
CHAPTER 7

CHEMICAL THERMODYNAMICS: FUNDAMENTAL PRINCIPLES

In this chapter we return to a formal study of chemical equilibrium, but the approach will be from a new direction. We look now at the energy evolved and consumed in chemical reactions and at the relation of this energy to equilibrium. This is a branch of physical chemistry called thermodynamics, a basic subject that permeates much of modern chemistry and geochemistry. As a predictive tool, thermodynamics has its greatest usefulness in the closed, carefully controlled systems of the chemical laboratory, but we shall find it an aid also in setting limits on what is possible and what is impossible in the more complex systems with which a geologist must deal.

7-1 THERMODYNAMIC SYSTEMS

In geochemistry we apply the principles of equilibrium thermodynamics to a well-defined macroscopic volume of the universe that is referred to as a *thermodynamic system* (Fig. 7-1). We are interested in what happens inside the system. That is, for a given set of conditions what chemical reactions will occur in the system? And how much reaction must take place to attain overall chemical equilibrium?

The dimensions of the system can be chosen to suit specific geochemical problems. We may choose systems that include the entire Earth and its atmosphere, or ones that are limited to a small portion of the Earth such as a hand specimen of rock. Another kind of system consists of experimental apparatus, for example a pressurized heating-vessel used in a laboratory. Thermodynamic systems are classified on the basis of whether or not energy (heat and work) and matter

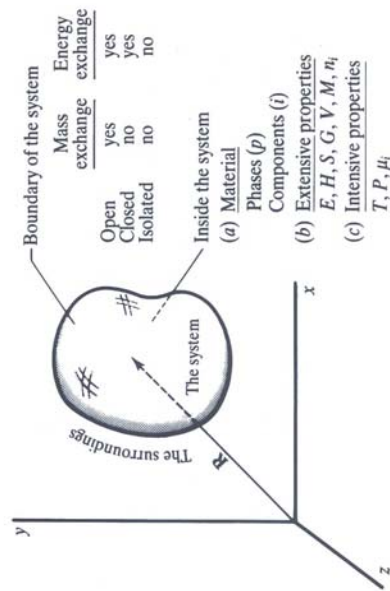


FIGURE 7-1

The thermodynamic system is located in space relative to a coordinate system by the vector (R). It is a well-defined volume separated from the surroundings by its boundaries, and classified in terms of its ability to exchange energy and mass with the surroundings. The interior, composed of phases whose composition is represented by chemical components, is described by a series of extensive and intensive properties.

can be transported across the boundaries outlining the system. There are three types: *isolated systems* cannot exchange energy or matter, *closed systems* can exchange energy but not matter, and *open systems* can exchange both energy and matter. Most thermodynamic systems of geologic interest belong to the last type, open to exchange of energy and matter. Some natural systems, however, have such slow rates of mass exchange with their surroundings that they can be treated as closed thermodynamic systems in a study of chemical equilibrium.

The material in a system is composed of *phases*, each phase having distinct physical and chemical properties. In geochemistry the phases are typically minerals that form rocks, plus fluids, including vapor, water, or magma, that are in contact with the minerals. The composition of each phase is described by a series of discrete chemical formula units, called *chemical components*. For example, we can represent the compositions of alkali feldspar minerals in Fig. 5-7 with the components NaAlSi₃O₈ and KAlSi₃O₈, or the minerals and aqueous solution of the phase diagram in Fig. 4-10 with the components K₂O, Al₂O₃, SiO₂, H₂O, and HCl.

Some properties of a system, like mass and volume, are defined by the system as a whole, and are called *extensive properties*. These properties are additive. For example, the mass of a system is equal to the sum of the masses of all the phases it contains. Internal energy (E), entropy (S), enthalpy (H), Gibbs free energy (G), and the number of moles of chemical components (n_i , where n is the number of moles of a specific component i) are all extensive properties that we will use in this chapter to describe chemical equilibrium. On the other hand, properties like pressure and

temperature take well-defined values at each point within the system, and do not depend on amounts of material. These are called *intensive properties*. They are *not* additive; the temperature of a system is *not* equal to the sum of the temperatures of the individual phases. One example of an intensive property that we will use in the following chapter to describe equilibrium among the phases in a system is chemical potential (μ_i). Handling equilibrium problems in terms of intensive variables is advantageous because these properties are independent of the mass of the system.

The *thermodynamic state* of a system is described by some specified group of independent intensive and/or extensive variables. Any particular property of the system that can be expressed in terms of these variables is called a *function of the state of the system*. As an example, consider a system with one phase, a gas, confined inside a cylinder with a piston at one end that allows the volume of the gas to expand or contract. If we describe the state of the system by specifying temperature (T) and pressure (P), then the volume (V) of the gas will be a function of the state of the system represented by the equation

$$V = F(T, P). \quad (7-1)$$

For one mol of an ideal gas this functional relationship is the familiar gas law,

$$\bar{V} = \frac{RT}{P}, \quad (7-2)$$

which permits calculation of the molar gas volume (\bar{V}) from the variables temperature and pressure.

Functions like Eq. (7-1) are commonly used in thermodynamics to calculate how certain properties respond to changes in the independent variables used to describe the system. For example, how does the volume of the gas in our cylinder respond to changes in temperature and pressure? Such a relationship is represented mathematically by the total derivative of Eq. (7-1),

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP, \quad (7-3)$$

and is graphically illustrated in Fig. 7-2. The change in volume is equal to the sum of two terms: the first is the rate of change in V with respect to T at constant P multiplied by the total change in temperature (dT), and the second is the rate of change in V with respect to P at constant T multiplied by the total change in pressure (dP).

The relation expressed by Eq. (7-3) for one mol of an ideal gas is obtained by first differentiating Eq. (7-2) with respect to pressure and temperature,

$$\left(\frac{\partial \bar{V}}{\partial P}\right)_T = -\frac{RT}{P^2} \quad (7-4)$$

and

$$\left(\frac{\partial \bar{V}}{\partial T}\right)_P = \frac{R}{P}, \quad (7-5)$$

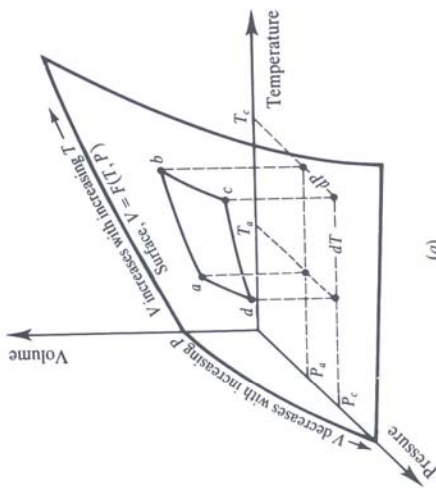


FIGURE 7-2 Schematic illustration of the differential change in volume (dV) when temperature and pressure change from T_a, P_a to T_c, P_c (diagram (a)). Because $V = F(T, P)$, the total derivative of volume [Eq. (7-3)] is composed of two parts: changes with T at constant P along path a to b as shown in diagram (b), and changes with P at constant T along path b to c in diagram (c). Note that the same total differential change in V is obtained along the alternate path a to d to c .

then substituting into Eq. (7-3):

$$dV = -\frac{R}{P^2} dP + \frac{R}{P} dT \tag{7-6}$$

To obtain the total change in molal volume this equation is integrated from the P and T conditions of the initial state ($P_{\text{initial}}, T_{\text{initial}}$) to that of the final state ($P_{\text{final}}, T_{\text{final}}$).

Note in Fig. 7-2 that it does not matter in which order we consider the differential operations involving temperature and pressure [Eq. (7-3)]. The change in volume (for volume in general, not only molal volumes) during a transformation that goes from an initial state to a final state is simply the difference in the volume written as $\Delta V = V_{\text{final}} - V_{\text{initial}}$. The change in volume with respect to changes in temperature and pressure will be the same because volume is a function of the state of the system and is independent of the path followed in changing the state of the system. This independence of path is characteristic of all extensive properties.

Chemical equilibrium will be described in this chapter in terms of the variables temperature, pressure, and composition, using a function of the state of a system called the Gibbs free energy (G),

$$G = F(T, P, n_i) \tag{7-7}$$

To develop relationships between equilibrium and these variables T, P , and n_i , we begin with the laws of thermodynamics, which introduce two additional functions of the state of the system, internal energy (E) and entropy (S).

7-2 THE LAWS OF THERMODYNAMICS

The laws of thermodynamics cannot be proved mathematically. They are simply generalizations derived from laboratory experiments and from ordinary experience that provide practical and useful explanations for many natural phenomena.

First Law: Conservation of Energy

The first law of thermodynamics expresses a relation between heat and work, specifically the heat added to or taken from a system and the associated work done by or done to the system. To give the law a mathematical statement, we postulate the existence of a function of the state of a system called its *internal energy*, E , which can be thought of as the sum of the kinetic and potential energies of its particles. The absolute value of E would be difficult to determine, but for most purposes we are interested only in its changes. Suppose that a change in E is brought about by addition of heat (Q) to a system from its surroundings, and that the system does mechanical work (W) on the surroundings as a result. The first law states that the change in internal energy is equal to the difference between the heat added and the work done, $\Delta E = E_{\text{final}} - E_{\text{initial}} = Q - W$, or in differential form

$$dE = dQ - dW \tag{7-8}$$

In this expression dQ has a positive sign because it represents energy added to the system from its environment, while dW is given a negative sign because it shows energy lost to the system when it does work on the environment. The law, in effect, is a restatement of the law of conservation of energy: an amount of energy is supplied to the system in the form of heat, an amount is removed in the form of work, and the difference is the change of energy within the system. Energy has

moved from one system to another, and a part of it has changed its form from heat to work, but the total amount of energy has remained constant.

To measure the work, suppose the system is arranged so that work is done by expansion against an external pressure. Specifically, suppose that the system is confined to a vertical cylinder and that expansion results in raising a mass (M) at the top of the cylinder against the force of gravity. If the vertical distance moved is Δh , the mechanical energy expended is $Mg\Delta h$, where g is the acceleration of gravity. This energy can also be expressed as $P\Delta V$, where P is pressure and ΔV is the total change in volume, since

$$P = \frac{\text{force}}{\text{area}} = \frac{Mg}{\text{area}} \quad \text{and} \quad \Delta V = \text{area} \times \Delta h.$$

If the expansion is performed reversibly, meaning that internal and external pressures never differ by more than infinitesimal amounts, P may be regarded not as the effect of an added mass, but as the prevailing external pressure acting on the system. Then we write in differential form

$$dW = PdV, \quad (7-9)$$

and Eq. (7-8) becomes

$$dE = dQ - PdV. \quad (7-10)$$

The energy E is a property of the system, determined by the nature and arrangements of its constituent particles. By contrast, Q and W are not properties of the system; their values are dependent on processes by which the state of the system is changed. By different experimental arrangements, the same change in energy, E , can be produced with different combinations of Q and W .

Second Law: Creation of Entropy

The second law of thermodynamics defines a function of the state of the system called *entropy* (S). Like energy, entropy is an extensive property of the system. The second law states that the change in S of a closed system due to a *reversible process* (that is, a process where infinitesimal changes can make the process reverse itself at any time) is equal to the heat absorbed during this process divided by the absolute temperature,

$$dS \equiv \frac{dQ}{T}. \quad (7-11)$$

Thus S is related to Q through the intensive variable T in much the same way as V is related to W by the intensive variable P [$dV = dW/P$, see Eq. (7-9)]. If an irreversible (nonequilibrium) process occurs in the system, the second law states that the total change in entropy will be greater than the heat adsorbed divided by T ,

$$dS > \frac{dQ}{T}. \quad (7-12)$$

This statement is very succinct, and commonly fails to convey the significance of the second law except to those who have had long practice in its use. To help make clear the meaning of entropy and its importance in geochemistry, we look first at two hypothetical experiments.

Suppose that an ideal gas is confined under pressure in a cylinder by a piston that moves without friction, and suppose that an amount of heat Q is added to the gas. The gas responds by expanding against the pressure P exerted by the piston and thereby does an amount of work $P\Delta V$, where ΔV is the total change in volume during the experiment ($\Delta V = V_{\text{final}} - V_{\text{initial}}$). Suppose further that the addition of heat and the resulting expansion take place slowly, so that the pressure of the gas on the piston is never more than infinitesimally higher than the external pressure, and so that the temperature of the gas remains constant. At any time during the expansion it would be possible, by an infinitesimal increase in the external pressure, to reverse the operation—to do work on the gas by moving the piston inward, the work being converted into heat which would escape to the surroundings. Under these conditions we say that the expansion takes place reversibly. In thermodynamics reversible and equilibrium are equivalent terms. The entropy change during the expansion ($\Delta S = S_{\text{final}} - S_{\text{initial}}$), then, is equal to the total amount of heat absorbed divided by the absolute temperature [Eq. (7-11)].

Suppose, still using an ideal gas, we perform the experiment differently: we insert a shutter at the original position of the piston, move the piston back to its position at the end of the preceding experiment, evacuate the space between shutter and piston, then withdraw the shutter and let the gas expand freely to fill the enlarged space. The end result of the experiment is identical with that of the first experiment, for an ideal gas undergoes no temperature change during free expansion. This time we have added no heat and obtained no work, so that both Q and W are zero. The total entropy change (ΔS), however, must be the same as before, since the initial and final states of the gas are identical in the two experiments.

The second experiment is considered to be highly *irreversible* (nonequilibrium): there is no possible way, while the gas is expanding, by an infinitesimal change in external conditions to make the molecules move back to their former restricted volume. The total change in entropy during this experiment is equivalent to that transferred to the system by the heat absorbed *if* the process were carried out reversibly as in the first experiment. The amount of entropy that is supplied from the surroundings in the second experiment is zero; but the total entropy acquired by the gas is of course the same in both experiments, since it depends only on the state of the gas and not on how the expansion is carried out. The entropy acquired by the gas in the second experiment is therefore *new* entropy which was not present originally. In an irreversible process total entropy is not conserved but increases. Since all actual processes are to some extent irreversible, this means that, in any energy change, the total entropy of all systems involved increases. The amount of the net entropy increase measures the extent of irreversibility.

These experiments illustrate the dual role that entropy plays. In a reversible process, the change in entropy of a closed system is proportional to heat exchange

with the surroundings. In an irreversible process the entropy change may have nothing to do with heat, but is defined by some change in the configuration of the system, in this case by the expansion of the gas to a greater volume. The *measure* of entropy change is still the heat that *would* be absorbed if the process were carried out reversibly, and the entropy change is the same whether the process is reversible or not. The differential change in entropy (dS) during any transformation in a closed system will thus be made up of two parts: dS_{ext} , which arises from the exchange of entropy between the system and its exterior,

$$dS_{\text{ext}} = \frac{dQ}{T}, \quad (7-13)$$

and dS_{int} which arises from the creation of entropy inside the system. That is,

$$dS = dS_{\text{ext}} + dS_{\text{int}}. \quad (7-14)$$

Entropy created inside the system is due only to irreversible (nonequilibrium) processes; it is always greater than zero during such processes and equal to zero at equilibrium,

$$dS_{\text{int}} \geq 0. \quad (7-15)$$

As we shall see later, the equality in Eq. (7-15) will provide an important thermodynamic criterion for judging chemical equilibrium in geologic systems.

Difficulty in understanding entropy often arises because of confusion regarding the systems under consideration. In an individual system, entropy may increase or decrease or remain constant during various parts of a cycle of changes. In reversible processes the entropy change in one system, or one part of a system, must be balanced by opposite changes in another system; in irreversible processes the entropy increase in some system or systems is not completely balanced by entropy decreases elsewhere.

Because adding heat to a system always increases its entropy, the meaning of entropy will perhaps become clearer from a general consideration of the possible effects of the added heat. In our hypothetical experiment with a heated gas expanding against a movable piston, the added entropy causes the gas to become more attenuated. Other familiar effects of heat are the melting of a crystalline solid, the evaporation of a liquid, the dissolving of increasing amounts of a salt in water. Thus an expanded gas has greater entropy than compressed gas, a liquid has greater entropy than the corresponding solid, a gas has greater entropy than the liquid from which it comes, and the entropy of a salt-plus-water system increases as more of the salt dissolves. A common theme here is increase in disorder—from a compressed state to an expanded state, or from the ordered arrangement of particles in a crystal structure to the random dispersion in a liquid or gas or solution. Thus addition of heat leads to disorder, and entropy may be regarded as a measure of the disorder. Of course heat is not necessary to produce disorder; a system can become disordered either by the addition of heat from the outside (exchange of entropy from one system to another, or dS_{ext}) or from a change in the state of the system without addition of heat (free expansion, evaporation, in other words dS_{int}). In either case, entropy increases as disorder increases. Because all processes are to some extent

irreversible, the entropy of the world is increasing—as an expression of the tendency of natural processes toward disorder.

Thus when we write a mathematical expression for the second law as

$$dS \geq \frac{dQ}{T}, \quad (7-16)$$

the equality refers to the entropy added in a reversible change, and the inequality defines the additional increase from the natural irreversible tendency toward disorder. The inevitable change toward disorder can be expressed in versions of the second law that emphasize the unique characteristics of heat as a form of energy: (1) Heat always flows from hot objects to cold objects, never spontaneously from cold to hot. (2) It is impossible for a self-acting machine to transfer heat from a cold object to a hot object. (3) In any energy transformation, some of the original energy always appears in the form of heat energy which is no longer available for conversion into other forms of energy. Entropy provides a means of making such statements quantitative.

Combined Laws: Thermodynamic Potentials

Combining equations representing the first and second laws provides useful mathematical expressions relating energy to equilibrium. For any reversible energy transformation in a closed system we can substitute $dQ = TdS$ and $dW = PdV$ into Eq. (7-8) to obtain

$$dE = TdS - PdV. \quad (7-17)$$

Changes in the internal energy are determined *only* by changes in entropy and volume, which we express in a form similar to Eq. (7-1) by writing $E = F(S, V)$.

We now consider a transformation in a closed system, where an irreversible chemical reaction occurs so that $dS_{\text{int}} > 0$. By combining Eqs. (7-13) and (7-14), we determine that dQ is equal to the difference between the total change in entropy (dS) and the entropy produced (dS_{int}) when both are multiplied by absolute temperature,

$$dQ = TdS - TdS_{\text{int}}. \quad (7-18)$$

Substituting this relationship into Eq. (7-10) gives another expression for dE , written specifically for an irreversible process,

$$dE = TdS - PdV - TdS_{\text{int}}. \quad (7-19)$$

Now imagine a reaction that occurs under constraints so that the total change in S and V is zero; that is $dS = dV = 0$ and $dE = -TdS_{\text{int}}$. Because internal entropy production, dS_{int} , is always greater than or equal to zero [Eq. (7-15)], we have

$$(dE)_{S, V} \leq 0. \quad (7-20)$$

The inequality means that any irreversible processes will always be accompanied by a decrease in internal energy when S and V are constant. Furthermore, at

equilibrium $dS_{\text{int}} = 0$, requiring that $(dE)_{S,V} = 0$; this corresponds to a minimum in the internal energy of the system. Thus internal energy (E) may be referred to as a thermodynamic potential associated with the variables S and V , in that it can be used to determine the direction of reaction and conditions of equilibrium.

For the geochemist it is not very practical to characterize equilibrium in terms of the variables S , V , and E . Other thermodynamic potentials called *enthalpy* and *free energy* will provide more practical information about chemical reactions and equilibria in both experimental and natural systems.

7-3 ENTHALPY

Definition

In thermodynamic terms, enthalpy (H) is an extensive property of a system that is closely related to heat energy. It is defined as

$$H = E + PV, \quad (7-21)$$

or

$$dH = dE + PdV + VdP. \quad (7-22)$$

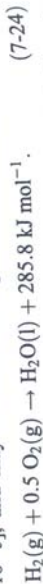
For any process that occurs at constant pressure Eq. (7-22) becomes

$$dH = dE + PdV = dQ. \quad (7-23)$$

Thus differential changes in H are equal to the heat adsorbed. For this reason H is often called the "heat content" of a system. As it was just defined, however, H has a broader meaning, not limited to isobaric processes, so that the name "enthalpy" is preferable. If a reaction takes place with both pressure and volume constant, $dH = dE$, so that the entire energy change is represented by the enthalpy.

Heats of Reaction

The simple and obvious way to measure the energy of a chemical reaction is to put the ingredients in a calorimeter and record the amount of heat energy absorbed or liberated as the reaction takes place. To standardize the results so that one reaction can be compared with another, we specify that the process shall take place at constant temperature and pressure, or at least that the products of reaction shall be brought back to the initial temperature and pressure before the heat change is measured. Under these conditions we speak of the heat given out or taken up as the *heat of reaction*. It is measured in joules [$1 \text{ joule (J)} = 1 \text{ kg}^2 \text{ m}^2 \text{ sec}^{-2}$ and $1 \text{ kilojoule (kJ)} = 10^3 \text{ J}$], and may be written as a part of the equation:



This means that 285.8 kJ of heat are evolved for each mol of liquid H_2O formed, when the reaction is carried out at 25°C and 1 bar.

From a slightly different point of view, we may think of the reactants as possessing a certain amount of chemical energy and the products a different

amount. In the example just cited, the product H_2O has less energy than does the combination of H_2 and O_2 , the excess being given up in the form of heat when the reaction takes place. In symbols,

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} = -285.8 \text{ kJ}. \quad (7-25)$$

The symbol ΔH means the change in H of the system when the reactants are transformed into the products. Here the H for the system becomes less during the reaction, so ΔH must have a negative sign. In general, ΔH is negative for exothermic reactions like this one, and positive for all endothermic reactions (see Sec. 1-6).

As was true for E , the absolute enthalpy of a substance or a mixture of substances is difficult to measure. The quantity that concerns us in discussing a reaction is not the individual H 's but the ΔH , the enthalpy change. This is easily measured as the heat change when the reaction takes place at constant temperature and pressure and is obviously the same number as the heat of reaction with the sign reversed. This odd procedure—introducing hypothetical quantities that cannot be measured, and using a negative sign for heat evolved—at first seems to make a simple subject needlessly complicated, but we shall find that it fits well into a large logical framework.

For the hydrogen-oxygen reaction, then, we write,



The enthalpy change is different at different temperatures and pressures, so we specify that $-285.8 \text{ kJ mol}^{-1}$ refers to the reaction when it is carried out at 25 °C and 1 bar (or when the resulting water is condensed and brought to these conditions). All enthalpy changes, unless otherwise specified, refer to these same conditions. Furthermore, ΔH obviously must be measured for a particular amount of substance; in our example the -285.8 kJ is the enthalpy change when 1 mol of hydrogen gas reacts with 0.5 mol of oxygen. We could write equally well,



In other words, a specific value of ΔH applies only to a particular formulation of the chemical equation. If the equation is multiplied by a number, the ΔH must be multiplied also, a relationship that is true for any extensive property of a chemical reaction. Obviously, if an equation is reversed, the sign of ΔH changes:



meaning simply that energy must be supplied to break water down into its elements. Thus the positive sign for ΔH indicates that the reaction in this direction is endothermic.

Computing Reaction Enthalpy

For any compound, the enthalpy change involved in forming it from its elements is called its *heat of formation*. Thus the heat of formation of water is $-285.8 \text{ kJ mol}^{-1}$ [Eq. (7-26)]. Heats of formation are useful for a variety of purposes, and have been

measured for many compounds of geochemical interest. The numbers given in tables usually refer to 25°C and 1 bar and to a single mol of the compound, unless conditions are specified otherwise. Tabulated values also refer to particular states of reactants and products, states described as *standard states*. In general the standard state of a pure element or compound is taken as its most stable form at 25°C and 1 bar, but the definition is less straightforward at elevated temperatures and pressures and for mixtures and solutions. We will consider standard states in more detail later, but for the moment we need only note that heats of reaction referred to standard states are symbolized with a superscript, ΔH_f° , and that some of the values of ΔH_f° for compounds of most interest in geochemistry are given in Appendix VIII.

By adding and subtracting heats of formation, the enthalpy change for any reaction can be computed. For example, the burning of hydrogen sulfide may be written,



The heats of formation are:



Now if these three reactions are doubled, if the second and third are added together, and if the first is subtracted from the sum, we obtain the original reaction. Hence we find ΔH° for the overall reaction by combining the ΔH_f° for the reactants minus those of the products: $\Delta H^\circ = -1124.0 \text{ kJ}$.

A more general formulation is expressed by the stoichiometric equation. This is a general mathematical expression used to represent the difference between the properties of products and reactants in a chemical reaction. For the enthalpy of reaction (ΔH_r°) at 1 bar and 25°C the stoichiometric equation is

$$\Delta H_r^\circ = \sum_i \nu_i \Delta H_{f,i}^\circ \quad (7-30)$$

where ΔH_r° is the heat of a specific chemical reaction denoted by the subscript r , and ν_i (the Greek letter nu) is the stoichiometric reaction coefficient for the i th species of the reaction, which by convention is positive for products and negative for reactants. Thus for Eq. (7-29) we have $\nu_{\text{SO}_2} = +2$, $\nu_{\text{H}_2\text{O}} = +2$, $\nu_{\text{O}_2} = -3$, and $\nu_{\text{H}_2\text{S}} = -2$. The term $\Delta H_{f,i}^\circ$ is the heat of formation of a particular species or compound (i) in the reaction. We now write Eq. (7-30) as

$$\Delta H_r = \nu_{\text{SO}_2} \Delta H_{f,\text{SO}_2}^\circ + \nu_{\text{H}_2\text{O}} \Delta H_{f,\text{H}_2\text{O}}^\circ + \nu_{\text{O}_2} \Delta H_{f,\text{O}_2}^\circ + \nu_{\text{H}_2\text{S}} \Delta H_{f,\text{H}_2\text{S}}^\circ$$

or substituting values of ν_i and $\Delta H_{f,i}^\circ$

$$\Delta H_r = 2(-296.8 \text{ kJ}) + 2(-285.8 \text{ kJ}) + (-3)(0 \text{ kJ}) + (-2)(-20.6 \text{ kJ}) = -1124.0 \text{ kJ}.$$

This is a general rule for obtaining enthalpy changes of a chemical reaction at 1 bar and 25°C from tabulated values of heats of formation.

Enthalpy at Elevated Temperatures: The Heat Capacity

Enthalpies of formation for substances of geologic interest, as noted above, are usually tabulated at 25°C. Because many geochemical problems concern processes that occur at elevated temperatures, a means for calculating heats of reactions at temperatures $> 25^\circ\text{C}$ is often necessary. For this purpose we introduce the property called *heat capacity*.

The heat capacity of a substance is the amount of heat required to raise the temperature of 1 mol by 1°C. More rigorously, it may be defined as the limit of the ratio of heat added to the temperature change produced, as the latter approaches zero:

$$C = \frac{dQ}{dT}. \quad (7-31)$$

If V is constant during the addition of heat, the heat absorbed equals the change in internal energy [see Eq. (7-10)]:

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V, \quad (7-32)$$

where the term C_V is heat capacity at constant volume. If P is constant rather than V , heat absorbed goes into both temperature rise and expansion; hence, combining Eq. (7-23) and (7-31), we obtain

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P, \quad (7-33)$$

which tells us that the change of H with respect to T is the heat capacity at constant pressure, C_P .

Measured values of C_P for the monoclinic feldspar microcline are shown in Fig. 7-3 as a function of temperature. The heat capacity curve for most minerals is

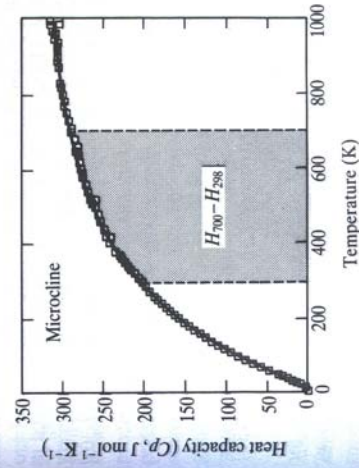


FIGURE 7-3 Heat capacity of microcline (KAlSi_3O_8) between 0 and 1000 K. (Symbols are data reported by Hemingway et al., 1981, and Openshaw et al., 1976). The shaded area under the C_P curve between $T = 700 \text{ K}$ and $T_{\text{ref}} = 298 \text{ K}$ represents the quantity $H_T - H_{T_{\text{ref}}}$ in Eq. (7-36).

similar to this one; that is, C_P increases rapidly from near 0 to approximately 400–600 K, then at higher temperatures the rate decreases and the relationship between C_P and temperature becomes approximately linear. Near temperatures where polymorphic phase transformation or atomic disordering occur in a mineral, there will be steep changes or discontinuities in the temperature dependence of C_P . Relations between C_P and temperature are more complex for H_2O and for aqueous electrolyte solutions. Water has a maximum in C_P at high temperatures and low pressures near its critical point (31°C and 221 bar), and electrolytes are characterized by even more extreme temperature variations in C_P at low pressures.

To facilitate calculations of reaction enthalpy we use an equation that approximates experimental measurements of C_P , such as the data represented by the symbols in Fig. 7-3. One simple equation that provides a reasonable fit to experimental C_P data for many common minerals is

$$C_P = a + bT - cT^{-2}. \quad (7-34)$$

The a , b , and c terms are constants derived from fitting the line to the experimental data, and they have characteristic values for each substance. More complex equations would be required to describe the heat capacity of minerals with temperature-dependent atomic transformations, H_2O , and electrolytes.

Using an equation like (7-34), we can compute the effect of temperature on the enthalpy of a substance. First we rearrange Eq. (7-33) to give $dH = C_P dT$, then integrate from some reference temperature (T_{ref} , which is usually 25°C, 298 K), to some specified elevated temperature (T),

$$\int_{H_{T_{\text{ref}}}}^{H_T} dH = \int_{T_{\text{ref}}}^T C_P dT. \quad (7-35)$$

The left-hand side of this equation integrates to give $H_T - H_{T_{\text{ref}}}$, and for C_P on the right-hand side we substitute the value given by Eq. (7-34) to obtain,

$$H_T - H_{T_{\text{ref}}} = a(T - T_{\text{ref}}) + \frac{b}{2}(T^2 - T_{\text{ref}}^2) + c\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right). \quad (7-36)$$

This relationship is illustrated graphically by the shaded area in Fig. 7-3.

The enthalpy of reaction at some elevated temperature may be calculated in two different ways. One method is to compute values of $H_T - H_{T_{\text{ref}}}$ for every substance in the reaction, then apply the stoichiometric equation [see Eq. (7-30)] to obtain

$$\sum_i \nu_i (H_T - H_{T_{\text{ref}}}) = \sum_i \nu_i H_T - \sum_i \nu_i H_{T_{\text{ref}}} = \Delta H_T - \Delta H_{T_{\text{ref}}}. \quad (7-37)$$

The heat of reaction is computed by solving for ΔH_T ,

$$\Delta H_T = \Delta H_{T_{\text{ref}}} + \sum_i \nu_i (H_T - H_{T_{\text{ref}}}). \quad (7-38)$$

In Eq. (7-38) the value of $\Delta H_{T_{\text{ref}}}$ is computed using heats of formation for the substances in the reaction [see Eq. (7-30)], and $H_T - H_{T_{\text{ref}}}$ is computed using Eq. (7-36).

Alternatively we may compute the change in heat capacity for the reaction (ΔC_P) using the stoichiometric equation,

$$\Delta C_P = \sum_i \nu_i C_{P,i}, \quad (7-39)$$

where $C_{P,i}$ is the heat capacity of the i th substance in the reaction. The heat of reaction is then determined by solving the integral

$$\int_{H_{T_{\text{ref}}}}^{H_T} d\Delta H = \int_{T_{\text{ref}}}^T \Delta C_P dT \quad (7-40)$$

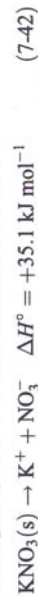
for ΔH_T :

$$\Delta H_T = \Delta H_{T_{\text{ref}}} + \int_{T_{\text{ref}}}^T \Delta C_P dT. \quad (7-41)$$

Enthalpy Change as a Measure of Reactivity

In Chapter 1 we set up as a major goal of geochemistry the ability to predict what will happen when one substance is mixed with another. Will a reaction take place, or will the substances exist side by side in chemical equilibrium? At first glance it looks as if enthalpy changes might be a key to answer such questions, for exothermic reactions often take place spontaneously while endothermic processes generally do not occur unless energy is supplied. Further, the more exothermic a reaction is (the higher its negative ΔH), the more energetically we expect it to proceed. The hydrogen–oxygen reaction [Eq. (7-26)], for example, is strongly exothermic and occurs with explosive violence if it is touched off with flame or spark. The reaction between water and carbon dioxide to form carbonic acid, on the other hand, is only mildly exothermic and reaches equilibrium with no obvious indication that a reaction is taking place at all.

To say that the energy available in a reaction mixture determines how readily and how violently the reaction will take place seems entirely natural. It conforms to our intuitive prejudices, derived from experience with mechanical systems, where, in general, energy available does determine whether a given process will go of its own accord and how much work or heat we can expect to get out. A little reflection, however, will suggest that the generalization cannot be strictly true for chemical processes. Some reactions take place spontaneously despite the fact that they are endothermic; of their own accord they extract the necessary heat from their surroundings, cooling adjacent objects below the general temperature level. A good example is the dissociation of potassium nitrate: when this salt is stirred in water, the container quickly becomes cold because the reaction



absorbs heat from its surroundings. Many other common dissolution processes are similarly endothermic. The enthalpy change, therefore, is by no means an infallible measure of the tendency of a reaction to take place.

It remains true that for very many reactions the size of the enthalpy change provides at least a gross indication of reactivity. In the absence of other data, enthalpy changes can be used fairly satisfactorily to make predictions about the behavior of unfamiliar substances. We might expect, therefore, that a quantity related to enthalpy would give us the necessary refinement to make the predictions exactly. This quantity is called the *free energy*.

7-4 FREE ENERGY

Definition

To see why enthalpy is not the only factor of importance in making a reaction take place, let us imagine a process in which there is no enthalpy change at all. We have two gases in containers separated by a partition; we remove the partition and let the gases mix. If we symbolize one gas by A, the other by B, and the mixture by A-B, the "equation" for the process is



The experiment is imaginary because we assume that A and B behave as perfect gases, a reasonable assumption as long as the pressure is low. The mixing of two perfect gases involves no energy change, so we may write for the reaction $\Delta H = 0$. Despite the lack of any evolved energy, the reaction takes place readily of its own accord.

Why does it take place? Because the mixture represents a state of greater disorder or randomness, or a state of higher probability, than the two separate pure gases. From ordinary experience we know that natural processes tend to produce disordered arrangements from ordered arrangements; think, for example, how quickly a neat pile of papers is scattered by a gust of wind, how readily the ordered arrangement of particles in a crystal disappears when salt dissolves in water, how effectively the processes of decay destroy the complexly organized structures of a dead animal. The mixing of two gases is a simple example of a general pattern in nature. Quite apart from energy changes, natural processes go spontaneously from states of order to states of disorder, and this tendency toward disorder is the other factor besides enthalpy that makes chemical reactions take place.

Thus the tendency of a reaction to take place can be thought of as dependent on two factors, the change in enthalpy and the change in degree of disorder:

$$\text{tendency to react} = \Delta H + \text{change in disorder}. \quad (7-44)$$

Now in a previous section (Sec. 7-2) we have noted that entropy can be used as a measure of the degree of disorder. As an energy term, then, we can express "change in disorder" by multiplying the change in entropy by temperature:

$$\text{change in disorder} = T\Delta S. \quad (7-45)$$

And if we now describe "tendency to react" as a new variable called "change in free energy," symbolized as ΔG , we can rewrite Eq. (7-44) in mathematical form:

$$\Delta G = \Delta H - T\Delta S. \quad (7-46)$$

The minus sign means that an entropy increase adds to the negative value of ΔH , in other words increases the tendency of a reaction to take place.

The new symbol we have introduced, G , stands for free energy, or more properly Gibbs free energy. This is an extensive property of a system, defined as

$$G \equiv H - TS \quad (7-47)$$

or

$$G = E - TS + PV. \quad (7-48)$$

Absolute values of G , as for the values H and E , would be difficult to obtain. Our chief concern is with *changes* in G during reactions:

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}. \quad (7-49)$$

Values of free energy differences, ΔG , like similar values for ΔH and ΔE , are commonly expressed in joules or kilojoules.

Free Energy as a Criterion of Equilibrium

Because the quantity ΔG expresses the ability of substances to react and the extent to which reactions will go, it plays an important role in making predictions about a great variety of geochemical processes. To demonstrate this relationship between free energy and equilibrium for a reaction mixture, we begin by differentiating Eq. (7-48) to obtain

$$dG = dE - TdS - SdT + VdP + PdV. \quad (7-50)$$

From Eq. (7-19) we see that

$$dE - TdS + PdV = -TdS_{\text{int}}, \quad (7-51)$$

so that Eq. (7-50) becomes

$$dG = -SdT + VdP - TdS_{\text{int}}. \quad (7-52)$$

Now imagine a chemical reaction occurring in a closed system under conditions of constant T and P , so that $dT = dP = 0$ and Eq. (7-52) reduces to

$$(dG)_{T,P} = -TdS_{\text{int}}, \quad (7-53)$$

or from Eq. (7-15)

$$(dG)_{T,P} \leq 0. \quad (7-54)$$

Thus Gibbs free energy is a thermodynamic potential associated with the variables T and P . Any spontaneous irreversible process in a closed system at constant T and P will cause a decrease in the Gibbs free energy, and equilibrium will occur when $(dG)_{T,P} = 0$, corresponding to a minimum in the function G . These energy relations are graphically illustrated in Fig. 7-4 for a hypothetical chemical reaction between substances A and B, where equilibrium of $A \rightleftharpoons B$ occurs when G is a minimum, and the spontaneous irreversible reactions $A \rightarrow B$ and $B \rightarrow A$ are accompanied by a decrease in the free energy of the system as shown in the figure.

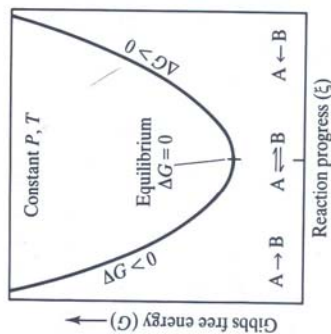


FIGURE 7-4

Gibbs free energy (G) is a thermodynamic potential that acts as an indicator of equilibrium for any process that occurs in a closed system at constant T and P [Eq. (7-54)]: any spontaneous irreversible process will cause a decrease in G , and equilibrium occurs when G is a minimum. This schematic diagram illustrates these relations for a reaction between two hypothetical substances, A and B , as a function of a reaction progress variable (ξ): positive changes ($d\xi > 0$) occur when $\Delta G < 0$ and $A \rightarrow B$, and negative changes ($d\xi < 0$) occur when $\Delta G > 0$ and $A \leftarrow B$. Equilibrium, $A \rightleftharpoons B$, corresponds to $\Delta G = 0$.

Now in terms of a chemical reaction, where ΔG is expressed by Eq. (7-49), the rules are very simple:

1. If $\Delta G = 0$, the reaction mixture is at equilibrium.
2. If $\Delta G < 0$, the reaction will take place spontaneously in the direction of lower Gibbs free energy (although the rate may be so slow that no reaction is apparent).
3. If $\Delta G > 0$, the reaction cannot take place as written unless energy is supplied from an external source.

Similar rules cannot hold for enthalpy changes, because some endothermic reactions (for which $\Delta H > 0$) take place spontaneously. Such endothermic reactions would have a negative ΔG , but a positive $T\Delta S$ term [Eq. (7-46)] larger numerically than ΔG , so that ΔH becomes positive. These reactions are not common, and by and large a negative ΔG means a negative ΔH , especially if the ΔG is a large number, say more than 40 kJ. But ΔG has the advantage over ΔH in that it gives an exact measure of the position of a reaction with respect to equilibrium for the constraints of constant temperature and pressure, whereas ΔH gives only a rough indication.

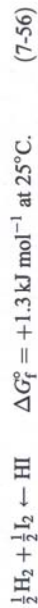
Values of ΔG for simple reactions can be combined, just as values of ΔH are combined, to give values for more complex reactions. And again like ΔH , values of ΔG for the formation of compounds from their elements can be usefully tabulated, with the same provisos about temperature, pressure, and standard states (*standard free energies of formation*, ΔG_f°). A list of such values for many compounds of geochemical importance is given in Appendix VIII.

Two examples will illustrate the use of free energy as a criterion of equilibrium. The reaction between sulfur and oxygen has a large negative ΔG ,



This means that a mixture of sulfur and oxygen is far from equilibrium: once ignited, the mixture will react until one or the other substance is almost entirely

converted to SO_2 . The reaction between hydrogen and iodine, on the other hand, has a small positive free energy change



Hence a mixture of hydrogen gas at 1 bar, hydrogen iodide gas at 1 bar, and solid iodine, would be approximately at equilibrium. A little of the hydrogen iodide would tend to break down into its elements, but much would still be present when true equilibrium was established.

Measurement of ΔG

The direct measurement of ΔG for most reactions is a difficult operation. One method, applicable to many oxidation-reduction processes, depends on measurements of electromotive force and use of the relation

$$\Delta G^\circ = -W' = nFE^\circ. \quad (7-57)$$

This equation expresses the fact that electromotive force (E°) multiplied by the amount of electric charge moving through a cell (the charge carried by a mol of electrons, f , times the number of mols, n) gives the maximum electrical work (W') that the cell reaction can accomplish (Sec. 9-2). Another possible method involves measurement of activities of reactants and products when a reaction has reached equilibrium, and use of the equation

$$\Delta G^\circ = -RT \ln K, \quad (7-58)$$

where K is the equilibrium constant (this is discussed in detail in the next chapter). But obviously it would be desirable to have a general method for determining free energy changes from heat measurements alone. Such a method might be based on the relation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7-59)$$

if ΔH° and ΔS° can be determined independently. The enthalpy term is easily found by measuring the heat of reaction in a calorimeter. Now if we had a way of obtaining entropy change also, the problem of measuring ΔG° would be solved.

It turns out that values of ΔS can be found by determining absolute entropies from heat capacity measurements. Since $dQ = TdS$ [Eq. (7-11)] we can express the heat capacity at constant pressure in terms of the change in entropy,

$$C_p = \left(\frac{dQ}{dT}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_p. \quad (7-60)$$

Upon rearranging

$$dS = C_p \frac{dT}{T} = C_p d \ln T, \quad (7-61)$$

or

$$\int_{S_{T_1}}^{S_{T_2}} dS = S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} C_p d \ln T. \quad (7-62)$$

Hence when C_p of a substance is known as a function of temperature, the change in S with temperature may be calculated.

If we knew an absolute value for S at one temperature, its value at any other temperature could be found by carrying out the integration of Eq. (7-62). Arbitrarily let us assign a value of zero to the entropy of some crystal form of each element at the absolute zero of temperature. Then the entropy of this crystal form at a temperature T can be determined by measuring its heat capacity over the temperature interval 0 to T (involving slight extrapolation at the lower limit, since absolute zero is experimentally unattainable) and integrating between these limits.

Now a striking experimental fact emerges if we then determine the entropy differences between various crystal forms of the same element: the differences become smaller and smaller as the temperature drops toward absolute zero. In other words, if we make the assumption of zero entropy at $T = 0$ for one crystal form, then the entropy of other crystal forms is also zero at this temperature. Even more striking is the experimental fact that entropy differences in reactions involving combinations of crystalline elements to form pure crystalline compounds also fall toward zero as T approaches zero. We can generalize from such experimental results: *if the entropy of each element in some crystal state is assumed to be zero at $T = 0$, the entropy of other pure crystalline solids is also zero at this temperature.* This statement is called the Third Law of Thermodynamics. Although formulated much later than the first and second laws and for a time seriously questioned, its validity has now been established by many different kinds of experiments.

The third law makes possible the determination of absolute entropies for most pure crystalline solids. For example, the standard third law entropy (S°) of a pure crystalline solid can be computed by integrating Eq. (7-62) from 0 K where $S = 0$ to 298.15 K,

$$S_{298.15\text{ K}}^\circ = \int_{T=0}^{T=298.15\text{ K}} C_p^\circ d \ln T. \quad (7-63)$$

This is graphically illustrated in Fig. 7-5 for the mineral phlogopite. Note that S is different from E and H , in that its absolute value can be found.

It should be noted that the relationship between C_p and T is complicated at very low temperatures and the integration is often best performed by graphical methods. In addition, purity and perfection of crystal form are essential in a careful evaluation of third law entropies; glassy solids, solid solutions, and imperfect crystals would all have finite positive entropies at absolute zero. If any phase transitions occur in the substance between 0 and 298.15 K, they must also be considered in evaluating the third law entropy. Entropies of liquids and gases are obtainable from those of the corresponding solids by adding the entropies of melting or vaporization (heats of fusion or vaporization divided by absolute temperature at the transition points). Absolute entropies of gases may be calculated also from spectroscopic data by the methods of statistical mechanics. Entropies of ions and undissociated molecules in solution may be found, with a few additional assumptions, from heats of solution. Thus absolute entropies are obtainable, at least

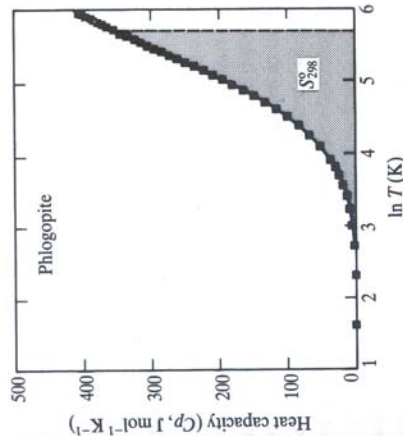


FIGURE 7-5
Low-temperature (5 to 400 K) heat capacity of phlogopite $[\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2]$. The shaded area schematically represents the third-law entropy of phlogopite at 298.15 K, as defined by Eq. (7-63). (Data from Robie and Hemingway, 1984.)

in principle, for most substances of geochemical interest. Some of these are listed in Appendix VIII.

The ΔS° 's for reactions are simply differences between the combined absolute entropies of reactants and products. These, multiplied by the absolute temperature and subtracted from ΔH° 's give values for ΔG . This is the most generally useful method of finding free energies of reaction.

Free Energy: Conventions and Qualifications

The conventions used in free energy calculations are summarized here for easy reference:

1. As we will use the term, free energy refers only to processes taking place at constant temperature and constant pressure (*Gibbs free energy*). The term may be defined equally well for constant temperature and volume processes (*Helmholtz free energy*), but because reactions of interest in geochemistry take place more commonly under conditions of constant pressure than under constant volume, Gibbs free energies are the more useful.
2. Numerical values of free energies, like those for enthalpies, are known only as relative quantities, never as absolute ones. All we ever get from experiment is a difference of enthalpy and a difference of free energy between the products and the reactants of a chemical process. We are concerned only with ΔG and ΔH , never with G and H themselves.
3. Free energies, like enthalpies, are expressed in joules (J) or kilojoules (kJ), or sometimes in calories or kilocalories. The convention of sign is similar: negative free energy means energy evolved; positive free energy means energy absorbed.

4. The free energy of formation of a compound (ΔG_f) is the free energy change accompanying the formation of 1 mol from its elements. The *standard* free energy of formation of a compound from its elements (ΔG_f°) is the free energy change when the reaction takes place with all substances in their specified *standard states*. A variety of standard states may be chosen for special purposes (this will be discussed further in Sec. 8-3), but the ones used most commonly in calculations of free energies are similar to those used for enthalpies of formation: a temperature of 25°C or 298.15 K, a pressure of 1 bar, and a provision that pure substances be in their most stable states under these conditions. For example, sulfur is assumed to be orthorhombic (rather than monoclinic), iron to have the crystal form called alpha-iron, and silica to be in the form of α -quartz, since these are the most stable states of these substances at the specified conditions. In reactions involving mercury or bromine, the standard state for the element would be the pure liquid. The standard state of gases is more difficult to define precisely, but for most purposes can be taken as the pure gas with an activity of 1 at a specified temperature and pressure (usually taken as 1 bar and any temperature).

5. Substances in solution also may pose a difficult problem with regard to choice of standard states, but in the relatively dilute solutions encountered most commonly in geochemistry a convenient choice is again unit activity, for both solvent and solutes. Thus for H_2S as a pure gas and in aqueous solution, we write



The symbol S_{th} means rhombic sulfur, $H_2(g)$ and $H_2S(g)$ mean hydrogen gas and hydrogen sulfide gas at 1 bar, and $H_2S(aq)$ means dissolved H_2S at an activity of 1.

6. For ions a further convention is needed, because ions are never produced singly. We can determine, for example, the free energy change in the reaction $Na + \frac{1}{2}Cl \rightarrow Na^+ + Cl^-$, but not for the separate processes Na going to Na^+ or $\frac{1}{2}Cl_2$ going to Cl^- . This means that one dissociation reaction must be arbitrarily assigned a free energy value, and the other dissociation processes can then be referred to it. The convention universally adopted is



The symbol H^+ means hydrogen ion at an activity of 1 and the symbol e^- refers to the electron removed from the hydrogen atom.

7. Values of the standard Gibbs free energy of formation are important because they can be added and subtracted to determine free energy changes of reactions (ΔG°), just as heats of formation are used to calculate enthalpy changes using Eq. (7-30). Written in terms of the stoichiometric equation the free energy change of a reaction is

$$\Delta G_r^\circ = \sum_i \nu_i \Delta G_f^\circ. \quad (7-67)$$

As in Eq. (7-30), ν_i is the stoichiometric reaction coefficient, positive for products and negative for reactants, so that the free energy of the reaction is the difference between the free energies of all the products and the free energies of the reactants.

SUMMARY: USES AND LIMITATIONS OF FREE ENERGY

In effect, by introducing the concept of free energy change we have developed a second method of describing the tendency of a mixture to react. The first device was the equilibrium constant, from which we could deduce the concentration ratios that exist at equilibrium, and thus determine in what direction a given mixture must react to attain equilibrium. The standard free energy change gives us the same sort of information, for it shows, by its sign and its magnitude, whether a mixture with unit concentrations will react one way or the other and to what extent. We shall see in the next chapter that the equilibrium constant is actually defined in terms of standard free energy changes. So what have we gained by introducing this second method for describing equilibrium?

Free energies have two great advantages: they are additive, and they require less space in tables. In tables a separate equilibrium constant must be listed for each reaction, whereas free energies of formation in a relatively brief list can be used to compute free energy changes (and equilibrium constants as we shall see in the next chapter) for a large number of reactions.

Free energies give us a quantitative measure of *stability*, a concept we have discussed at some length earlier (Sec. 1-7). A mixture of substances all of whose possible reactions have zero free energy could undergo no change, hence would be stable; a mixture permitting reactions with negative free energy changes would be unstable, and the magnitude of the possible free energy changes would indicate the degree of instability. As in the earlier discussion, it should be emphasized that this kind of stability refers only to possible energy changes, not to the rate at which these energy changes actually occur. A piece of coal exposed to the air is apparently stable, but the stability is due only to the slowness with which coal reacts with oxygen at ordinary temperatures. In this book *stability* or *true stability* will always refer to stability with respect to energy changes, and the apparent stability of some mixtures due to slow reaction rates will be called *metastability*.

The inability to give information about reaction rates is one of the severe limitations on the application of free energy reasoning in geochemistry. A second serious limitation is the inability of free energy reasoning to deal with geologic processes that take place in open systems, systems in which matter is continually being added from the outside or is continually flowing away, so that real chemical equilibrium is not attained. Consider the movement of fluid through a vein, for example, or the rush of gases through a volcanic orifice. Even when flow is not an important factor, the slowness of reaction and incompleteness of mixing may prevent attainment of equilibrium, as is obvious for immature soils and for half-digested inclusions in granites. Despite these restrictions, we shall find that

reasoning on the basis of free energy and equilibrium will help in setting limits to geologic processes, in telling us at least which reactions are possible and which are completely out of the question. In restricted areas of geology, particularly in chemical sedimentation, metamorphism, and the crystallization of magmas, equilibrium reasoning can be carried further and leads to exact predictions that can be checked against natural occurrences.

PROBLEMS

1. The area, a , of a rectangle is a function of the height, h , and the length, l ; that is $a = F(h, l)$ where $a = hl$.

The independent variables are h and l ; a is the dependent variable. Two other possible dependent variables are the perimeter, p ,

$$p = F(h, l) \quad \text{where} \quad p = 2h + 2l$$

and the diagonal, d ,

$$d = F(h, l) \quad \text{where} \quad d = (h^2 + l^2)^{0.5}$$

Find the values of the following partial derivatives in terms of h and l , or find a numerical answer:

$$\left(\frac{\partial a}{\partial h}\right)_l; \left(\frac{\partial a}{\partial l}\right)_h; \left(\frac{\partial p}{\partial h}\right)_l; \left(\frac{\partial p}{\partial l}\right)_h; \left(\frac{\partial d}{\partial h}\right)_l; \left(\frac{\partial d}{\partial l}\right)_h$$

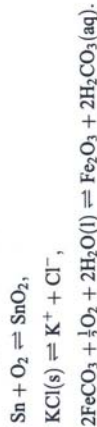
2. Prove that the expression for work performed by an ideal gas is $dW = RdT - (RT/P)dP$.

3. The coefficients of expansion and compression for a substance are defined as

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad \text{and} \quad \beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

Derive expressions for α and β in terms of density (ρ). At the critical point, where $(\partial P/\partial V)_T = 0$, show that both α and β are infinite.

4. Using the data of Appendix VIII, find the standard enthalpy changes and free energy changes for the following reactions at 25°C:



To reach equilibrium, which of these reactions would go as written, i.e., from left to right? Which is more stable at ordinary temperatures in contact with air, tin or tin oxide? Hematite or siderite?

5. Using the data of Appendix VIII, find the standard free energy change and enthalpy change for the reaction



From these numbers calculate the standard entropy change for the reaction, and compare your result with the value calculated directly from the standard entropies of formation listed in Appendix VIII. (Any discrepancy probably means that the different numbers were determined by different investigators at different times, and the difference is just expectable experimental error.) Is the reaction exothermic or endothermic? In what sort of environment would you expect to find it occurring in nature?

6. In each of the following pairs, which has the greater amount of entropy? Assume that all variables not mentioned are the same for both members of a pair.

- (a) A mol of calcite at 0°C, (a') a mol of calcite at 100°C.
- (b) A sample of air under a pressure of 1 bar, (b') the same sample under 10 bar.
- (c) Crystalline salt plus water, (c') a solution formed by dissolving the salt in water.
- (d) Crystalline basalt, (d') the magma from which the basalt crystallized.

7. Calcite is more soluble at low temperatures than at high temperatures. What does this tell you about the sign of ΔH° for the reaction $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3$? Verify your answer by calculating the standard change in enthalpy for this reaction.

8. Because the standard state adopted for minerals is unit activity of the pure phase at any temperature and pressure, we can define the standard molal Gibbs free energy of a mineral at some elevated temperature (T) and pressure (P) by the equation

$$\Delta G_{\text{mineral}, T, P}^\circ = \Delta G_{\text{mineral}}^\circ + (G_{T, P}^\circ - G_{T_{ref}, P_{ref}}^\circ)$$

The term $\Delta G_{\text{mineral}, T, P}^\circ$ is called the *apparent standard molal Gibbs free energy* of the mineral at the specified T and P . $\Delta G_{\text{mineral}}^\circ$ is the free energy of formation of the mineral from its elements at the reference conditions of 25°C and 1 bar, and the parenthetical term is the difference in the absolute value of the standard molal Gibbs free energy of the mineral at the temperature and pressure of interest and in the reference conditions (25°C and 1 bar).

- (a) To compute the value of $\Delta G_{\text{mineral}}^\circ$ at a temperature greater than 25°C and at the reference pressure of 1 bar, the parenthetical term in the above equation is written as

$$(G_{T, P_{ref}}^\circ - G_{T_{ref}, P_{ref}}^\circ) = -S_{T_{ref}, P_{ref}}^\circ (T - T_{ref}) + \int_{T_{ref}}^T C_{P_{ref}}^\circ dT - T \int_{T_{ref}}^T \frac{C_{P_{ref}}^\circ}{T^2} d \ln T$$

Derive this expression.

- (b) Using the above equations and the data given in the table below, compute the temperature of equilibrium between kyanite and andalusite at a pressure of 1 bar. The letters a, b, and c in the table correspond to the coefficients in Eq. (7-34) for the temperature dependence of heat capacity. (Reference: Helgeson, H. C., J. M. Delany, H. W. Nesbitt, and D. K. Bird: "Summary and critique of the thermodynamic properties of rock-forming minerals," *American Journal of Science*, vol. 278A, 229 pp., 1978; see pages 28-29.)

Mineral	$\Delta G_{\text{mineral}}^\circ$ J/mol	$S_{T_{ref}, P_{ref}}^\circ$ J/mol K	a	b $\times 10^3$ J/mol K ²	c $\times 10^{-5}$ J K/mol
Andalusite	-2,429,176	92.88	172.8444	26.3282	51.8485
Kyanite	-2,430,720	83.68	173.1887	28.5202	53.8987