - \sum_r \Delta H_f(r)$$

In this equation, the negative sign for the enthalpies of formation of the reactants is a result of the fact that we need reversed formation reactions for the reactants and for each of these, the enthalpy change is the negative of the enthalpy of formation of the substance.

In the application of the rule for calculation of enthalpy change it is necessary to include in the sums a contribution from every mole of product and every mole of reactant. Furthermore, the enthalpy change for a reaction depends on how the reaction is written.
For example, for
\[ \text{CO}(g) + \frac{1}{2} \text{O}_2(g) = \text{CO}_2(g), \]
\[ \Delta H^\circ = \Delta H^\circ_f(\text{CO}_2(g)) - \Delta H^\circ_f(\text{CO}(g)) \]
whereas for
\[ 2 \text{CO}(g) + \text{O}_2(g) = 2 \text{CO}_2(g), \]
\[ \Delta H^\circ = 2\Delta H^\circ_f(\text{CO}_2(g)) - 2\Delta H^\circ_f(\text{CO}(g)) \]
provided in each case that the reactants and products are all in their standard states. We do not need a contribution from the oxygen in either of these equations because the standard enthalpy of formation for oxygen gas is zero. The enthalpy change for the second reaction is just twice that for the first reaction, because in the second reaction two moles of carbon dioxide are formed, whereas in the first reaction only one mole of carbon dioxide is formed.

In the procedure just described there is no mention of zero of energy and there exist ways of measuring enthalpies of formation of substances. Even when the formation reaction itself cannot be carried out, the enthalpy of formation of a substance can be determined by measuring the enthalpy change for a reaction in which the only unknown enthalpy of formation is the desired one. By these means, extensive tables of enthalpies of formation have been produced.

We have just concluded that the enthalpy change for a chemical reaction can be calculated from enthalpies of formation for the reactants and products by the equation,
\[ \Delta H = \sum_p \Delta H_f(p) - \sum_r \Delta H_f(r) \]
From what was said at the beginning of this section, we should conclude that the enthalpy change for a chemical reaction can also be written
\[ \Delta H = \sum_p \bar{H}(p) - \sum_r \bar{H}(r) \]
where \( \bar{H}(p) \) is the enthalpy per mole of a product molecule and \( \bar{H}(r) \) is the enthalpy per mole of a reactant molecule. From the similarity in appearance of the two equations for \( \Delta H \), there is a temptation to think of the enthalpy of formation of a substance as being the enthalpy per mole of the substance. This is so tempting that it is in fact a common
textbook error. The enthalpy per mole of a substance depends only on the physical properties of the substance itself, whereas the enthalpy of formation for a substance depends on the properties of the substance and on the properties of the elemental substances needed to form the substance. Therefore, the enthalpy per mole and the enthalpy of formation are two very different quantities.

Enthalpies of formation can be used to determine enthalpy changes that accompany physical processes as well. We simply write the physical change as if it were a chemical reaction. For example, for the sublimation of graphite, we can write

\[ C(\text{graphite}) = C(g) \]

Then, for this process,

\[ \Delta H = \Delta H_f(C(g)) - \Delta H_f(C(\text{graphite})) \]

From a table,

\[ \Delta H = (1 \text{ mol})(716.68 \text{ kJ mol}^{-1}) - 0 = 716.68 \text{ kJ}. \]

d. Enthalpy of combustion

An extremely important application of enthalpies of reaction is the calculation of the amount of energy released in a combustion reaction. We will define a combustion reaction to be the reaction of a substance with oxygen gas. For a compound of C, H, and O, it is the reaction of one mole of the substance with gaseous oxygen to produce gaseous carbon dioxide and liquid water. The enthalpy change for this reaction with all of the reactants and products in their standard states at some temperature is the standard enthalpy of combustion of the substance.

For example, a balanced chemical equation for the combustion of methanol is

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

This equation is not in the form of a standard combustion reaction because it is the equation for the combustion of two moles of methanol. The standard combustion reaction for this substance is

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

and for this reaction,

\[ \Delta H^\circ = \Delta H^\circ_{\text{com}} = 2\Delta H_f^\circ(\text{H}_2\text{O}(l)) + 1\Delta H_f^\circ(\text{CO}_2(g)) - 1\Delta H_f^\circ(\text{CH}_3\text{OH}(l)) \]

We put in the number 1’s to emphasize that a stoichiometric coefficient is equal to 1 when it is omitted in a chemical reaction. Furthermore, the stoichiometric coefficients have
units of moles in thermodynamic calculations, as we see, for example, if we calculate the
standard enthalpy of combustion for methanol from a table of enthalpies of formation.

\[ \Delta H_{\text{com}}^0(\text{CH}_3\text{OH}(l)) = (2 \text{ mol})(-285.83 \text{ kJ mol}^{-1}) + (1 \text{ mol})(-393.51 \text{ kJ mol}^{-1}) \\
- (1 \text{ mol})(-238.86 \text{ kJ mol}^{-1}) \\
= -726.31 \text{ kJ} \]

e. **Bond enthalpies**

If a diatomic molecule dissociates, the enthalpy change for the process is called the *bond enthalpy*. If the water molecule dissociates into a hydrogen atom and an OH radical, the enthalpy change is the bond enthalpy for the OH bond. If the OH radical further dissociates into an oxygen and a hydrogen atom, that could also be called the OH bond enthalpy. To what extent are these two values of the OH bond enthalpy the same? The answer is

\[
\begin{align*}
\text{H}_2\text{O}(g) & \rightleftharpoons \text{H}(g) + \text{OH}(g) \quad \Delta H = 499 \text{ kJ} \\
\text{OH}(g) & \rightleftharpoons \text{H}(g) + \text{O}(g) \quad \Delta H = 428 \text{ kJ}
\end{align*}
\]

It can be seen that the two values are not the same, although they are not greatly different.

It turns out to be useful to construct a table of *mean bond enthalpies* by computing the average value of the bond enthalpy for a large number of examples of a particular chemical bond. With such a table, it is possible to estimate the enthalpy change for a reaction. As an example, we calculate a variation of the combustion enthalpy for ethylene, which is the enthalpy change for the reaction,

\[
\text{C}_2\text{H}_4(g) + 3 \text{O}_2(g) = 2 \text{CO}_2(g) + 2 \text{H}_2\text{O}(g)
\]

(The combustion reaction, as we have defined it, should have \(\text{H}_2\text{O}(l)\) rather that \(\text{H}_2\text{O}(g)\), but bond enthalpies require gas phase species.) For this reaction, we find by using enthalpies of formation that

\[ \Delta H = 2(-241.82) + 2(-393.51) - (+52.26) = -1323 \text{ kJ} \]

To estimate this value by using bond enthalpies, we use the relation,

\[ \Delta H \equiv \sum_r B_r - \sum_p B_p \]

where \(B_r\) is the *mean bond enthalpy* for a bond in a reactant molecule and \(B_p\) is the *mean bond enthalpy* for a bond in a product. Note the difference between the following two expressions:
\[ \Delta H = \text{sum of enthalpies of formation of products minus reactants; } \]

\[ \Delta H \equiv \text{sum of mean bond enthalpies of reactants minus products. } \]

The expression in terms of enthalpies of formation is exact, whereas the expression in terms of mean bond enthalpies is only approximate, as we will now see for the combustion of ethylene.

\[ \Delta H \equiv 4B(C-H) + B(C=C) + 3B(O=O) - 4B(C=O) - 4B(O-H) \]

\[ = 4(412) + (612) + 3(497) - 4(743) - 4(463) = -1073 \text{ kJ} \]

The result using bond enthalpies is about 250 kJ different from the correct result. Nevertheless, the bond enthalpy result is a useful estimate of the correct value, and its usefulness is greatly increased when there are not too many bonds broken and made in the chemical reaction of interest.

t. \textit{Temperature dependence of the enthalpy change for a process}

We have seen that the enthalpy change for a process can be computed by first writing the process as a balanced chemical equation and then calculating the sum of the enthalpies of formation of the products minus the sum of the enthalpies of formation of the reactants. This works extremely well if the enthalpies of formation are known for the temperature of interest, but if the process is to be carried out at a different temperature, then it is necessary either to correct the enthalpies of formation to the new temperature or to correct the overall reaction enthalpy to the new temperature. It is usually easier to do the latter.

To develop a procedure for calculation of the enthalpy change at a temperature \( T_2 \) from the value at temperature \( T_1 \), we write the following equations in terms of the enthalpies per mole of the reactants and products:

\[ \Delta H_{T_2} = \sum_p \bar{H}_{T_2}(p) - \sum_r \bar{H}_{T_2}(r) \]

\[ \Delta H_{T_1} = \sum_p \bar{H}_{T_1}(p) - \sum_r \bar{H}_{T_1}(r) \]

Then,

\[ \Delta H_{T_2} - \Delta H_{T_1} = \sum_p \left( \bar{H}_{T_2}(p) - \bar{H}_{T_1}(p) \right) - \sum_r \left( \bar{H}_{T_2}(r) - \bar{H}_{T_1}(r) \right) \]

Now, for any substance \( i \), the enthalpy per mole at temperature \( T_2 \) minus the enthalpy per mole at temperature \( T_1 \) is the integral of the heat capacity \( C_p \) between the two
temperatures. But, if the two temperatures are not too different, so there is not much change in the heat capacity between the two temperatures, this may be calculated by multiplying the heat capacity by the temperature difference, as follows:

\( \bar{H}_{T_2}(i) - \bar{H}_{T_1}(i) = \int_{T_1}^{T_2} \bar{C}_p(i) \,dT \equiv \bar{C}_p(i)(T_2 - T_1) \)

Therefore,

\( \Delta H_{T_2} = \Delta H_{T_1} + \left( \sum_p \bar{C}_p(p) - \sum_r \bar{C}_p(r) \right)(T_2 - T_1) \)

Sometimes, this is written,

\( \Delta H_{T_2} = \Delta H_{T_1} + \Delta C_p \Delta T \)

and called *Kirchhoff's Law*. In this equation \( \Delta T = T_2 - T_1 \) and

\( \Delta C_p = \sum_p \bar{C}_p(p) - \sum_r \bar{C}_p(r) \)

We emphasize that in these sums over reactants and products, every mole of reactant and product must be summed over. Thus, if there are two moles of CO_2(g) in the balanced equation, the heat capacity per mole for this substance must be multiplied by two in the sum.

As an example, we calculate the standard enthalpy of formation of NH_3(g) at 400 K given that it is -46.11 kJ at 298 K. The molar heat capacities of N_2(g), H_2(g), and NH_3(g) are 29.13, 28.82, and 36.00 J K^{-1}, respectively. The formation reaction is

\( \frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) = NH_3(g) \)

(Note that the equation has been written to produce one mole of ammonia, as required for the formation reaction.)

Then,

\( \Delta C_p = 36.00 - \frac{1}{2}(29.13) - \frac{3}{2}(28.82) = -21.80 \text{ J K}^{-1} = -0.02180 \text{ kJ K}^{-1} \)

Since \( \Delta T = 400 - 298 = 102 \text{ K} \),

\( \Delta H_{400} = -46.11 \text{ kJ} + (-0.02180 \text{ kJ K}^{-1})(102 \text{ K}) = -48.33 \text{ kJ} \)
g. *Relation between $\Delta H$ and $\Delta U$ for a chemical reaction*

From the definition of $\Delta H$, we find

$$\Delta H = \Delta U + \Delta (pV)$$

Here,

$$\Delta (pV) = \sum_p (pV)_p - \sum_r (pV)_r$$

That is, $\Delta (pV)$ is the sum of the value of $pV$ for each product molecule minus the sum of the value of $pV$ for each reactant molecule. Now, for each mole of any reactant or product that may be assumed to be an ideal gas, $pV = RT$. If there are $n$ moles of a gaseous reactant or product in the equation, the contribution to $\Delta (pV)$ is $pV = nRT$.

The contributions from liquids or solids to $\Delta (pV)$ is normally so small that it can be ignored. (If the reaction contains only liquids and solids, there may be occasions when $\Delta (pV)$ must be calculated). The usual desired relationship between $\Delta H$ and $\Delta U$ is

$$\Delta H = \Delta U + \Delta nRT$$

For this relation, we look at the balanced chemical equation and determine $\Delta n$ from

$$\Delta n = \text{no. of moles of gaseous products} - \text{no. of moles of gaseous reactants}$$