CHAPTER
8

CHEMICAL THERMODYNAMICS: PHASE EQUILIBRIA

The idea embodied in free energy as a measure of equilibrium may be expressed in a variety of ways. Here we develop a practical means for using free energy to describe heterogeneous equilibrium in complex geologic systems.

8-1 CHEMICAL POTENTIAL

We begin by considering a very simple kind of heterogeneous equilibrium, the equilibrium between liquid water and water vapor in a closed container,

$$H_2O(\text{vapor}) \rightleftharpoons H_2O(\text{liquid}). \qquad (8\text{-}1)$$

The condition that equilibrium exists we can state by saying that, if a very small amount of liquid is vaporized and if a small amount of vapor is condensed, the change in the free energy is zero. One may think of the liquid water as capable of vaporizing, or as tending to vaporize, or as seeking to "escape" from the liquid into the vapor phase. Thus we can assign to the water a certain *escaping tendency* with respect to the vapor. Similarly we can describe the vapor as having a certain escaping tendency with respect to the liquid. The condition of equilibrium would then be simply that the two escaping tendencies are equal. If the temperature is raised, the escaping tendency of the liquid increases more than that of the vapor, so that additional liquid must vaporize before equilibrium is reestablished.

As a measure of the escaping tendency, we may use the free energy per mol, or *molal free energy*, of water and its vapor. We designate molal free energy with a bar over the letter symbol: $\overline{G} = G/n$, where G represents the free energy of n mols. The condition of equilibrium at constant temperature and pressure requires that the free energy of the reaction be zero so that $\overline{G}_{\text{liquid}} = \overline{G}_{\text{vapor}}$. Alternatively, we may express this condition by thinking of the vaporization of an infinitesimal amount of water—the escape of dn mols of water from the liquid phase into the gas phase. The free energy lost by the liquid is $\overline{G}_{\text{liquid}}\,dn$, and that gained by the vapor is $\overline{G}_{\text{vapor}}\,dn$. If equilibrium exists, the net free energy change must be zero:

$$dG = \overline{G}_{\text{liquid}}\,dn - \overline{G}_{\text{vapor}}\,dn = 0. \tag{8-2}$$

This is clearly equivalent to $\overline{G}_{\text{vapor}} = \overline{G}_{\text{liquid}}$. Molal free energies so defined are not a very practical measure for evaluating equilibrium, since numerical values of absolute free energies are unknown. For actual use we would substitute free energies of formation assigned on the basis of conventions described in Chapter 7.

The molal free energy may be given another name, *chemical potential*, suggesting that this quantity represents a sort of energy level of a substance in one phase of a system. An actual transfer of energy attendant on vaporization or condensation is expressed by the chemical potential multiplied by the number of mols transferred—in other words, by the total free energy change. Analogously in mechanics an object suspended above the Earth can be said to have a mechanical potential, measured by its height times the acceleration of gravity, **gh**; energy released when the object falls is the product of this potential multiplied by its mass, **Mgh**. Or in electricity: an electric charge has a certain electric potential (measured in volts) with respect to another charged object, and electrical energy released when the charge moves is the product of electric potential and the amount of charge. Chemical potential is less easily visualized, but it plays the same role in chemical reactions that these more familiar potentials play in mechanical and electrical processes. We may rephrase our condition of chemical equilibrium [Eq. (8-2)] by saying that the chemical potentials of H_2O in the liquid and vapor phases must be equal.

The idea of chemical potential becomes more useful when we consider complicated systems involving solutions. Suppose we change our simple example by stirring salt into the liquid water: the equilibrium will readjust itself, and we inquire how the necessary condition for equilibrium between liquid and vapor can best be expressed. If we try to use equality of the molal free energies of H_2O in the two phases, we meet the difficulty that we have not yet defined the molal free energy of H_2O in the solution. It cannot be simply the free energy of the water present divided by the number of mols, because dissolving the salt involves an energy change. In other words, the free energy of H_2O is now a complex function of concentration as well as of temperature and pressure.

We can still set up a number to represent the molal free energy, however, if we consider the change in free energy of the solution produced by an infinitesimal change in the amount of water. Instead of a quotient of macroscopic quantities, G/n, which we can use for a pure substance, we set up a differential coefficient in terms of a specific chemical component represented by the subscript i,

$$\lim_{\Delta n_i \to 0}\left(\frac{\Delta G}{\Delta n_i}\right) = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j} \equiv \mu_i. \tag{8-3}$$

The subscript T, P, n_j means that differentiation is carried out for constant pressure, temperature, and the concentrations of all other components of the solution except the ith (represented by the term n_j). In mathematical language this is a partial derivative (see Fig. 7-2), and the quantity it represents is therefore called the *partial molal free energy*. The term chemical potential is a synonym for this expression, as well as for the molal free energy of pure substances; it is often designated by the Greek letter mu, μ, usually with a subscript denoting the chemical component and a superscript representing the phase, such as $\mu_{H_2O}^{\text{vapor}}$.

A general statement of the condition of equilibrium can now be proposed for any system, however complex: *the chemical potential of each component must be the same in all phases of the system.* To prove this we again consider two different types of experiments, each with identical initial and final states, so that changes in functions of the state of the system will be the same for both experiments.

The first experiment is the one we used to derive Eq. (7-19): an irreversible chemical reaction occurs in a closed system producing entropy within the system, so that the change in the internal energy is

$$dE = TdS - PdV - TdS_{\text{int}}. \tag{7-19}$$

An example would be the irreversible hydrolysis of K-feldspar in an acid solution to produce the clay mineral kaolinite,

$$\underset{\text{K-feldspar}}{KAlSi_3O_8} + H^+ + \tfrac{1}{2}H_2O \rightarrow K^+ + \tfrac{1}{2}\underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + 2SiO_2(aq)\,. \tag{8-4}$$

The initial state consists of one mol of K-feldspar and an acid solution, and the final state has half a mol of kaolinite and a solution enriched in K^+ and $SiO_2(aq)$.

In the second experiment the initial and final states of the first experiment are exactly reproduced, but without any chemical reaction whatsoever. This is accomplished by making the boundaries of the system open to the transport of mass, so material inside the system can be exchanged with material from the surroundings. First we remove the one mol of K-feldspar and all the solution from our system. Next, we place inside the system half a mol of kaolinite and a solution of the exact composition produced by the first experiment.

The initial and final states of our two experiments are identical, so that changes in E, S, and V are equal. In the first experiment a portion of the energy change was also due to irreversible entropy production inside the system ($-TdS_{\text{int}}$). But in the second experiment there is no entropy production. Instead the energy was altered by exchange of mass between the system and its surroundings. We represent this energy change by the number of mols of each component (dn_i) multiplied by the chemical potential of that component [see Eq. (8-2)]. So for the second experiment the change in internal energy is

$$dE = TdS - PdV + \sum_i \mu_i dn_i. \tag{8-5}$$

Since the differential changes in E, S, and V are the same in both experiments, Eqs. (7-19) and (8-5) are combined to give

$$-TdS_{\text{int}} = \sum_i \mu_i dn_i. \tag{8-6}$$

Thus the condition for chemical equilibrium defined by the second law [$dS_{\text{int}} = 0$, Eq. (7-15)] can be stated as

$$\sum_i \mu_i dn_i = 0. \tag{8-7}$$

This general equation is clearly equivalent to the specific equation [Eq. (8-2)] we deduced earlier for liquid–vapor equilibrium of H_2O based on escaping tendency alone.

We now assume that Eq. (8-7) can be used to express changes in internal energy within a closed system when the redistribution of elements among phases is due to chemical reactions within the system. The criterion for equilibrium of a chemical reaction is now written as

$$\sum_i \mu_i \nu_i = 0, \tag{8-8}$$

where the change in the number of mols of a reaction species [dn_i in Eq. (8-7)] is equal to the stoichiometric reaction coefficient, ν_i [which is taken to be positive for products and negative for reactants as in Eq. (7-30)]. To illustrate this we write Eq. (8-8) for the liquid–vapor equilibrium of H_2O [Eq. (8-1)],

$$\mu_{H_2O}^{\text{liquid}}(+1) + \mu_{H_2O}^{\text{vapor}}(-1) = 0 \tag{8-9}$$

or

$$\mu_{H_2O}^{\text{liquid}} = \mu_{H_2O}^{\text{vapor}}, \tag{8-10}$$

and for equilibrium between quartz and an aqueous solution,

$$\underset{\text{quartz}}{SiO_2} \rightleftharpoons SiO_2(aq), \tag{8-11}$$

Eq. (8-8) becomes

$$\mu_{SiO_2}^{\text{aqueous}}(+1) + \mu_{SiO_2}^{\text{quartz}}(-1) = 0 \tag{8-12}$$

or

$$\mu_{SiO_2}^{\text{aqueous}} = \mu_{SiO_2}^{\text{quartz}}. \tag{8-13}$$

These relationships, developed from the basic principles of thermodynamics, demonstrate that: *at equilibrium the chemical potential of a thermodynamic component is the same in all phases.*

Other useful relationships between chemical potential and Gibbs free energy are derived by substituting the identity of Eq. (8-6) into Eq. (7-52),

$$dG = -SdT + VdP + \sum_i \mu_i dn_i. \tag{8-14}$$

This equation shows that changes in G are determined by changes in T, P, and n_i; that is, G is a function of temperature, pressure, and composition, as stated earlier in Eq. (7-7),

$$G = F(T, P, n_{i(i=1,2,3,\ldots)}). \tag{8-15}$$

The subscript $i = 1, 2, 3, \ldots$ represents chemical components used to describe the composition of all phases in our system. Differentiating Eq. (8-15) leads to an expression for the total derivative of G,

$$dG = -\left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j} dn_i, \tag{8-16}$$

and comparison with Eq. (8-14) gives the following identities,

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,n_i}; \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,n_i}; \quad \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j}. \tag{8-17a, b, c}$$

We now see that our function of the state of the system called G has the following properties: its partial change with respect to temperature is simply the negative of the entropy of the system, its partial change with respect to pressure is the volume of the system, and its partial change with respect to composition is the chemical potential.

The extensive parameters G, S, and V in Eqs. (8-17a, b) refer to the entire system. However, similar types of equations can also be written for a chemical reaction,

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P; \quad \Delta V = \left(\frac{\partial \Delta G}{\partial P}\right)_T, \tag{8-18a, b}$$

or for a specific phase (represented here by the subscript ψ,

$$S_\psi = -\left(\frac{\partial G_\psi}{\partial T}\right)_P; \quad V_\psi = \left(\frac{\partial G_\psi}{\partial P}\right)_T. \tag{8-19a, b}$$

These identities have many practical uses in geochemistry. They may be integrated or used graphically to predict the effects of temperature and pressure on the free energy of substances or chemical reactions.

As an example, consider what happens to the liquid–vapor reaction of water [Eq. (8-1)] when temperature is changed at constant pressure. From Eq. (8-19a) we see that the entropy of the two phases (S_{liquid} and S_{vapor}) will determine how the free energies (G_{liquid} and G_{vapor}) change with temperature. Because the entropy of vapor is greater than that of the liquid, the slope of a curve for G_{vapor} will be steeper than that for G_{liquid} when both are plotted against T, as shown schematically in Fig. 8-1(*a*). The curves intersect at the temperature where ΔG is zero and the liquid and vapor are in equilibrium. At lower temperatures, because $S_{\text{vapor}} > S_{\text{liquid}}$, the free energy curve for the vapor will be above that for the liquid. Here ΔG is negative and the liquid is the stable phase. For higher temperatures, where ΔG is positive, the vapor will be stable. These relationships are easily visualized in a graph like Fig. 8-1(*a*), where the stable phase is always the one with the lower free energy, and the phase with the larger entropy (the vapor in this case) is stable at high temperatures.

Similar relations can be deduced by qualitatively evaluating the pressure dependence of free energy using Eq. (8-19b). An example for the liquid–vapor reaction of water is shown in Fig. 8-1(*b*). Because water as a vapor has a higher molal volume than the liquid, its free energy curve will be steeper when plotted against pressure. As a consequence, at pressures greater than liquid–vapor equilibrium the phase with the smaller volume (the liquid) will have the lower free energy and thus be the stable phase.

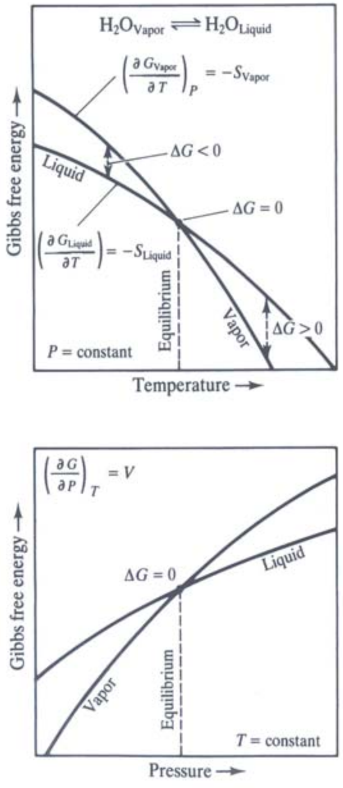

FIGURE 8-1
Schematic illustration of the difference in the Gibbs free energy of formation of H_2O liquid and H_2O vapor as a function of temperature at constant pressure (*a*) and as a function of pressure at constant temperature (*b*). In both diagrams the stable phase is the one with the lower free energy, and equilibrium between the two phases exists when $\Delta G = 0$. The stable phase at high temperatures is the one with the higher entropy (the vapor), and the stable phase at high pressures is the one with the higher density or smaller volume (the liquid).

Other important relations between chemical potential and free energy are obtained if we integrate Eq. (8-16) over the entire mass of the system. Noting that T and P are independent of mass, we find that G is uniquely defined by the sum of the chemical potentials multiplied by the number of mols of each chemical component (i),

$$G = \sum_i \mu_i n_i. \tag{8-20}$$

And upon differentiation we obtain

$$dG = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i, \tag{8-21}$$

which can be combined with Eq. (8-14) to give

$$0 = SdT - VdP + \sum_i n_i d\mu_i. \tag{8-22}$$

The latter equation is called the Gibbs–Duhem equation. It defines relationships among changes in the intensive variables T, P, and μ_i for systems in a state of internal equilibrium. We shall see later that these three equations form a useful basis for describing equilibrium phase relations in complex geologic systems, but first we introduce the concepts of fugacity, activity, and standard states.

8-2 FUGACITY

Mathematically the partial molal free energy has the drawback that it approaches an infinite negative value as the concentration becomes indefinitely small. To circumvent this difficulty, it is often convenient to use still another measure of escaping tendency, called *fugacity*, defined by the equation

$$\left(\frac{\partial \ln f_i}{\partial \mu_i}\right)_{P.T} = \frac{1}{RT}, \tag{8-23}$$

where f_i is the fugacity and μ_i is the chemical potential as defined by Eq. (8-3). Alternatively this may be expressed in the integrated form

$$\mu_i - \mu_i' = RT \ln \frac{f_i}{f_i'}, \tag{8-24}$$

where μ_i and μ_i' are the partial molal free energies, and f_i and f_i' the fugacities, of one substance (i) at two different concentrations (or, for gases, at two different pressures). The fugacity, in effect, is a sort of idealized vapor pressure. It is measured in bars, and is equal to the vapor pressure when the vapor behaves as a perfect gas.

Fugacities may be used for solids and liquids as well as for gases. We may speak of the fugacity of a vapor above a liquid, or the fugacity of the liquid itself, just as the vapor pressure of a liquid may be considered a property of either the vapor or the liquid.

The relation between fugacity and vapor pressure can be made clear by an argument based on the equation for change in free energy with pressure (8-17b) for a perfect gas, where nRT/P may be substituted for V,

$$\left(\frac{\partial G}{\partial P}\right)_T = \frac{nRT}{P}. \tag{8-25}$$

Differentiation with respect to n at constant T and P gives

$$\left(\frac{\partial}{\partial n}\left(\frac{\partial G}{\partial P}\right)_T\right)_{T,P} = \left(\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial n}\right)_{T,P}\right)_T = \left(\frac{\partial \mu}{\partial P}\right)_T = \frac{RT}{P}. \tag{8-26}$$

If dP is moved to the right side of the equation, integration gives

$$\int_{\mu'}^{\mu} d\mu = \int_{P'}^{P} \frac{RT}{P} dP, \tag{8-27}$$

and

$$\mu - \mu' = RT \ln \frac{P}{P'}. \tag{8-28}$$

For a specific chemical component (i) of the gas we substitute Dalton's law ($P_i = X_i P$, which states that the partial pressure of a gas, P_i, is equal to its mol fraction, X_i, times the total pressure, P, noting that $X_i \equiv X_i'$) so that,

$$\mu_i - \mu_i' = RT \ln \frac{P_i}{P_i'}. \tag{8-29}$$

This has the same form as Eq. (8-24), indicating that vapor pressure may be used as an approximation for fugacity to the same extent that a perfect gas approximates the behavior of a real gas.

Deviation from ideal gas behavior is measured by the ratio of the fugacity to the partial pressure of a chemical component (i) in the gas; this ratio is given the name *fugacity coefficient* (χ_i),

$$\frac{f_i}{P_i} = \chi_i. \tag{8-30}$$

Upon substituting Dalton's law we obtain the following relation between fugacity and composition for a nonideal gas,

$$f_i = X_i \chi_i P. \tag{8-31}$$

8-3 ACTIVITY AND STANDARD STATES

In very dilute solutions the fugacity of a volatile solute becomes equal to its vapor pressure, and this in turn is proportional to its concentration in the solution, a relationship called Henry's law. To express the deviation of more concentrated solutions from Henry's law, it is convenient to use *relative fugacities*, fugacities referred to the fugacity in some assumed standard state:

$$\mu_i - \mu_i^\circ = RT \ln \frac{f_i}{f_i^\circ}. \tag{8-32}$$

This equation is identical with Eq. (8-24) if μ_i' and f_i' are defined as the values of these quantities in a standard state. The standard state may be selected in different ways for different kinds of problems. For solids and solvent components of fluids the standard state usually chosen is one of unit activity of the pure substance at some specified T and P, or for some range of T and P. For solutes a convenient standard state is a hypothetical solution of unit concentration that obeys Henry's law (practically all real solutions deviate considerably from Henry's law at concentrations near 1m).

The ratio f_i/f_i° in Eq. (8-32) is defined as the *activity* of the ith species or component (a term introduced in Sec. 2-6). Thus Eq. (8-32) can be rewritten as

$$\mu_i - \mu_i^\circ = RT \ln a_i. \tag{8-33}$$

In this way the chemical potential of a thermodynamic component in our system is considered to be the sum of two terms: the chemical potential in some specified standard standard state (μ_i°) and a term including the activity (a_i),

$$\mu_i = \mu_i^\circ + RT \ln a_i. \tag{8-34}$$

Note that the last term is simply a measure of the difference in the chemical potentials of a component in our system and the component in some chosen standard state, that is

$$a_i \equiv \frac{f_i}{f_i^\circ} = \exp\left(\frac{\mu_i - \mu_i^\circ}{RT}\right). \tag{8-35}$$

Like fugacity, activity is related to concentration. It is, in fact, a sort of idealized concentration, the concentration that would be expected if the solution obeyed Henry's law at all concentrations. The ratio of activity to concentration (m_i) or to mol fraction (X_i),

$$\frac{a_i}{m_i} = \gamma_i \tag{8-36}$$

and

$$\frac{a_i}{X_i} = \lambda_i, \tag{8-37}$$

expresses the extent to which solutions deviate from Henry's law; this ratio is given the name *activity coefficient*. The concepts of activity and activity coefficient described here may be generalized to apply to volatile as well as nonvolatile solutes and to any kind of solution. We have met the terms before in our discussion of solubility equilibria in Chapter 2.

The best units to use for activities are not agreed upon by all writers. If the activity of a solute in a saturated solution is defined as in Sec. 2-6, that is, as the equilibrium concentration extrapolated to zero ionic strength, the appropriate unit would be the same as the unit used to express concentration. With the more general definition given above [Eq. (8-35)], however, *activity is the ratio of two fugacities*, hence *it is a dimensionless quantity*. There is no discrepancy in the two definitions; they can easily be reconciled by adjusting the definitions of standard fugacity or of the activity coefficient. The way these related quantities are defined is largely a matter of choice, and practically it makes little difference, since numerical values of activity are the same with either usage.

8-4 THE EQUILIBRIUM CONSTANT

In Chapter 1 we introduced the equilibrium constant as a quotient of concentrations based on qualitative observations, and used it in later chapters to describe conditions of equilibrium between aqueous solutions and minerals. Here we derive an exact formulation of the equilibrium constant based on thermodynamic principles.

For constant temperature and pressure, where dT and dP are zero, the relationships among G, μ_i, and n_i defined by Eqs. (8-14), (8-21), and (8-22) reduce to

$$0 = \sum_i n_i d\mu_i \tag{8-38}$$

and

$$dG = \sum_i \mu_i dn_i. \tag{8-39}$$

The latter equation can be written for a chemical reaction as

$$\Delta G = \sum_i \mu_i \nu_i, \tag{8-40}$$

an equation similar in form to stoichiometric equations derived earlier involving free energy, composition, and chemical potential [Eqs. (7-49), (7-67), (8-2), (8-7), and (8-8)]. Now if we substitute for μ_i the standard state and activity relations defined by Eq. (8-34), noting that

$$\Delta G^\circ = \sum_i \mu_i^\circ \nu_i, \tag{8-41}$$

we obtain

$$\Delta G = \Delta G^\circ + RT \sum_i \nu_i \ln a_i. \tag{8-42}$$

The superscript in the symbol ΔG° indicates that this is the *standard Gibbs free energy* of reaction, the free energy change for the reaction that would occur when all substances are present in their standard states (Sec. 7-4).

Equilibrium at constant T and P requires that the free energy of reaction, ΔG, must be equal to zero, so we can rewrite Eq. (8-42) for the condition of equilibrium (converting to the more familiar base 10 logarithm) as

$$-\Delta G^\circ = 2.303\, RT \sum_i \nu_i \log a_i. \tag{8-43}$$

Thus for equilibrium among the hypothetical components X, Y, Z, and Q represented by the reaction

$$x\mathrm{X} + y\mathrm{Y} \rightleftharpoons z\mathrm{Z} + q\mathrm{Q}, \tag{8-44}$$

where x, y, z, and q are stoichiometric reaction coefficients, we have

$$\Delta G^\circ = -2.303\, RT\,(z \log a_\mathrm{Z} + q \log a_\mathrm{Q} - x \log a_\mathrm{X} - y \log a_\mathrm{Y}) \tag{8-45}$$

or

$$\Delta G^\circ = -2.303\, RT\,(\log a_\mathrm{Z}^z + \log a_\mathrm{Q}^q - \log a_\mathrm{X}^x - \log a_\mathrm{Y}^y). \tag{8-46}$$

Rearrangement of Eq. (8-46) gives, for equilibrium,

$$\frac{-\Delta G^\circ}{2.303\, RT} = \log \left(\frac{a_\mathrm{Z}^z \cdot a_\mathrm{Q}^q}{a_\mathrm{X}^x \cdot a_\mathrm{Y}^y} \right). \tag{8-47}$$

The quotient on the right-hand side of the equation must be constant if ΔG is to remain zero. The separate activities may change, but any change is compensated by other changes so that the value of the quotient remains constant. We call this quotient the equilibrium constant, K, for the reaction of Eq. (8-44):

$$K = \left(\frac{a_\mathrm{Z}^z \cdot a_\mathrm{Q}^q}{a_\mathrm{X}^x \cdot a_\mathrm{Y}^y} \right). \tag{8-48}$$

The following general relations can now be written among K, the standard Gibbs free energy, and the activities of components in a chemical reaction:

$$\log K = \frac{-\Delta G^\circ}{2.303RT} = \sum_i \nu_i \log a_i \tag{8-49}$$

and

$$K = 10^{\left(\frac{-\Delta G^\circ}{2.303RT}\right)} = \prod_i a_i^{\nu_i}. \tag{8-50}$$

The right-hand expression in Eq. (8-50) is a general statement for the stoichiometric activity product of a chemical reaction; it is explicitly stated by the quotient in Eqs. (1-6) and (8-48).

From the derivations above we see that the equilibrium constant has a value that is determined by the standard states (μ_i°) chosen for all the substances in the reaction. It is a function of T and P, and is independent of the compositions of the phases involved in the actual reaction. In earlier chapters the equilibrium constant was treated as a product of concentrations [Eq. (1-6)]; actually the number refers to activities [Eqs. (8-48) to (8-50)], so that K is a dimensionless quantity (as noted earlier, Sec. 1-8).

As an example of the relationship between the equilibrium constant and standard molal Gibbs free energy we look again at the solubility of anhydrite previously considered in Sec. 1-5. At equilibrium $CaSO_4(\text{anhydrite}) \rightleftharpoons Ca^{2+} + SO_4^{2-}$ [Eq. (1-26)] and, if the anhydrite is pure so that $a_{\text{anhydrite}} = 1$, the constant is $K = a_{Ca^{2+}} a_{SO_4^{2-}}$. For a solution of $CaSO_4$ in pure water, the concentrations of Ca^{2+} and SO_4^{2-} are so small that the difference between concentrations and activities is unimportant, and the experimental value of K is $m_{Ca^{2+}} m_{SO_4^{2-}} = 3.4 \times 10^{-5}$. From this value the standard free energy change can be computed:

$$\Delta G^\circ = -2.303RT \log K = +25.5 \text{ kJ}. \tag{8-51}$$

The positive number means that the reaction tends to go to the left when all substances are at unit activities, that is, solid $CaSO_4$ and the two ions Ca^{2+} and SO_4^{2-} each at an activity of unity. This, of course, agrees with laboratory experience: in a solution that contains such a high concentration of Ca^{2+} and SO_4^{2-}, solid $CaSO_4$ (in the form of gypsum) will precipitate rapidly until equilibrium is established.

For another example, consider the oxidation of galena to anglesite:

$$\underset{\text{galena}}{PbS} + 2O_2 \rightarrow \underset{\text{anglesite}}{PbSO_4}\,. \tag{8-52}$$

The standard free energy of this reaction is computed from Eq. (7-67), which reduces to the difference in free energies of formation of anglesite and galena ($\Delta G^\circ = -714$ kJ). The equilibrium constant, computed from Eq. (8-50), is $K = 10^{125}$. Both the high negative ΔG° and the enormous exponent in K indicate that this reaction goes practically to completion toward the right. For the reaction

$$\underset{\text{galena}}{PbS} + SO_4^{2-} \leftarrow \underset{\text{anglesite}}{PbSO_4} + S^{2-} \qquad \Delta G^\circ = +115.9 \text{ kJ} \tag{8-53}$$

on the other hand, $K = 10^{-20.3}$; here the high positive ΔG° and the large negative exponent in K both mean that this reaction is displaced far to the left. For the reaction

$$\underset{\text{galena}}{PbS} + 2H^+ \rightleftharpoons H_2S + Pb^{2+} \qquad \Delta G^\circ = +46.4 \text{ kJ} \tag{8-54}$$

K is $10^{-8.1}$. Here the small positive ΔG° and the small exponent in K mean that the reaction is displaced toward the left, but that all four substances can exist together in appreciable amounts at equilibrium—as is shown by the experimental observations that lead sulfide is precipitated when H_2S is passed through an acid solution of a lead salt, and that a perceptible odor of H_2S is evident when a fairly strong acid is dropped on galena.

8-5 EQUILIBRIUM CONSTANTS: TEMPERATURE AND PRESSURE DEPENDENCE

Thermodynamic relations presented above allow us to express quantitatively how equilibrium constants change with temperature and pressure, and thus to determine conditions of equilibrium for the geologic processes summarized in Fig. 1-1.

The equilibrium constant is a function of T and P expressed mathematically as

$$K = F(T, P). \tag{8-55}$$

Differential changes in K are described by the total derivative of this equation (see Fig. 7-1), which in logarithmic form appears as

$$d \ln K = \left(\frac{\partial \ln K}{\partial T}\right)_P dT + \left(\frac{\partial \ln K}{\partial P}\right)_T dP. \tag{8-56}$$

To see how K changes with variations in T and P, we need equations for the two partial derivatives in Eq. (8-56) written in terms of measurable thermodynamic quantities, specifically T, P, ΔH°, and ΔV°.

Temperature Dependence

First we derive the change in ln K with respect to T at constant P. Combining Eq. (8-49) and Eq. (7-59) allows the equilibrium constant to be expressed in terms of ΔH° and ΔS°:

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}. \tag{8-57}$$

Differentiating with respect to T at constant P gives

$$\begin{aligned} \left(\frac{\partial \ln K}{\partial T}\right)_P &= \frac{-1}{R}\left(\frac{\partial \Delta G^\circ/T}{\partial T}\right)_P \\ &= \frac{-\Delta H^\circ}{R}\left(\frac{\partial T^{-1}}{\partial T}\right)_P - \frac{1}{RT}\left(\frac{\partial \Delta H^\circ}{\partial T}\right)_P + \frac{1}{R}\left(\frac{\partial \Delta S^\circ}{\partial T}\right)_P. \end{aligned} \tag{8-58}$$

On the right-hand side of the equation we differentiate the first term, then substitute for the last two partial derivatives their definitions in terms of ΔC_P° [Eqs. (7-33) and (7-60)],

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H^\circ}{RT^2} - \frac{\Delta C_P^\circ}{RT} + \frac{\Delta C_P^\circ}{RT}. \tag{8-59}$$

The last two terms cancel, leaving

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H^\circ}{RT^2}. \tag{8-60}$$

Using the more familiar decimal logarithms, we have

$$\left(\frac{\partial \log K}{\partial T}\right)_P = \frac{\Delta H^\circ}{2.303RT^2}. \tag{8-61}$$

This equation, referred to as the van't Hoff equation, shows that differential changes in log K with respect to T are proportional to the standard heat of reaction and inversely proportional to the square of temperature.

The importance of the heat of reaction in determining how the equilibrium constant responds to changes in temperature can be summarized as follows: if ΔH° is zero, the value of K will not change when temperature is changed; if the reaction is endothermic, log K increases with increasing temperature, and the larger the value of ΔH° the greater the change with temperature; and if the reaction is exothermic, log K decreases with increasing temperature, the magnitude of change again depending on the value of ΔH°. This agrees with qualitative predictions from Le Chatelier's rule. For example, when ΔH° is positive, meaning that the reaction is endothermic, the differential coefficient of Eq. (8-61) is also positive; in other words, K increases as T increases, so that the equilibrium is displaced in the direction which shows absorption of heat.

We can now attach numbers to the temperature dependence of mineral solubilities and phase assemblages discussed in Chapter 4. Consider first the solubility of quartz presented in Fig. 4-4. The reaction is

$$\underset{\text{quartz}}{SiO_2} \rightleftharpoons SiO_2(aq), \tag{4-35}$$

and the equilibrium constant is merely the activity of aqueous silica, since the activity of pure quartz is chosen to be unity at any temperature and pressure, by convention. In dilute solutions the activity of aqueous silica may be taken as equal to its concentration, and this may be expressed as the measured solubility of quartz, that is, $\log K = \log a_{SiO_2(aq)} \approx \log m_{SiO_2(aq)}$. The temperature dependence of quartz solubility can now be expressed by Eq. (8-61) as

$$\left(\frac{\partial \log m_{SiO_2(aq)}}{\partial T}\right)_P = \frac{\Delta H^\circ}{2.303RT^2}. \tag{8-62}$$

For pressures above 1 kbar quartz solubility increases with increasing temperature at constant pressure, as shown in Fig. 4-4; for these conditions the reaction must be endothermic [ΔH° is positive in Eq. (8-62)]. The maximum in quartz solubilities at pressures below 1 kbar in Fig. 4-4 corresponds to pressures and temperatures where ΔH° is equal to zero and Eq. (8-62) becomes

$$\left(\frac{\partial \log m_{SiO_2(aq)}}{\partial T}\right)_P = 0. \tag{8-63}$$

At lower temperatures the reaction is endothermic, but at temperatures higher than that for maximum solubility and at these low pressures we deduce that quartz solubility is exothermic because of the negative slopes of the curves in diagrams

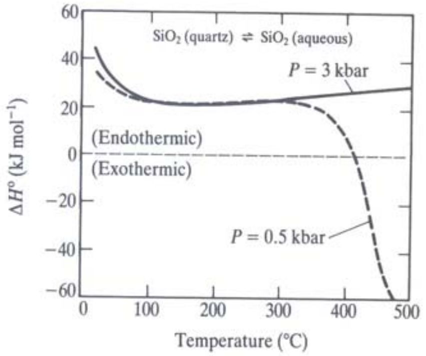

FIGURE 8-2
Computed values of the enthalpy of reaction for quartz solubility at 3 kbar and 0.5 kbar. Note that the enthalpy of reaction is essentially constant over the temperature range of 100°C to 300°C where it is nearly independent of changes in pressure. However, at high temperatures and low pressures (for example 0.5 kbar) the enthalpy of reaction changes rapidly with increasing temperature. (Curves computed from equations and data reported by Walther and Helgeson, 1977.)

where log K is plotted as a function of T. These predictions are borne out by the computed values of ΔH° for Eq. (4-35) shown in Fig. 8-2.

Applying the same type of reasoning to experimental phase relations shown in Fig. 4-6, we see that reactions of kaolinite going to diaspore [Eq. (4-9)], and of pyrophyllite to kaolinite [Eq. (4-10)], are endothermic reactions because these phase boundaries have positive slopes in a plot of log K as a function of temperature. On the other hand, reactions involving K-feldspar, muscovite, kaolinite, and quartz in Eqs. (4-26) and (4-27) are exothermic because: (1) the equilibrium constants are both equal to $\log K = 2 \log (a_{K^+}/a_{H^+})$, (2) their temperature derivative is

$$\left(\frac{\partial \log(a_{K^+}/a_{H^+})}{\partial T}\right)_P = \frac{\Delta H^\circ}{4.606RT^2}, \tag{8-64}$$

and (3) the measured ratio of KCl to HCl in solution decreases with increasing temperature (Fig. 4-10); thus ΔH° must be negative. We see from these examples that solubility and phase equilibrium experiments provide useful information about the heat energy of chemical reactions.

To evaluate the absolute change in log K with temperature we integrate Eq. (8-61) from some reference temperature (T_{ref}, which is usually 25°C (298 K) where values of $\log K_{T_{ref}}$ and ΔH° are known) to some specified temperature (T) of interest,

$$\int_{K_{T_{ref}}}^{K_T} d\log K = \int_{T_{ref}}^{T} \frac{\Delta H^\circ}{2.303RT^2}\, dT \tag{8-65}$$

and

$$\log K_T = \log K_{T_{ref}} + \int_{T_{ref}}^{T} \frac{\Delta H^\circ}{2.303T^2}\, dT. \tag{8-66}$$

If ΔC_P° of the reaction is zero, so that ΔH° is independent of temperature [Eq. (7-33)], the equilibrium constant will be a linear function of T^{-1}:

$$\log K_T = \log K_{T_{\text{ref}}} - \frac{\Delta H^\circ}{2.303R}\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right). \tag{8-67}$$

Otherwise we need equations like Eqs. (7-34) and (7-39), describing the temperature dependence of ΔC_P°, to solve the integral of Eq. (8-66).

As an example of how Eq. (8-67) is used, we consider the familiar equilibrium among K-feldspar, muscovite, quartz, and an aqueous solution represented by

$$\underset{\text{K-feldspar}}{3\text{KAlSi}_3\text{O}_8} + 2\text{H}^+ \rightleftharpoons 2\text{K}^+ + \underset{\text{muscovite}}{\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2} + \underset{\text{quartz}}{6\text{SiO}_2}, \tag{4-26}$$

for which log K at 1 bar and 25°C is 9.58 and the heat of reaction is −26.3 kJ. On the assumption that ΔH° is independent of temperature, we can calculate values of log K at some higher temperature, say 250°C, by Eq. (8-67) (note $R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$),

$$\log K_{T=523} = 9.58 - \frac{-26,300\ \text{J mol}^{-1}}{2.303 \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{523\text{K}} - \frac{1}{298\text{K}}\right) = 7.6. \tag{8-68}$$

In other words, the equilibrium constant has decreased two orders of magnitude as the temperature rises from 25 to 250°C. This is the direction of change we would predict qualitatively from Le Chatelier's principle for a reaction with negative ΔH°. So if pure K-feldspar, muscovite, and quartz were in equilibrium with a dilute solution where $m_{\text{K}^+} = 10^{-3}$, the pH of the solution at 25°C would be

$$\log K = 2\log a_{\text{K}^+} - 2\log a_{\text{H}^+} = 2\log a_{\text{K}^+} + 2\text{pH},$$

$$\text{pH} = 0.5\log K - \log a_{\text{K}^+} = 0.5(9.58) - (-3.0) = 7.8,$$

and at 250°C it would be

$$\text{pH} = 0.5\log K - \log a_{\text{K}^+} = 0.5\,(7.6) - (-3.0) = 6.8.$$

The heat capacities of aqueous species and water change dramatically with increasing temperature at low pressures, so our assumption about the temperature independence of reaction enthalpy for Eq. (4-26) is not strictly valid. The equilibrium constant computed at 250°C above is only a first approximation. Accurate computation of the solution pH at 250°C requires additional information on the temperature dependence of ΔH° [see Eqs. (7-38) and (7-41)].

As a second example of the use of van't Hoff's equation, let us try the reverse problem: given values of the equilibrium constant over a range of temperature, to calculate the enthalpy change of the reaction. We use a simple reaction considered earlier, the dissolving of quartz in water represented by Eq. (4-35). Experimental values for the solubility of quartz over a temperature range of 70 to 250°C are shown in Fig. 8-3. Solubilities are plotted as logarithms, and temperatures as reciprocals of the absolute temperature times 1000. The reason for this procedure lies in the form

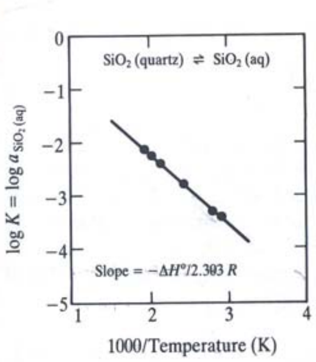

FIGURE 8-3
The logarithm of the equilibrium constant for quartz solubility [Eq. (4-35)] as a function of the reciprocal of temperature times 1000. The symbols represent experimental measurements reported by Morey et al., 1962. The line is a linear fit to the experimental data: log $K = -1.346\ (1000T^{-1}) + 0.491$.

of Eq. (8-67), which can be rewritten as

$$\log K_T = -\frac{\Delta H^\circ}{2.303R}\frac{1}{T} + \left(-\log K_{T_{\text{ref}}} + \frac{\Delta H^\circ}{2.393R}\frac{1}{T_{\text{ref}}}\right). \tag{8-69}$$

This is an equation for a straight line which has the form of

$$y = mx + b,$$

where y corresponds to the dependent variable (log K_T), m is the slope of the line ($-\Delta H^\circ/2.303R$), x represents the independent variable ($1/T$), and b is a constant equal to the parenthetical term in Eq. (8-69). The experimental data shown in Fig. 8-3 clearly fit this requirement over this limited temperature interval. (See for comparison Fig. 4-4.)

When the data are plotted and the best straight line is fitted to the points, the slope of the line is equal to $-\Delta H^\circ/2.303R$. Hence ΔH° in kJ mol^{-1} can be found by multiplying the slope by $2.303R$ (19.477 J mol^{-1} K^{-1}). In Fig. 8-3 the slope is −1.346 K, and ΔH° for dissolving quartz is 25.85 kJ. This number can be used to estimate the enthalpy of formation of aqueous silica because $\Delta H^\circ = \Delta H^\circ_{\text{f, SiO}_2\text{(aq)}} - \Delta H^\circ_{\text{f, SiO}_2\text{(quartz)}}$ [Eq. (7-30)]: from Appendix VIII, the value of $\Delta H_{\text{f,quartz}}$ is −910.65 kJ mol^{-1}; the figure for aqueous silica must then be 25.85 kJ more positive than this or approximately 884.8 kJ mol^{-1}. This is a widely used method for obtaining enthalpy changes for reactions and enthalpies of formation that would be difficult to measure directly.

Pressure Dependence

We can also differentiate Eq. (8-49) with respect to P at constant T to obtain an expression for the pressure dependence of K:

$$\left(\frac{\partial \log K}{\partial P}\right)_T = -\frac{1}{2.303RT}\left(\frac{\partial \Delta G^\circ}{\partial P}\right)_T. \tag{8-70}$$

The right-hand partial derivative is equal to the standard volume of reaction [Eq. (8-17b)],

$$\left(\frac{\partial \log K}{\partial P}\right)_T = -\frac{\Delta V^\circ}{2.303RT}. \qquad (8\text{-}71)$$

Thus the pressure dependence of the equilibrium constant will be determined by the standard volume of reaction and temperature. Qualitatively, if the volume change of the reaction is less than zero, log K will increase and ΔG° [Eq. (8-49)] will decrease with increasing pressure. In other words the reaction is displaced to the right, in the direction of decreasing volume, as Le Chatelier's rule requires.

Integration of Eq. (8-71) from a reference pressure (P_{ref}), where the value of $K_{P_{\text{ref}}}$ is known, to some specified pressure (P) gives

$$\log K_P = \log K_{P_{\text{ref}}} - \frac{1}{2.303RT}\int_{P_{\text{ref}}}^{P} \Delta V^\circ \, dP. \qquad (8\text{-}72)$$

To use this equation we must express ΔV° as a function of P before we can integrate. If ΔV° is independent of P the integral becomes

$$\log K_P = \log K_{P_{\text{ref}}} - \frac{\Delta V^\circ}{2.303RT}(P - P_{\text{ref}}), \qquad (8\text{-}73)$$

and log K will be a linear function of P at constant T. The slope of a plot of log K versus P will be $-\Delta V^\circ/2.303RT$.

As an example of the use of Eq. (8-73) we again consider equilibrium of K-feldspar, muscovite, quartz, and solution [Eq. (4-26)], for which we computed a value of log K at 250°C of 7.6 using numbers for K and ΔH° at 1 bar and 25°C. Now, how will this value for the equilibrium constant change if pressure is increased to 5000 bar and temperature is held constant at 250°C? To estimate this we use a value of ΔV° of -34.8 cm^3 mol^{-1} (computed from molal and partial molal volumes of reaction species at 250°C), assume that ΔV° is independent of pressure, and use a conversion factor of 10 cm^3 bar = 1 J:

$$\log K_{P=5000} = 7.59 - \frac{-34.8\ \text{cm}^3\ \text{mol}^{-1}}{2.303 \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 523\ \text{K}}\left(\frac{4999\ \text{bar}}{10\ \text{cm}^3\ \text{bar}}\right) = 9.3. \qquad (8\text{-}74)$$

Because the volume change of reaction is negative, the differential coefficient for Eq. (8-71) is positive and log K increases with increasing pressure as shown in Fig. 8-4. This change with pressure is opposite to the change in K we computed earlier for a temperature increase from 25 to 250°C. The effects of increasing both T and P may, under circumstances when both ΔH° and ΔV° are of the same sign, cancel each other in Eq. (8-56); thus in the present example, log K at 1 bar and 25°C is nearly equal to that at 5000 bar and 250°C.

As our final example we use Eq. (8-73) to predict pressures for reactions deep in the Earth from assemblages and compositions of minerals found on the surface. This procedure, referred to as geobarometry, helps geologists evaluate physical conditions of igneous and metamorphic processes that cannot be directly observed

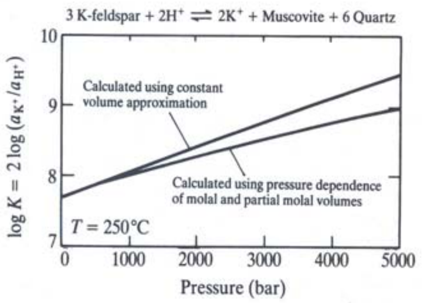

FIGURE 8-4
Computed values of the equilibrium constant for the reaction of K-feldspar, muscovite, quartz, and solution [Eq. (4-26)] as a function of pressure at a constant temperature of 250°C. The upper curve is computed assuming that the volume change of reaction is independent of pressure, while the lower curve accounts for the pressure dependence of the volume of aqueous species in the reaction.

or measured. Of the many reactions we could consider, the one we choose involves only three minerals, the familiar minerals quartz and albite and a Na–Al pyroxene called jadeite ($NaAlSi_2O_6$). Pyroxenes rich in jadeite are found with quartz and sometimes albite in blueschist metamorphic rocks, rocks that formed at high pressures and low temperatures in regions where plates of the lithosphere are being subducted into the mantle. In these rocks jadeitic pyroxene exhibits a wide range of isomorphic substitutions with the components diopside ($CaMgSi_2O_6$) and acmite ($NaFe^{3+}Si_2O_6$). In contrast, the quartz and albite are nearly pure phases. The equilibrium reaction is

$$\underset{\text{jadeite}}{NaAlSi_2O_6} + \underset{\text{quartz}}{SiO_2} \rightleftharpoons \underset{\text{albite}}{NaAlSi_3O_8}. \qquad (8\text{-}75)$$

Because quartz and albite are nearly pure their activities are taken as unity, so the equilibrium constant equals the reciprocal of the activity of the jadeite component in pyroxene. We assume, as a first approximation, that the jadeite is an ideal solid solution so that the activity of jadeite in the pyroxene is equal to the mol fraction of jadeite [X_{jadeite}, Eq. (8-37)] and the equilibrium constant for Eq. (8-75) becomes

$$K = a_{\text{jadeite}}^{-1} \approx X_{\text{jadeite}}^{-1}. \qquad (8\text{-}76)$$

If we assume that the pyroxene has not changed in composition since it formed, the mol fraction of jadeite will be a measure of the equilibrium constant at the T and P of metamorphism. If an independent estimate of temperature can be made, the measured pyroxene compositions can be used to predict metamorphic pressures.

The pressure dependence of the pyroxene compositions is given by combining Eqs. (8-76) and (8-71),

$$\left(\frac{\partial \log X_{\text{jadeite}}}{\partial P}\right)_T = \frac{\Delta V^\circ}{2.303RT}. \qquad (8\text{-}77)$$

The volume change for Eq. (8-75) is positive (approximately 17 cm^3 mol^{-1} at 1 bar and 25°C), so by analogy with Fig. 8-1(b) we see that the assemblage jadeite + quartz has the greater density and will be the mineral assemblage stable at high pressure. One can predict, then, that the mol fraction of jadeite in pyroxene in equilibrium with quartz and albite will increase with increasing pressure [the differential coefficient in Eq. (8-77) is positive].

To use the composition of jadeitic pyroxene as a geobarometer at some specified temperature (T), we integrate Eq. (8-77) (assuming that the reaction volume is independent of pressure). One of the integration limits (P_{ref}) will represent the pressure of equilibrium for pure jadeite, quartz, and albite, so that $\log K_{P_{\text{ref}}} = -\log X_{\text{jadeite}} = 0$; the other integration limit (P) will correspond to the pressure of equilibrium for albite, quartz, and a pyroxene of some measured composition represented by X_{jadeite}. The resulting equation is

$$\log X_{\text{jadeite}} = \frac{\Delta V^\circ}{2.303RT}(P - P_{\text{ref}}), \tag{8-78}$$

which is an equation for a straight line on a diagram of $\log X_{\text{jadeite}}$ plotted as a function of P; the line (Fig. 8-5) has a slope of $\Delta V^\circ/2.303RT$. Solving for pressure gives

$$P = \frac{2.303RT}{\Delta V^\circ}\log X_{\text{jadeite}} + P_{\text{ref}}, \tag{8-79}$$

an equation that allows us to estimate metamorphic pressures from measured compositions of pyroxene in equilibrium with albite and quartz.

For example, at a temperature of 600°C, where the equilibrium pressure (P_{ref}) for pure jadeite, quartz, and albite is experimentally determined to be 16.85 kbar (Fig. 8-5), Eq. (8-79) becomes

$$P = \frac{2.303 \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 873\ \text{K}}{17\ \text{cm}^3\ \text{mol}^{-1} \times 0.1\ \text{J cm}^{-3}\ \text{bar}^{-1}}\log X_{\text{jadeite}} + 16{,}850\ \text{bar}. \tag{8-80}$$

As with our previous examples the conversion factor of 1 J = 10 cm^3 bar is required to maintain the correct units. So if X_{jadeite} is 0.5 and the temperature of metamorphism is about 600°C, the predicted pressure is approximately 14 kbar, as shown in Fig. 8-5.

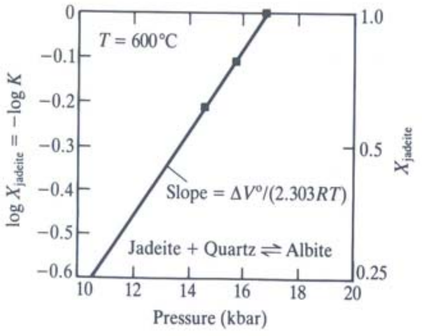

FIGURE 8-5
Calculated (line) and experimental (symbols) relations between pyroxene composition and pressure at 600°C for jadeitic–pyroxene, quartz, and albite equilibrium [Eq. (8-75)]. The symbols are unpublished experimental data of Jun Liu, Stanford University.

8-6 THE PHASE RULE

The equations developed in this chapter provide a thermodynamic basis for calculating equilibrium phase relations among minerals and solutions using the variables temperature, pressure, molal concentrations, and mol fractions. One important question remains for consideration: What determines the number of phases when a mixture of substances is in equilibrium? Or, in different phrasing, how many thermodynamic variables must be fixed to establish equilibrium in an assemblage of phases?

Consider, for example, the equilibrium of muscovite, quartz, K-feldspar, sillimanite, and water shown in Fig. 1-2, where the state of equilibrium is specified as a function of the variables temperature and pressure. How many of these variables must be fixed to ensure that equilibrium exists? Here the answer is *one*: if we fix pressure, say at 3 kbar, the temperature is automatically determined at about 630°C. We are free to choose one of the variables arbitrarily, but not two. For another example, take the equilibrium of quartz and water shown as a function of three intensive variables: temperature, pressure, and $m_{SiO_2(aq)}$ in Fig. 4-4(a). (Note that the third term, $m_{SiO_2(aq)}$, can be considered to represent the chemical potential of SiO_2 because of the relation $\mu_{SiO_2} = \mu^\circ_{SiO_2} + RT\ln a_{SiO_2} = \mu^\circ_{SiO_2} + RT\ln m_{SiO_2}$). This time the number of variables that can be chosen arbitrarily is *two*: if we pick only one, say a temperature of 200°C, we still do not know whether we are on a line representing equilibrium unless either pressure or concentration is specified also.

A general answer to such questions about the number of variables that must be fixed to establish equilibrium lies in a simple relationship called the *phase rule*. This is one more useful tool whose original formulation we owe to the American chemist J. Willard Gibbs toward the end of the 19th century. The rule tells us that the number of phases (p) and number of chemical components (c) needed to describe the composition of all the phases determines the number of intensive variables that must be specified at equilibrium. The number of variables to which arbitrary values can be assigned is called the *variance* or number of *degrees of freedom*. It is commonly given the symbol f.

In symbolic terms the phase rule is stated as

$$\text{f} = c + 2 - p. \tag{8-81}$$

To illustrate its use, we apply it to the two examples considered above. The muscovite–quartz–K-feldspar–sillimanite–water equilibrium has 5 phases made up of 4 components (K_2O, Al_2O_3, SiO_2, and H_2O), so that Eq. (8-81) becomes f = 4 + 2 − 5 = 1. This agrees with our conclusion from Fig. 1-2: *one* of the intensive variables, either temperature or pressure, can be arbitrarily specified, and the other is thereby determined. A reaction of this sort is described as *univariant*. The quartz–water equilibrium has 2 phases and 2 components (SiO_2, H_2O), so that the variance is f = 2 + 2 − 2 = 2; thus values of two variables, say temperature and pressure, can be fixed arbitrarily, and by fixing these we automatically determine the equilibrium value of the third, $m_{SiO_2(aq)}$ [Fig. 4-4(a)]. Such a reaction is said to be *divariant*.

The equation for the phase rule [Eq. (8-81)] can be arrived at in a number of ways. It can be deduced qualitatively by considering equilibrium in simple systems, like the ones discussed above, or it can be obtained from a series of equalities among the chemical potentials of thermodynamic components and constraints imposed by the mol fractions used to describe the composition of all phases in the system. Here we derive the rule using the fundamental thermodynamic relation of the Gibbs–Duhem equation [Eq. (8-22)].

Consider again the equilibrium of quartz and water in the system SiO_2–H_2O. An explicit statement of the Gibbs–Duhem equation can be written for each of the two phases: for quartz we have

$$S_{\text{quartz}}\,dT - V_{\text{quartz}}\,dP + n_{\text{SiO}_2,\,\text{quartz}}\,d\mu_{\text{SiO}_2} = 0, \tag{8-82}$$

and for the solution

$$S_{\text{solution}}\,dT - V_{\text{solution}}\,dP + n_{\text{SiO}_2,\,\text{solution}}\,d\mu_{\text{SiO}_2} + n_{\text{H}_2\text{O},\,\text{solution}}\,d\mu_{\text{H}_2\text{O}} = 0. \tag{8-83}$$

These two equations determine the possible changes of intensive variables (T, P, and μ_i) in quartz and in the solution. At equilibrium the value of each intensive variable will be constant throughout the phases. Thus the state of the system is determined by the two variables, temperature and pressure, plus the chemical potential of each component in the system; that is, a total number of $c + 2$ variables. For our particular example the number is $2 + 2 = 4$. Since we have only 2 independent equations and 4 independent variables, we must arbitrarily specify two of the variables in order to have a unique solution to the equations; in other words, the number of unknowns must equal the total number of independent equations. The equality of Eq. (8-81) is now apparent: if we have p phases, then the number of degrees of freedom is the difference between the number of unknowns ($c + 2$) and the total number of independent statements of the Gibbs–Duhem equation (p), or $f = c + 2 - p$.

The phase rule has many uses in geochemistry, especially in evaluating experimental observations and in constructing theoretical phase diagrams. Its application to geologic systems is complicated by the large number of components needed to describe the composition of all the phases and by the fact that geologic systems are typically open to the transport of chemical components, especially those in the fluid phase. Nevertheless, the phase rule is another useful tool in geochemistry for which we shall find many applications in the study of metamorphic and magmatic processes in later chapters.

SUMMARY

The various concepts we have introduced here are treated at length in textbooks of physical chemistry and thermodynamics listed in the references at the end of this chapter. The important considerations are, in summary: the idea of chemical equilibrium may be visualized in terms of escaping tendencies, the tendency of each constituent to escape from one phase into another; escaping tendencies may be expressed quantitatively by chemical potentials (molal free energies for pure substances, partial molal free energies for constituents of solutions), by fugacities, or by activities and equilibrium constants once appropriate standard states are adopted; and the deviation of solutions from ideal behavior may be expressed by activity and fugacity coefficients. Variation of the equilibrium constant with temperature and pressure is determined by the heat and volume of reaction, a relation that provides a theoretical basis for estimating temperatures and pressures of geological processes. First order approximations of the temperature and pressure dependence of the equilibrium constant can often be made by using the assumption of constant heat and volume of reaction, which greatly simplifies the computations. It should be noted, however, that the validity of any thermodynamic calculation is determined by the extent to which the equations, data, and approximations used are consistent with reliable experimental and geologic observations. In subsequent chapters we will build upon the principles developed here to evaluate complex phase relations and reaction paths in a wide variety of geochemical environments.

PROBLEMS

1. For the reaction of water and carbon to make a combustible fuel (the "water–gas reaction"),

$$H_2O(g) + C \rightleftharpoons H_2 + CO,$$

ΔH° at 25°C is +131 kJ and the equilibrium constant K is $10^{-16.0}$. Calculate K for 100°C and for 200°C on the assumption that ΔH° is constant. What is the fugacity ratio of f_{H_2} to f_{H_2O} in equilibrium with 0.1 bar of CO at these two temperatures? Assume that fugacity is equal to partial pressure.

2. From the data of Appendix VIII, calculate the equilibrium constant at 25°C and at 250°C for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3.$$

In volcanic gas escaping from a fumarole at 600°C, would you expect the nitrogen to exist largely in the form of ammonia or largely as the free element? Assume ΔH° for the reaction is independent of temperature.

3. From the data of Appendix VIII, calculate the solubility product at 25°C for the reaction,

$$\underset{\text{galena}}{PbS} \rightleftharpoons Pb^{2+} + S^{2-}.$$

What would be the solubility of PbS in pure water if this were the only reaction taking place? The measured solubility is 3×10^{-4} g/liter. Explain why the two values differ so markedly.

4. In theories of formation of sulfide veins, a critical factor is the amount of free S^{2-} present in the vein solutions. Would the concentration of this ion resulting from dissociation of H_2S be greater or less at 100°C than at 25°C? Calculate the change in the two dissociation constants of H_2S between these temperatures. Assume ΔH° for the reactions are independent of temperature.

5. It is often suggested that solutions which transport and deposit metallic sulfides are alkaline. At ordinary temperatures would galena dissolve appreciably in an alkaline solution to form $Pb(OH)_3^-$? In this and similar questions, assume that "appreciable