Thermodynamics

The science of thermodynamics originally evolved from a variety of observational evidence which indicated that mechanical energy is transformable into heat. For example, Benjamin Thompson (1753–1814) of Woburn, Massachusetts, better known as Count Rumford of the Holy Roman Empire, was impressed by the amount of heat generated during the boring of cannon at the arsenal in Munich. In 1798 he proposed that the heat was formed by conversion of the mechanical energy expended by the boring and actually calculated the amount of heat generated by one horse turning the borer for one hour. Count Rumford’s ideas about the equivalence of work and heat were supported by Sir Humphry Davy (1778–1829), who demonstrated in 1799 that two pieces of ice could be made to melt by rubbing them together by a clockwork mechanism in a vacuum. Nevertheless, the scientific community did not accept this idea for nearly 50 years until James P. Joule (1818–1889), working in his father’s brewery in Manchester, England, carefully measured the rise in temperature caused by stirring water with a mechanical paddle wheel. His research between 1840 and 1849 clearly demonstrated that the expenditure of a certain amount of work always produced the same amount of heat (Moore, 1955).

The observation that work is transformable into heat is an extension of the principle of conservation of energy. It can be restated by saying that whenever work is done, heat energy is consumed, implying that one must always pay a price by the expenditure of energy if work is to be accomplished.

Thermodynamics is founded on three basic principles, which arise from common experience but cannot be proved or disproved. They must be accepted as articles of faith. The science of thermodynamics has evolved from these so-called laws by careful deductive reasoning aided by mathematics.

13.1 Definitions

Thermodynamics describes the world the way it appears to an observer in terms of certain measurable properties of matter, such as volume, pressure, temperature, and chemical composition. Matter is regarded as continuous and indistinguishable. In this regard thermodynamics is the opposite of statistical mechanics in which matter is treated as a collection of particles in motion. In order to enter the world of thermodynamics we must first become familiar with certain definitions and conventions that may differ from common usage.

The basic entity for consideration in thermodynamics is the system, which is that part of the universe whose properties are under consideration. The system is separated from the rest of the universe, known as the surroundings, by a boundary whose properties can be defined. A system is said to be open when matter can pass across the boundary and closed when matter is prevented from entering or leaving the system. The boundary may prevent not only matter but also heat and any other form of energy from passing through it. Systems that have such impervious boundaries are said to be isolated. The investigator must identify the system to be studied and specify the properties of its boundary.
The properties of a system are classified as being either *intensive* or *extensive*. Intensive properties, such as pressure, temperature, and density, are independent of the amount of matter that is present, whereas the extensive properties, such as volume, depend on the mass and are therefore additive. When the properties of a system are changed, it experiences a change in its *state*. For example, when a quantity of gas in a cylinder is compressed by moving a frictionless piston, the system undergoes a *change in state*.

The chemical composition of thermodynamic systems is expressed in terms of *components* and *phases*. Nordstrom and Munoz (1986, p. 67) defined a *phase* as “a uniform, homogeneous, physically distinct, and mechanically separable portion of a system.” When the system under consideration is a rock, the minerals of which the rock is composed are the phases. Phases need not be solids, but can also be liquids or gases. For example, a system containing ice, water, and water vapor has three phases (solid, liquid, and gas). The aqueous phase in such a system may also contain a number of ionic or molecular species in solution.

The *components* of a system are the chemical constituents by means of which the chemical compositions of the phases of a system can be completely described. The choice of components is arbitrary. For example, the chemical composition of a rock specimen can be expressed in terms of oxides or in terms of chemical elements. However, the number of components required to describe the compositions of all the phases present in a system at equilibrium is constrained by the *Gibbs phase rule*.

The number of variables that must be specified in order to define the state of a system is equal to the number of components plus the number of intensive properties, such as pressure and temperature. The state of the system is completely defined when the number of variables is equal to the number of independent relations between them. If the number of independent equations is *less* than the number of variables, the system has *variance* or *degrees of freedom*. In this case, the state of the system cannot be completely constrained. When the number of variables exceeds the number of independent equations by one, the system is *univariant* and has one degree of freedom. Univariant systems can be constrained by specifying the value of *one* of the variables. When the number of variables exceeds the number of equations by *two*, the system is *divariant*, and so on.

When a chemical system is at equilibrium, the number of phases (p), the number of components (c), and the number of degrees of freedom (f) must satisfy the Gibbs phase rule (Nordstrom and Munoz, 1986).

$$p + f = c + 2 \quad (13.1)$$

Therefore, systems in which the number of phases is *equal* to the number of components have two degrees of freedom. In other words, pressure and temperature must be specified in this case in order to completely define the state of the system.

All systems contain a certain amount of *heat*, which is defined as that which flows across the boundary of a closed system during a change in its state by virtue of a difference in temperature between the system and its surroundings. Moreover, heat always flows from a point of higher to a point of lower temperature. Thermodynamics defines heat as though it were an invisible fluid whose *direction* of flow is indicated by its algebraic sign. Heat is *positive* when it flows from the surroundings to the system and *negative* when it flows from the system to the surroundings. We can remember this important convention by recognizing that systems are “selfish.” When a system gains heat, the added heat has a positive sign, and when it loses heat the sign is negative.

*Work* is defined in mechanics as the product of force times distance, whereas in thermodynamics work is defined as a quantity that flows across the boundary of a system during a change in its state and is completely convertible into the lifting of a weight in the surroundings. Work,
like heat, is an algebraic quantity, but the sign convention of work is opposite to that of heat. When work flows to the surroundings it has a positive sign, and when it flows to the system it has a negative sign. Another way to visualize the sign convention for work is to say that when the system does work, the work is positive, but when the surroundings do it, the work is negative.

With these definitions and conventions we have now set the stage to introduce the first law of thermodynamics. The presentation will be selective and based on plausibility rather than mathematical rigor. More complete and rigorous presentations can be found in college level textbooks on physical chemistry. Thermodynamics for use by geologists is presented in books by Kern and Weisbord (1967), Wood and Fraser (1976), Fraser (1977), and Nordstrom and Munoz (1986).

\[ \Delta E = (E_2 - E_1) + (E_1 - E_2) = 0 \quad (13.3) \]

The first law of thermodynamics states that the increase in the internal energy of a system during a reversible change in its state is equal to the heat that flows across its boundary from the surroundings \((q)\) minus the work done by the system \((w)\). Therefore, the net change in the internal energy of the system is

\[ \Delta E = q - w \quad (13.4) \]

The first law of thermodynamics implies that work and heat are related and that some of the heat that flows into the system during a change in state is converted into work and therefore does not augment the internal energy.

We can imagine that a reversible change in state can be carried out in small incremental steps such that the internal energy changes by small amounts designated by \(dE\). Now we can restate the first law in differential form,

\[ dE = dq - dw \quad (13.5) \]

where \(dq\) and \(dw\) are very small increments of heat and work, respectively. The most common form of work a system can do during a change in its state is to expand against the constant pressure of the surroundings. Thus we can specify that

\[ dw = PdV \quad (13.6) \]

where \(P\) is the external pressure and \(dV\) is an incremental change in the volume of the system.
A simple demonstration indicates that \( PdV \) does have the dimensions of work (force \( \times \) distance).

\[
PdV = \frac{\text{force} \times (\text{distance})^3}{(\text{distance})^2} = \text{force} \times \text{distance}
\]

(13.7)

Therefore, we can express the first law by the equation

\[
dE = dq - PdV
\]

(13.8)

13.3 Enthalpy

The statement of the first law represented by equation 13.8 enables us to predict the change in the internal energy of a system during a change in its state. The equation indicates that the increase in the internal energy of the system is equal to the heat absorbed from the surroundings minus the work done by the expansion of the system against the pressure exerted by the surroundings. We can carry out such a change in state by integrating equation 13.8 from state 1 to state 2.

\[
\int_{1}^{2} dE = \int_{1}^{2} dq - P \int_{1}^{2} dV
\]

(13.9)

The integration yields

\[
E_2 - E_1 = (q_2 - q_1) - P(V_2 - V_1)
\]

(13.10)

We simplify this result by replacing \( q_2 - q_1 \) by \( q_p \), which is an amount of heat added at constant pressure. In addition, we multiply the \( PV \) terms.

\[
E_2 - E_1 = q_p - PV_2 + PV_1
\]

(13.11)

By rearranging the terms of this equation we obtain

\[
(E_2 + PV_2) - (E_1 + PV_1) = q_p
\]

(13.12)

It is advantageous at this point to define a new kind of energy called the enthalpy \( H \),

\[
H = E + PV
\]

(13.13)

The enthalpy is a function of the state of the system like the internal energy. Therefore, the enthalpy of the system in states 1 and 2 is

\[
H_1 = E_1 + PV_1
\]

(13.14)

\[
H_2 = E_2 + PV_2
\]

(13.15)

Substituting equations 13.14 and 13.15 into equation 13.12 yields

\[
H_2 - H_1 = q_p = \Delta H
\]

(13.16)

In other words, the change in the enthalpy of a system \( (\Delta H) \) during a reversible change in its state at constant pressure is also equal to the heat absorbed by the system during that change in state.

This is a very important and concrete result because \( q_p \) is a measurable quantity. For example, when a chemical reaction is carried out in a well-insulated vessel called a calorimeter, the heat evolved or consumed is indicated by the change in temperature inside the calorimeter. Therefore, equation 13.16 enables us to measure the change in the enthalpy of a system as a result of a chemical reaction, but we still do not know the amount of enthalpy the system contains.

In order to establish a scale for enthalpy we now define a reference state for chemical elements and their compounds. The reference state is defined in terms of certain standard properties that define the so-called standard state. The temperature of the standard state is equal to 25°C (298.15 K), the pressure is 1 atm (recently redefined as 1 bar which is equal to \( 10^5 \) dyne/cm\(^2\), or 0.987 atm, 29.53 mm Hg), and the activity of ions and molecules in aqueous solution is equal to one. In addition, we specify that the enthalpies of the pure elements in their stable state of aggregation in the standard state are equal to zero. Thus we have the definition
The enthalpy of formation of compounds and their ions and molecules in aqueous solution is the heat absorbed or given off by chemical reactions in which the compounds, ions, and molecules form from the elements in the standard state.

We represent this important thermodynamic parameter by the symbol \( H_f^o \), where the superscript \( f \) identifies the standard state and the subscript \( f \) symbolizes "formation."

The standard enthalpies of formation and other thermodynamic constants of many compounds, ions, and molecules have been measured experimentally and are tabulated in the CRC Handbook of Chemistry and Physics (Weast et al., 1986), in Technical Notes of the National Bureau of Standards, and in compilations by Kelley (1962), Robie et al. (1978), Barin et al. (1989), and Woods and Garrels (1987). However, it is important to remember that standard enthalpies of formation and other thermodynamic constants are measurements and are subject to experimental errors. Consequently, the values reported by different investigators for a given compound commonly differ from each other by amounts that may or may not be within the error of the measurements. Such discrepancies in thermodynamic constants affect the results of calculations in which they are used and cause internal inconsistencies. Some of the standard enthalpies of formation listed in the Appendix are average values of two or more determinations that appear to be compatible within the errors of measurement. However, no assurance can be given that these values are accurate to within the stated number of significant figures or that the listed values are internally consistent.

### 13.4 Heats of Reaction

When two compounds or elements, \( A \) and \( B \), react to form a product \( A_2B_3 \) by the reaction

\[
2 A + 3 B \rightarrow A_2B_3 \quad (13.17)
\]

a certain amount of heat is either used up or given off. We can now calculate the amount of this heat \( (q_R) \) from the enthalpy change of the system when the reaction takes place in the standard state. In other words, we treat the reaction as a change in state and calculate the difference in the enthalpy \( (\Delta H_R^o) \) between the final state \( (A_2B_3) \) and the initial state \( (2 A + 3 B) \). Therefore, the change in enthalpy of the reaction in the standard state is

\[
\Delta H_R^o = H_f^o(A_2B_3) - [2H_f^o(A) + 3H_f^o(B)] \quad (13.18)
\]

where \( \Delta H_R^o \) is the heat of the reaction in the standard state and \( H_f^o \) is the standard enthalpy of formation of \( A_2B_3 \), \( A \), and \( B \), respectively. Note that the heat is evolved or absorbed as a result of, or during, the reaction and not when the reaction is at equilibrium. After a reaction has reached equilibrium, the heat of the reaction \( (\Delta H_R) \) is zero because the rates of the forward and backward reactions are exactly equal. Thus, we can state that at equilibrium \( \Delta H_R = 0 \). However, the reference state is a defined condition in which equilibrium does not occur. Therefore \( \Delta H_R^o \) is never zero. In general, \( \Delta H_R^o \) is calculated by summing the standard enthalpies of the products and by subtracting the enthalpies of the reactants.

\[
\Delta H_R^o = \sum_i n_i H_f^o(\text{products}) - \sum_i n_i H_f^o(\text{reactants}) \quad (13.19)
\]

where \( n \) is the molar coefficient of each reactant and product taken from a balanced equation representing the reaction and \( i \) identifies the compounds or ions that participate in the reaction.

Standard enthalpies are expressed in units of kilocalorie per mole (kcal/mol), where the normal calorie is defined as the amount of heat required to raise the temperature of 1 g of water from 14.5 to 15.5 °C. The calorie is equivalent to 4.1840 Joules (J) so that 1 kcal/mol is equal to 4.1840 kJ/mol. At the present time both units are in use.
When $\Delta H^e_R$ of a reaction is positive, the reaction is **endothermic**, which means that heat flows from the surroundings to the system. Conversely, when $\Delta H^e_R$ is negative, the reaction is **exothermic** and heat flows from the system to the surroundings. Endothermic reactions consume heat, whereas exothermic reactions produce heat.

In order to illustrate how heats of reaction are calculated, we choose the reaction between hydrogen and oxygen to form water in the gaseous state, symbolized by (g).

$$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g})$$ (13.20)

The amount of heat absorbed or given off when this reaction occurs at 1 atm and 25°C is given by

$$\Delta H^e_R = 2H^o_f(\text{H}_2\text{O}(\text{g})) - [2H^o_f(\text{H}_2(\text{g})) + H^o_f(\text{O}_2(\text{g}))]$$ (13.21)

The standard enthalpies of H₂ and O₂ are both equal to zero by definition, so that in this case

$$\Delta H^e_R = 2H^o_f(\text{H}_2\text{O}(\text{g}))$$ (13.22)

The standard enthalpy of formation of water vapor is $-57.80$ kcal/mol (Appendix). Therefore,

$$\Delta H^e_R = 2(-57.80) = -115.6 \text{ kcal}$$ (13.23)

We conclude that this reaction is strongly **exothermic**. In fact, this reaction is commonly used to demonstrate the explosive nature of some chemical reactions. Note that the reaction is **endothermic** when equation 13.20 is reversed.

Heat effects are also associated with the disassociation of salts into ions, with phase transformations, and with mixing or dilution of solutions. For example, heat is absorbed from the surroundings when water evaporates to form water vapor.

$$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$$ (13.24)

When the evaporation occurs in the standard state

$$\Delta H^e_R = H^o_f(\text{H}_2\text{O}(\text{g})) - H^o_f(\text{H}_2\text{O}(\text{l}))$$ (13.25)

From the Appendix

$$\Delta H^e_R = (-57.80) - (-68.32) = +10.52 \text{ kcal}$$ (13.26)

Evidently, the evaporation of water at 25°C and 1 atm pressure is an **endothermic** process that requires heat from the surroundings and thereby causes the temperature to decrease. The heat required to evaporate one mole of a liquid is called the **latent heat of evaporation**. When the vapor condenses to form the liquid, the heat given off is called the **latent heat of condensation**.

In other words, evaporation is endothermic, whereas condensation of water vapor is exothermic, and the latent heat of evaporation is equal in magnitude to the heat of condensation. Similarly, fusion or melting of solids is endothermic, whereas crystallization of liquids is exothermic, and the **latent heat of fusion** is equal to the **latent heat of crystallization**.

Note that we are unable to calculate the latent heat of fusion or crystallization of water because it takes place at 0°C rather than at 25°C. Therefore, in order to calculate the latent heat of fusion of water, we must first extrapolate the enthalpies of formation from 25 to 0°C. In general, chemical reactions on the surface of the Earth occur at temperatures between 0 and 100°C, and their heats of reaction therefore commonly differ from those calculated at 25°C.

The response of a reaction at equilibrium to a change in temperature can be predicted on the basis of Le Châtelier's principle. If the forward reaction is exothermic, an **increase** in the temperature favors the backward reaction because it consumes heat and therefore counteracts the increase in the temperature. Consequently, the equilibrium will shift to the left making the equilibrium constant smaller. Similarly, a **decrease** in temperature favors the forward reaction. Therefore, the equilibrium constant increases.

13.5

We must now consider the temperature dependence of the standard equilibrium constant.
13.5 Heat Capacity

When heat is added to a solid, a liquid, or a gas, the temperature of the substance increases. This familiar observation can be stated as an equation

\[ dq = C_dT \]  \hspace{1cm} (13.27)

where \( dq \) is an increment of heat added, \( C \) is a constant known as the heat capacity, and \( dT \) is the corresponding incremental increase in the temperature expressed in kelvins (K). In thermodynamics, temperatures are always expressed on the “absolute” or Kelvin scale, which has its zero point at \(-273.15^\circ C\), when all molecular motion stops and the heat content of pure crystalline materials becomes equal to zero.

The heat capacity is a characteristic property of chemical elements and their compounds that must be measured experimentally. It turns out that heat capacities actually vary with temperature and that it makes a difference whether the heat is added at constant pressure or at constant volume. On the surface of the Earth pressure is constant, and we therefore work with the “heat capacity at constant pressure” symbolized by \( C_p \). Consequently, we restate equation 13.27 as

\[ dq_p = C_p dT \]  \hspace{1cm} (13.28)

We may also expect that exothermic reactions take place spontaneously because they do not require heat from the surroundings. However, this generalization is not correct. It turns out that not all of the heat that enters a system during a reversible change in its state is available to do work. Similarly, the direction in which a reaction proceeds spontaneously is not determined solely by the enthalpy change because systems have an additional property called entropy. We return to this phenomenon in Section 13.6.

We now recall that the heat added to a closed system during a reversible change in its state at constant pressure is equal to the increase in the enthalpy of the system. This conclusion was expressed by equation 13.16, which we now restate in terms of differentials.

\[ dq_p = dH \]  \hspace{1cm} (13.29)

Substituting equation 13.29 into 13.28 yields

\[ dH = C_p dT \]  \hspace{1cm} (13.30)

This equation can be integrated between appropriate temperature limits and therefore enables us to extrapolate enthalpies of formation of compounds from the standard temperature \( (T^\circ) \) to some other temperature \( (T) \) above or below it.

\[ \int_{T^\circ}^T dH = C_p \int_{T^\circ}^T dT \]  \hspace{1cm} (13.31)

By carrying out the integration we obtain

\[ H_T - H_{T^\circ} = C_p (T - T^\circ) \]  \hspace{1cm} (13.32)

Equation 13.32 enables us to calculate the enthalpy of formation of a compound at temperature \( T \) if we know its standard enthalpy and its heat capacity, provided the temperature dependence of \( C_p \) can be neglected.

In reality, use of equation 13.32 to extrapolate enthalpies is limited because the heat capacity is in fact a function of the temperature and there-
fore cannot be treated as a constant in the integration. Moreover, the range of temperatures over which the integration is carried out must not include phase transformations, such as boiling or freezing, which cause a discontinuity in the heat capacity and involve their own enthalpy changes. These restrictions generally are not severe provided the environmental conditions remain between 0 and 100°C at 1 atm pressure. Therefore, the most straightforward procedure is to recalculate the enthalpies of formation of the reactants and products to the desired temperature (between 0 and 100°C) and then to calculate the enthalpy change of the reaction at that temperature.

A more accurate and elegant procedure is based on equations that express the variation of \( C_P \) as a function of temperature in the form

\[
C_P = a + (b \times 10^{-3})T + (c \times 10^{-6})T^2 \tag{13.33}
\]

where \( a, b, \) and \( c \) are constants derived by fitting an algebraic equation to experimentally determined data in coordinates of \( C_P \) and \( T \). Substituting equation (13.33) into equation 13.31 yields

\[
\int_a^T dH = a \int_a^T dT + b \times 10^{-3} \int_a^T TdT + 10^{-6} \int_a^T T^2dT \tag{13.34}
\]

By integrating this equation we obtain

\[
H_T - H_a = a(T - T^0) + \frac{b \times 10^{-3}}{2} [T^2 - (T^0)^2] + \frac{c \times 10^{-6}}{3} [T^3 - (T^0)^3] \tag{13.35}
\]

Equation 13.35 can be applied to the reactants and products of a chemical reaction as specified by equation 13.19. As a result, we calculate \( \Delta a, \Delta b, \) and \( \Delta c \) for the reaction and then evaluate the enthalpy change of the reaction at temperature \( T (\Delta H_{R,T}) \) from the equation

\[
\Delta H_{R,T} - \Delta H_{R}^0 = \Delta a(T - T^0) + \frac{\Delta b \times 10^{-3}}{2} [T^2 - (T^0)^2] + \frac{\Delta c \times 10^{-6}}{3} [T^3 - (T^0)^3] \tag{13.36}
\]

The relationship between \( C_P \) and \( T \) is sometimes expressed in ways that differ from equation 13.33, but the application of these equations is limited by the availability of experimental data.

### 13.6 The Second Law

In the 19th century much work was done by means of steam engines in which hot steam expands in a cylinder and pushes a piston. The steam cools as it expands and is returned to the reservoir at a lower temperature. An important scientific problem of that time was to understand the factors that limit the efficiency of steam engines. This problem was solved in 1824 by the French engineer Sadi Carnot (1796–1832). Without going into the details, we can say that the efficiency of steam engines can never be 100% because some of the heat added to the system must be discharged when the expanded steam returns to the reservoir.

The work of Carnot was a very important contribution to thermodynamics and from it arose a new principle known as the second law of thermodynamics. The essence of the second law is that all systems possess a property called **entropy**, named by the German physicist Rudolf Clausius (1822–1888). One way to explain entropy is to say that a certain fraction of the enthalpy of a system is not convertible into work because it is consumed by an increase in the entropy. Another way to explain the meaning of entropy is to compare it to the property of "randomness" rec-

O,nized in statistical mechanics. We shall, however, defer the prediction of these particles, one of the most probable ways of randomization that Carnot pointed out, on the assumption of maximum entropy. The statement that the entropy increases when energy is spent to reverse a process.

When energy is added to a system, it can be rearranged in order. We have already seen the consequences of limited order. This will affect the natural tendency toward popular societies of high entropy and low entropy as described previously, including the "entropy principle" that governs evolution and the "entropy of a state of perfect order 

The second law of thermodynamics states that:

In any process, the entropy of the universe must increase or remain constant.

In any process, the entropy of the universe will increase if the process is reversible and remain constant if the process is irreversible.

Entropy, a measure of the disorder or randomness of a system, is a fundamental concept in thermodynamics. It is used to describe the concentration of pure substances into a mixture.
ognized in statistical mechanics. When one tries to predict the behavior of a collection of particles, one comes to the conclusion that they will most probably assume a condition of maximum randomness. This conclusion leads to the generalization that every system that is left to itself will, on the average, change toward a condition of maximum randomness. The implication of this statement is that the entropy of a system increases spontaneously and that energy must be spent to reverse this tendency.

When entropy is thought of as randomness, it can be recognized in many natural phenomena. We have all learned from the common experiences of life that work must be done to counteract the natural tendency toward disorder. Many popular science books have been written about entropy and its manifestations in everyday life including one by Rifkin (1980) who claimed that "entropy is the supreme law of nature and governs everything we do."

The second law introduces entropy by the statement

In any reversible process the change in the entropy of the system \( dS \) is equal to the heat received by the system \( dq \) divided by the absolute temperature \( T \).

\[
dS = \frac{dq}{T} \quad \text{(reversible process)} \quad (13.37)
\]

In any spontaneous irreversible process the change in entropy is greater than this amount.

\[
dS > \frac{dq}{T} \quad \text{(irreversible process)} \quad (13.38)
\]

Entropy, like internal energy and enthalpy, is a property whose magnitude depends on the state of the system. However, unlike internal energy and enthalpy, the absolute value of the entropy of a system can be determined by virtue of the third law of thermodynamics.

Measurements indicate that the heat capacities of pure crystalline materials decrease with decreasing temperature and approach zero at absolute zero. This evidence has been elevated into the third law of thermodynamics which states

\[
\text{The heat capacities of pure crystalline substances become zero at absolute zero. Since } dq = C_d dT \text{ (equation 13.28) and } dS = dq/T \text{ (equation 13.37), it follows that }
\]

\[
dS = C \left( \frac{dT}{T} \right) \quad (13.39)
\]

If the heat capacity is equal to zero at absolute zero, then \( dS = 0 \). Therefore, when a system composed of pure crystalline substances undergoes a reversible change in state at absolute zero, the entropy change \( \Delta S \) is equal to zero. The German physicist Walther Hermann Nernst (1864–1941) expressed these insights by stating that at absolute zero the molar entropies of pure crystalline solids are equal to zero. Therefore, the third law enables us to calculate entropies by integrating equation 13.39 from absolute zero to some higher temperature \( T \).

\[
\int_0^T dS = \int_0^T C \left( \frac{dT}{T} \right) \quad (13.40)
\]

In order to calculate the entropy of an element or compound in the standard state from equation 13.40, the temperature dependence of its heat capacity must be determined experimentally. The standard molar entropies of many elements and compounds have been determined and are listed in reference books including the CRC Handbook of Chemistry and Physics (Weast et al., 1986). Molar entropies are expressed in "entropy units" or calories per degree (cal/deg). When the standard molar entropies of the reactants and products of a chemical reaction are known, the change in the entropy \( \Delta S^\circ_R \) of a chemical reaction or phase transformation can be calculated from the statement

\[
\Delta S^\circ_R = \sum n_i S^\circ_i \text{(products)} - \sum n_i S^\circ_i \text{(reactants)} \quad (13.41)
\]
When $\Delta S_R$ is positive, the entropy of the system increases as a result of the change in state, whereas when $\Delta S_R$ is negative, it decreases. For example, when liquid water evaporates in the standard state to form water vapor

$$H_2O(l) \rightarrow H_2O(g) \quad (13.42)$$

the change in entropy is (Krauskopf, 1979)

$$\Delta S_R = 45.10 - 16.71 = +28.39 \text{ cal/deg} \quad (13.43)$$

The increase in the entropy is consistent with our expectation that water molecules in the gas phase are more randomly distributed than molecules of liquid water. Similarly, when solid NaCl dissociates to form ions,

$$NaCl(s) \rightarrow Na^+ + Cl^- \quad (13.44)$$

the change in entropy is (Krauskopf, 1979)

$$\Delta S_R = 14.0 + 13.5 - 17.2 = +10.3 \text{ cal/deg} \quad (13.45)$$

Evidently, the entropy increases when NaCl dissolves to form ions in aqueous solution because the ions occupy fixed lattice positions in the crystal whereas the ions in the solution are mobile. However, for other reactions $\Delta S_R$ may be negative, which implies a reduction in the entropy of the system.

J. Willard Gibbs (1839–1903) to define a new form of energy, now known as the Gibbs free energy ($G$),

$$G = H - TS \quad (13.46)$$

where $H$ is the enthalpy and $S$ is the entropy. The change in the Gibbs free energy of a chemical reaction in the standard state is

$$\Delta G_R = \Delta H_R - T\Delta S_R \quad (13.47)$$

The Gibbs free energy is a function of the state of the system like the internal energy and the enthalpy. It is therefore subject to the same conventions regarding the standard state as enthalpy and is measured in kilocalories per mole.

The standard Gibbs free energy of formation of a compound ($G_f^\circ$) is the change in the free energy of the reaction by which it forms from the elements in the standard state.

Numerical values of $G_f^\circ$ for compounds and ions in aqueous solution are listed in the Appendix together with values of $H_f^\circ$. The value of $\Delta G_R$ for a reaction is calculated by summing the values of $G_f^\circ$ of the products, each multiplied by its molar coefficient, and by subtracting from it the sum of the $G_f^\circ$ values of the reactants.

$$\Delta G_R = \sum n_i G_f^\circ(\text{products}) - \sum n_i G_f^\circ(\text{reactants}) \quad (13.48)$$

The algebraic sign and magnitude of $\Delta G_R$ depend on the sign and magnitude of $\Delta H_R$ and $\Delta S_R$ in equation 13.47. If the forward reaction is exothermic ($\Delta H_R$ is negative) and the entropy increases ($\Delta S_R$ is positive), then the two terms of equation 13.47 combine to make $\Delta G_R$ negative. If, however, the entropy decreases ($\Delta S_R$ is negative), then $T\Delta S_R$ in equation 13.47 is positive. If $\Delta H_R$ is negative, $\Delta G_R$ will be less negative than $\Delta H_R$ and may even become positive if $T\Delta S > \Delta H$. Note that $T\Delta S$ is in fact a form of

enthalpy change. Therefore, a reaction proceeds spontaneously if $\Delta G < 0$ and if $\Delta H < 0$.

When a reaction occurs in the forward direction, the entropy of the system increases. When the reaction occurs in the reverse direction, the entropy decreases.

If $\Delta G_R$ is large, the reaction will not proceed in the forward direction. If $\Delta G_R$ is small, the reaction will proceed in the forward direction. In general, the smaller the $\Delta G_R$, the greater the chance that the reaction will occur. In other words, the reaction will have a greater force on the system if $\Delta G_R$ is large.

If, however, $\Delta G_R$ is small, the change in entropy is large.

Therefore, the entropy change is very important because it determines the direction of the process. The smaller the $\Delta G_R$, the greater the efficiency of the reaction and the smaller the constant temperature change.

In the reverse reaction, the entropy decreases.
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enthalpy because \( \Delta S = \Delta H/T \) at constant pressure and temperature (equations 13.16 and 13.37). Therefore, \( T \Delta S \) has the dimensions of \( \Delta H \) and the two terms can be added or subtracted from each other.

When \( \Delta G_R^o \) of a reaction is negative, the forward reaction has excess energy when it occurs in the standard state. When \( \Delta G_R^o \) is positive, there is a deficiency of energy for the forward reaction in the standard state and the reaction will therefore run in the backward direction. In general, \( \Delta G_R^o \) is a measure of the driving force of a chemical reaction such as equation 13.17,

\[ 2A + 3B \rightarrow A_2B_3 \]

If \( \Delta G_R^o \) of this reaction is negative, the reaction proceeds as written from left to right in the standard state. When the reaction ultimately reaches equilibrium, the product is more abundant than the reactants so that the equilibrium constant \( K \) is large.

\[ \frac{[A_2B_3]}{[A][B]^3} = K \]

\[ (13.49) \]

If, however, \( \Delta G_R^o \) for reaction 13.17 in the standard state is positive, the reaction runs the other way.

\[ 2A + 3B \rightarrow A_2B_3 \]

\[ (13.50) \]

Therefore, the equilibrium constant is small because the reactants are more abundant than the product. Evidently, the sign and magnitude of \( \Delta G_R^o \) of a reaction can be used to predict both the direction in which a reaction runs in the standard state and the magnitude of the equilibrium constant.

In conclusion, we calculate \( \Delta G_R^o \) for the familiar reaction

\[ \text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} \]

\[ (13.51) \]

calcite

using the data in the Appendix.

\[ \Delta G_R^o = [(-132.3) + (-126.17)] - [(-269.9)] \]

\[ = +11.43 \text{ kcal} \]

\[ (13.52) \]

Since \( \Delta G_R^o \) is positive, the reaction runs from right to left in the standard state and calcite precipitates. The equilibrium constant for reaction 13.51 should therefore be a small number, as we know it to be. It is not surprising that the reaction (equation 13.51) runs to the left in the standard state because the activities of the ions in the standard state are each equal to one and the ion activity product is therefore much larger than the equilibrium constant.

We can also calculate \( \Delta H_R^o \) and \( \Delta S_R^o \) for reaction 13.51 using values of \( H_f^o \) from the Appendix and of \( S_f^o \) from Krauskopf (1979).

\[ \Delta H_R^o = [(-129.7) + (-161.84)] - [(-288.6)] \]

\[ = -2.94 \text{ kcal} \]

\[ (13.53) \]

\[ \Delta S_R^o = [(-12.7) + (-13.6)] - [(+22.2)] \]

\[ = -48.5 \text{ cal/deg} \]

\[ (13.54) \]

Note that \( \Delta S_R^o \) for the dissociation of calcite into ions is negative, implying a decrease in the entropy. Note also that the entropy change is expressed in calories per degree (cal/deg) rather than in kilocalories (kcal). We can now combine \( \Delta H_R^o \) and \( \Delta S_R^o \) for reaction 13.51 and calculate \( \Delta G_R^o \), thereby testing the internal consistency of the thermodynamic data.

\[ \Delta G_R^o = \frac{-2.94 - \frac{298.15(-48.5)}{1000}}{1000} \]

\[ (13.55) \]

where 298.15 is the temperature of the standard state and we divide the \( T \Delta S \) term by 1000 in order to convert calories to kilocalories.

The result is

\[ \Delta G_R^o = +11.5 \text{ kcal} \]

\[ (13.56) \]
which is in satisfactory agreement with $\Delta G^\circ_R = +11.43$ kcal calculated from equation 13.52. Note that $\Delta G^\circ_R$ for the dissociation of calcite into ions is positive even though the reaction is exothermic, that is, $\Delta H^\circ_R$ is negative. This occurs because more heat energy is consumed to decrease the entropy than is produced by the dissociation. Therefore, in this case $\Delta H^\circ_R$ is not a reliable predictor of the direction in which the reaction runs in the standard state.

The sign of $\Delta H^\circ_R$ does, however, enable us to use Le Châtelier’s principle to predict how the equilibrium constant of reaction 13.51 varies with temperature. Since the reaction is exothermic as written, it produces heat which increases the temperature. Therefore, if reaction 13.51 is at equilibrium and the temperature is decreased, the reaction moves to the right because that tends to increase the temperature. When equilibrium is reestablished at a lower temperature, the equilibrium constant is larger than it was before. Therefore, the solubility-product constant of calcite increases with decreasing temperature and calcite becomes more soluble. As we discussed in Section 12.4, thermodynamics provides a rational explanation for the temperature dependence of the solubility of calcite and allows us to predict the course of other chemical reactions provided the necessary data are available.

### 13.8 Derivation of the Law of Mass Action

Because the Gibbs free energy is defined in terms of both the first and second laws of thermodynamics, we can express it in terms of directly measurable properties. We can replace $H$ in equation 13.46 by equation 13.13 and obtain

$$ G = E + PV - TS \quad (13.57) $$

For an infinitesimal change in state at constant temperature $dT = 0$ and

$$ dG = dE + PdV + VdP - TdS \quad (13.58) $$

Substituting equation 13.8 for $dE$ yields

$$ dG = dq - PdV + PdV + VdP - TdS \quad (13.59) $$

Since $dS = dq/T$, $dq = TdS$ and equation 13.59 therefore reduces to

$$ dG = VdP \quad (13.60) $$

We can use equation 13.60 to calculate the change in the Gibbs free energy of one mole of an ideal gas as a function of pressure at constant temperature. Since the volume of gases varies with pressure, we must express the volume in equation 13.60 by an equation that relates volume to pressure. According to the ideal gas law, for one mole of gas

$$ V = \frac{RT}{P} \quad (13.61) $$

where $R$ is the gas constant.

Substituting into equation 13.60 yields

$$ dG = RT \left( \frac{dP}{P} \right) \quad (13.62) $$

Integrating from the standard pressure ($P^\circ$) to some other pressure ($P$)

$$ \int_{P^\circ}^{P} dG = RT \int_{P^\circ}^{P} \frac{dP}{P} \quad (13.63) $$

yields

$$ G_p - G^\circ = RT(\ln P - \ln P^\circ) \quad (13.64) $$

Since $P^\circ = 1$ atm, $\ln P^\circ = 0$. Therefore, equation 13.64 reduces to

$$ G_p - G^\circ = RT \ln P \quad (13.65) $$

where $G_p$ is the molar free energy of the ideal gas at pressure $P$, $G^\circ$ is the molar free energy in the standard state, and $T$ is the temperature of the standard state in kelvins. The molar free energy is also a function of the number of moles of each component in the reaction.

The free energy change $\Delta G$ can be calculated as

$$ \Delta G = \sum n_i G_{i1} - \sum n_i G_{i2} \quad (13.66) $$

According to Le Châtelier’s principle, if a mixture of gases is at equilibrium and a pressure is applied to one of the gases, the pressure will change by a factor corresponding to the number of moles of that gas. Therefore

$$ \sum n_i \Delta G_{i1} = \sum n_i \Delta G_{i2} \quad (13.67) $$

Next, we can go back to the sign of the free energy change and relate it to the sign of the reaction

$$ \sum n_i G_{i1} - \sum n_i G_{i2} = \sum n_i (G_{i1} - G_{i2}) $$

then we can do the following:

$$ \sum n_i G_{i1} - \sum n_i G_{i2} = \sum n_i (G_{i1} - G_{i2}) $$

Similarly,

$$ \sum n_i (G_{i1} - G_{i2}) = \sum n_i G_{i1} - \sum n_i G_{i2} $$

and $RT \ln P$ is the molar free energy of the ideal gas at pressure $P$, $G^\circ$ is the molar free energy in the standard state, and $T$ is the temperature of the standard state in kelvins. The molar free energy

is also a function of the number of moles of each component in the reaction.

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$$ \sum n_i \Delta G_{i1} = \sum n_i \Delta G_{i2} \quad (13.67) $$

Next, we can go back to the sign of the free energy change and relate it to the sign of the reaction

$$ \sum n_i G_{i1} - \sum n_i G_{i2} = \sum n_i (G_{i1} - G_{i2}) $$

then we can do the following:

$$ \sum n_i G_{i1} - \sum n_i G_{i2} = \sum n_i (G_{i1} - G_{i2}) $$

Similarly,

$$ \sum n_i (G_{i1} - G_{i2}) = \sum n_i G_{i1} - \sum n_i G_{i2} $$

and $RT \ln P$ is the molar free energy of the ideal gas at pressure $P$, $G^\circ$ is the molar free energy in the standard state, and $T$ is the temperature of the standard state in kelvins. The molar free energy

is also a function of the number of moles of each component in the reaction.
is also called the chemical potential \( \mu \), and equation 13.65 can be written as

\[
\mu = \mu^0 + RT \ln P \quad (13.66)
\]

The free energy of \( n \) moles of an ideal gas can be calculated by multiplying equation 13.65 by \( n \).

\[
nG_p - nG^0 = nRT \ln P \quad (13.67)
\]

According to Dalton’s law, the total pressure of a mixture of ideal gases is the sum of the partial pressures exerted by each gas in the mixture. Therefore, for a mixture of \( i \) ideal gases,

\[
\sum n_i G_i = RT \sum n_i \ln P_i \quad (13.68)
\]

Next, we assume that the mixture of ideal gases is the result of a chemical reaction and specify that the molar coefficients (\( n \)) of the products are positive and those of the reactants are negative. The provision is not new or arbitrary but goes back to the convention regarding the algebraic sign of heat. If we choose to represent the chemical reaction by the equation

\[
aA + bB \rightarrow cC + dD \quad (13.69)
\]

then we can evaluate what equation 13.68 tells us to do. For example, \( \sum n_i G_i \) means

\[
\sum n_i G_i(\text{products}) - \sum n_i G_i(\text{reactants}) = \Delta G_R \quad (13.70)
\]

Similarly, \( \sum n_i G_i^\circ \) means

\[
\sum n_i G_i^\circ(\text{products}) - \sum n_i G_i^\circ(\text{reactants}) = \Delta G_R^\circ \quad (13.71)
\]

and \( RT \sum n_i \ln P_i \) means

\[
RT(c \ln P_C + d \ln P_D - a \ln P_A - b \ln P_B) = RT \ln \left( \frac{P_C^{P_C} P_D^{P_D}}{P_A^{P_A} P_B^{P_B}} \right) = RT \ln \left( \frac{P_C / P_D}{P_A / P_B} \right) = RT \ln Q \quad (13.72)
\]

where \( Q \) is the reaction quotient. Therefore, we now restate equation 13.68 as

\[
\Delta G_R = \Delta G_R^\circ = RT \ln Q \quad (13.73)
\]

which is valid for a reacting mixture of ideal gases.

The reaction quotient \( Q \) varies continuously as the reaction proceeds until the reaction reaches a state of equilibrium. After equilibrium has been established, the partial pressures of the reactant and product gases become constant because the forward and backward reactions are occurring at the same rate. Therefore, at equilibrium the reaction quotient becomes constant and is known to us as the equilibrium constant.

Next, we consider a very important point: the free energy change of a chemical reaction at equilibrium is equal to zero. This statement becomes obvious if we recall that \( \Delta G_R \) is regarded as the driving force of a chemical reaction. When a reaction is in equilibrium, there is no driving force pushing it one way or the other. However, note that \( \Delta G_R^\circ \) is not zero because it is the change in the Gibbs free energy when the reaction takes place in the standard state. Therefore, \( \Delta G_R^\circ \) is a constant, whereas \( \Delta G_R \) varies as the reaction proceeds from the standard state toward equilibrium. When the reaction reaches equilibrium, \( \Delta G_R \to 0 \), but \( \Delta G_R^\circ \) remains the same.

Returning to equation 13.73 we can now state that for a mixture of ideal gases at equilibrium \( \Delta G_R = 0 \) and therefore

\[
\Delta G_R^\circ = -RT \ln K \quad (13.74)
\]

where \( K \) is the equilibrium constant at the standard temperature. This remarkable equation establishes the functional relationship that exists between \( \Delta G_R^\circ \) and \( K \), both of which are constants that apply to chemical reactions in the standard state and at equilibrium, respectively. In the process of deriving this relationship we have also proved the validity of the Law of Mass Action for reactions among ideal gases. These two results are among the most important contribu-
tions thermodynamics has made to science. Equation 13.74 allows us to calculate the numerical values of equilibrium constants at 25°C for all chemical reactions for which we can calculate $\Delta G_R^o$ from existing measurements of the standard free energies of formation.

We reduce equation 13.74 to a formula by converting the equation to logarithms to the base 10 and by substituting $R = 1.987$ cal/deg·mol and $T = 298.15$ K.

$$\Delta G_R^o = \frac{-2.3025 \times 1.987 \times 298.15}{1000} \log K$$

$$= -1.364 \log K$$ (13.76)

The right side of equation 13.75 must be divided by 1000 because $R$ is expressed in calories, whereas $\Delta G_R^o$ is in kilocalories. Therefore, the equilibrium constant $K$ is related to $\Delta G_R^o$ by the formula

$$K = 10^{-\Delta G_R^o/1.364}$$ (13.77)

This is a very useful result, but it applies only to reactions among ideal gases unless we take steps to make it applicable to real gases and to ions and molecules in aqueous solutions.

### 13.9 Fugacity and Activity

In order to make equations 13.74 and 13.77 applicable to reactions among real gases we define the fugacity as the partial pressure a real gas would have if it were ideal. Therefore, fugacities satisfy equation 13.74. In order to apply equation 13.74 to real solutions of any kind we define the activity ($a$) of a solute as

$$a = \frac{f}{f^o}$$ (13.78)

where $f$ is the fugacity of the solute in the solution and $f^o$ is its fugacity when the vapor is in equilibrium with the pure substance in the standard state. Since fugacities are measured in atmospheres or other units of pressure, the activity as defined by equation 13.78 is a dimensionless number. It also follows from equation 13.78 that for a pure substance

$$a = 1.0$$ (13.79)

because the fugacity $f$ of a pure substance is equal to $f^o$.

Binary mixtures of two nonelectrolytes $A$ and $B$ obey Raoult’s law, which states that the fugacity of component $A$ is given by

$$f_A = f^o_A N_A$$ (13.80)

where $N_A$ is the mole fraction of $A$ defined as

$$N_A = \frac{n(A)}{n(A) + n(B)}$$ (13.81)

where $n(A)$ and $n(B)$ are the numbers of moles of $A$ and $B$, respectively. When the solution is dilute, that is, $n(A) \ll n(B)$, the vapor obeys Henry’s law.

$$f_A = k N_A$$ (13.82)

By dividing both sides of equation 13.82 by $f^o_A$, we obtain

$$\frac{f_A}{f^o_A} = \frac{k}{f^o_A} N_A = a_A$$ (13.83)

Next, we note that for a dilute solution of solute $A$ in solvent $B$ the number of moles of $A$ is much smaller than the number of moles of $B$. Therefore, if $n(A) \ll n(B)$, equation 13.81 can be restated to a very good approximation as

$$N_A = \frac{n(A)}{n(B)}$$ (13.84)

The mole fraction of $A$ in a dilute solution can be transformed to an activity ($a_A$) by combining equation 13.83.

$$a_A = \frac{n(A)}{n(B)} = \frac{f_A}{f^o_A} = \frac{k}{f^o_A}$$

where $MW_A$ is the molecular weight of solute $A$.

Since $n(A)$ and $n(B)$ are known we substitute into equation 13.83 to obtain

$$a_A = \frac{k}{f^o_A}$$

and $k'$ is a constant that we substitute into equation 13.83 to obtain

$$a_A = \frac{k'}{f^o_A}$$

By combining equations 13.83 and 13.87 we obtain

$$a_A = \frac{k}{f^o_A} = \frac{k'}{f^o_A}$$

where $k_A$ is a constant

This relation holds regardless of the size or of the solute, provided that the volatile nonvolatile mixture is in water, where $k_A$ is the consequence of activity and the activity of a component. Equation 13.78 is an expression of the dissociation of a solute or a compound in water or in a solvent. It is also useful for calculating the activity of the solute or the solvent. However, it does not hold for a solution of a gas in water, whether the gas is a component of the solution.

The conclusion is quite different for the solutions in 11.2 and 11.3.
be transformed into the molal concentration of A (\(m_A\)) by converting \(n(B)\) to kilograms of B.

\[
m_A = \frac{n(A) \times 1000}{n(B) \times MW(B)}
\]

(13.85)

where \(MW(B)\) is the gram-molecular weight of B. Since \(n(A)/n(B) = N_A\) in dilute solutions of A in B,

\[
m_A = \frac{N_A \times 1000}{MW(B)} = N_A k'
\]

(13.86)

and \(k'\) is a constant equal to \(1000/MW(B)\). When we substitute equation 13.86 into equation 13.83, we obtain

\[
a_A = \frac{k}{f^*_A} N_A = \frac{k m_A}{f^*_A k'}
\]

(13.87)

By combining the three constants in equation 13.87 we obtain

\[
a_A = \gamma_A m_A
\]

(13.88)

where \(\gamma_A\) is the activity coefficient.

This relationship applies to all solutions regardless of the vapor pressures of the solutes or of the solvent. If the solution is a mixture of volatile nonelectrolytes such as acetone dissolved in water, we have no difficulty detecting the presence of acetone vapor and the definition of the activity of acetone in the solution given by equation 13.78 makes sense. Ions produced by the dissociation of salts, acids, and bases in water also produce vapors, but their partial pressures or fugacities are so low that they may be undetectable. However, this experimental difficulty does not alter the validity of relationships derived by consideration of vapors in equilibrium with solutes and solvents regardless of whether they are electrolytes or nonelectrolytes.

The concept of activity presented above is quite different from that discussed in Sections 11.2 and 12.3. We can reconcile the two representations by saying that activities are introduced in thermodynamics in order to extend the Law of Mass Action from reacting mixtures of ideal gases to chemical reactions among molecules and ions in nonideal aqueous solutions. This is accomplished by means of activity coefficients which convert molal concentrations of ions and molecules into activities. When activity coefficients are regarded as dimensionless conversion factors, their activities have the same units as concentrations.

### 13.10 The van't Hoff Equation

Thermodynamics enables us to calculate the equilibrium constants of chemical reactions at 25°C. In order to extrapolate the equilibrium constant from the standard temperature to other temperatures between 0 and 100°C, we return briefly to equation 13.74,

\[
\Delta G_R^o = -RT \ln K
\]

By solving this equation for \(\ln K\) we obtain

\[
\ln K = -\frac{\Delta G_R^o}{RT}
\]

(13.89)

Next, we differentiate equation 13.89 with respect to \(T\).

\[
\frac{d \ln K}{dT} = - \left( \frac{1}{R} \right) \frac{d}{dT} \left( \frac{\Delta G_R^o}{T} \right)
\]

(13.90)

Since \(\Delta G_R^o = \Delta H_R^o - T \Delta S_R^o\), it follows that

\[
\frac{\Delta G_R^o}{T} = \frac{\Delta H_R^o}{T} - \Delta S_R^o
\]

(13.91)

and

\[
\frac{d}{dT} \frac{\Delta G_R^o}{T} = - \frac{\Delta H_R^o}{T^2} - 0
\]

(13.92)
Substituting into equation 13.90 yields

$$\frac{d \ln K}{dT} = \left(-\frac{1}{R}\right)\left(-\frac{\Delta H^\circ R}{T^2}\right) = \frac{\Delta H^\circ R}{RT^2} \quad (13.93)$$

Multiplying by $dT$ gives

$$d \ln K = \left(\frac{\Delta H^\circ R}{R}\right)\left(\frac{dT}{T^2}\right) \quad (13.94)$$

We integrate equation 13.94 from the standard temperature ($T^\circ$) to some other temperature ($T$), which may be higher or lower than $T^\circ$.

$$\int_{T^\circ}^{T} d \ln K = \frac{\Delta H^\circ R}{R} \int_{T^\circ}^{T} \left(\frac{dT}{T^2}\right) \quad (13.95)$$

The result of the integration is

$$\ln K_T - \ln K_{T^\circ} = \left(-\frac{\Delta H^\circ R}{R}\right)\left[\frac{1}{T} - \frac{1}{T^\circ}\right] \quad (13.96)$$

Equation 13.96 is the important van't Hoff equation, which we now restate in terms of logarithms to the base 10.

$$\log K_T = \log K_{T^\circ} - \frac{\Delta H^\circ R}{2.3025R} \left[\frac{1}{T} - \frac{1}{298.15}\right] \quad (13.97)$$

Note that equation 13.97 can be used to calculate $K$ at any temperature between 0 and 100°C if we know the value of $K$ at the standard temperature. However, if the reference temperature differs from 25°C, then $\Delta H^\circ R$ must be evaluated at that temperature by means of heat capacities as shown in equation 13.32 or 13.35.

We have now completed this selective presentation of thermodynamics, which has enabled us to prove the validity of the Law of Mass Action and to calculate equilibrium constants of chemical reactions not only at the standard temperature but also at other temperatures between 0 and 100°C.

### 13.11 Solubility of Amorphous Silica between 0 and 100°C

At the end of Chapter 11 we calculated the solubility of amorphous silica in water as a function of pH at 25°C. We are now in a position to investigate how the solubility of amorphous silica varies as a function of temperature at different values of the pH. The thermodynamic constants required for this calculation are listed in the Appendix.

Amorphous silica reacts with water to form silicic acid.

$$\text{SiO}_2(\text{amorph.}) + 2 \text{H}_2\text{O}() \rightarrow \text{H}_4\text{SiO}_4^+ \quad (13.98)$$

The change in Gibbs free energy of this reaction in the standard state is

$$\Delta G^\circ_k = \left[(-312.66) - \left[-(203.33) + 2(-56.687)\right]\right]$$

$$= +4.044 \text{ kcal} \quad (13.99)$$

and the equilibrium constant $K_T$ is

$$K_T = 10^{-\left[4.044/1.364\right]} = 10^{-2.96} \quad (13.100)$$

The change in enthalpy in the standard state is

$$\Delta H^\circ_k = -349.1 - \left[-215.94 + 2(-68.315)\right]$$

$$= +3.47 \text{ kcal} \quad (13.101)$$

The reaction is endothermic, suggesting that its equilibrium constant increases with temperature. From the van't Hoff equation (13.97)

$$\log K_T = -2.96 - \frac{3.47 \times 10^3}{2.3025 \times 1.987} \left[\frac{1}{T} - \frac{1}{298.15}\right] \quad (13.102)$$

where $R = 1.987 \text{ cal} / \text{deg} \cdot \text{mol}$. Note that $\Delta H^\circ_k$ must be evaluated at the reference temperature.
must be converted to calories in order to be compatible with R. Equation 13.102 reduces to

\[ \log K_T = -2.96 - 758.4 \left( \frac{1}{T} - 0.00335 \right) \]  

(13.103)

When \( T > 298.15 \) K, \( \frac{1}{T} - 0.00335 \) is negative and the algebraic sign of the second term in equation 13.103 changes to plus. Therefore, at \( T = 273.15 \) K (0°C) equation 13.103 yields \( K_T = 10^{-3.20} \), whereas at 373.15 K (100°C) \( K_T = 10^{-2.45} \). Evidently, the equilibrium constant of reaction 13.98 increases with increasing temperature as predicted.

The first dissociation of silicic acid forms \( H_2SiO_4^- \) and \( H^+ \).

\[ H_2SiO_4 \rightarrow H_2SiO_4^- + H^+ \]  

(13.104)

The standard free energy change is \( \Delta G^\circ = +13.24 \) kcal, and the standard enthalpy change is \( \Delta H^\circ = +7.0 \) kcal. Note that the \( G^\circ \) and \( H^\circ \) for \( H^+ \) are both equal to zero. The equilibrium constant of reaction 13.104 at 25°C is \( K = 10^{-9.74} \) and varies with temperature in accordance with the van't Hoff equation.

\[ \log K_T = -9.71 - 1530.03 \left( \frac{1}{T} - 0.00335 \right) \]  

(13.105)

Consequently at 0°C, \( K_T = 10^{-10.19} \), whereas at 100°C, \( K_T = 10^{-8.68} \). Once again, the equilibrium constant increases with rising temperature because reaction 13.104 is endothermic.

These calculations illustrate the point that thermodynamics not only confirms our qualitative predictions based on Le Châtelier’s principle but actually permits us to determine the numerical values of the equilibrium constants of all kinds of chemical reactions between temperatures of 0 and 100°C or other appropriate temperature limits.

Although this is a very important advance in geochemistry, the calculations can become quite

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**Figure 13.1** Solubility of amorphous silica as a function of temperature at different pH values. The equilibrium constants at 25°C were calculated from equation 13.77 using the standard free energies of formation from the Appendix. Equilibrium constants at other temperatures were derived from the van’t Hoff equation (13.97) based on \( K \) and \( \Delta H^\circ \). The activity coefficients of all ions and molecules were assumed to be equal to one. The resulting curves indicate that the concentration of \( SiO_2 \) in milligrams per liter in saturated solutions of amorphous silica in water increases both with increasing temperature and pH.
tedious. Therefore, it is helpful to summarize the results of thermodynamic calculations by means of suitable diagrams. In the case at hand, we want to depict the concentration of SiO$_2$ in saturated solutions of amorphous silica at different values of the pH and temperature. We therefore carry out the calculations first made in Section 11.6 at a series of temperatures for selected pH values and plot the results in Figure 13.1 as a set of curves in coordinates of the concentration of SiO$_2$ and temperature. The diagram depicts the increase in the solubility of amorphous SiO$_2$ with increasing temperature at specified values of the pH. Such diagrammatic representations of chemical reactions are widely used in geochemistry and therefore are the subject of Chapter 14.

13.12 Summary

Thermodynamics is based on three statements regarding the relationship between heat and other forms of energy that do not require proof because they are self-evident. Starting from these basic premises, thermodynamics has grown into a large body of knowledge by rigorous deductive reasoning aided by mathematics. The products of this development include the concepts of enthalpy and Gibbs free energy and a proof of the Law of Mass Action for reacting mixtures of ideal gases.

These results of thermodynamics have great practical value in geochemistry because they permit us to calculate the equilibrium constants of chemical reactions at any desired temperature, limited only by the availability of the necessary thermodynamic parameters and constrained by the stabilities of the reactants and products. Consequently, we can now explore the behavior of chemical reactions on the surface of the Earth and use the results to specify the stability limits of the common rock-forming minerals. Many of the reactions that take place in the natural environment can be studied in the laboratory only with great difficulty because these reactions are so slow. Thermodynamics enables us to make predictions about the outcome of these reactions that can be tested by evidence in the field.

Problems

1. Calculate the enthalpy change when fluorite (CaF$_2$) dissolves in water in the standard state.

2. Based on the result in Problem 1, predict how the solubility of fluorite varies with temperature.

3. Calculate the standard free energy change of the reaction by which fluorite dissociates into ions.

4. Calculate the solubility of fluorite in water at 10, 20, and 30 °C and express each in terms of the concentration of Ca$^{2+}$ in mg/L. (Assume γ = 1 for all species.)

5. Calculate K$_{sp}$ for the reaction between albite (NaAlSi$_3$O$_8$), water, and H$^+$ to form kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$) and silicic acid.

6. Apply the Law of Mass Action to the reaction in Problem 5, take logarithms to the base 10, and express the resulting equation in terms of log [Na$^+$]/[H$^+$] and log [H$_2$SiO$_4$].

7. The water of the Mississippi River at Baton Rouge, Louisiana, has the following chemical composition at pH = 7.2.

<table>
<thead>
<tr>
<th>ppm</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO$_3^-$</td>
<td>101</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>41</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>15</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>1.9</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>34</td>
</tr>
</tbody>
</table>
Calculate log [Na⁺]/[H⁺] and log [H₄SiO₄] for this water using the necessary activity coefficients.

8. Use the results of Problems 6 and 7 to determine the direction of the reaction in Problem 5 in the Mississippi River at Baton Rouge, that is, determine whether albite or kaolinite is produced.

9. Make the necessary calculation (assuming \( T = 25 \text{°C} \)) to determine whether the Mississippi River at Baton Rouge is saturated or undersaturated with respect to (a) calcite, (b) gypsum, (c) amorphous silica, (d) quartz, and (e) dolomite.

10. Calculate the value of \( G_f^\circ \) for BaF₂ given that the concentration of Ba²⁺ in a saturated solution at 25°C, having an ionic strength of 0.01, is \( 1.12 \times 10^{-2} \) m/L. Assume that Ba²⁺ and F⁻ are derived entirely from BaF₂ and that hydrolysis is negligible.

References


