

Mass Transfer Among Minerals and Hydrothermal Solutions

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Ample field and laboratory evidence indicates that incongruent reactions among silicates and aqueous electrolyte solutions are responsible for deposition of sulfides in many hydrothermal ore deposits. The extent to which these reactions take place depends on the composition of the solution, the mineralogy of the system, and the rate at which the aqueous phase moves through the depositional environment. Fluid inclusion analyses indicate that hydrothermal solutions commonly contain relatively high concentrations of NaCl, KCl, and CaCl₂, with lesser concentrations of MgCl₂, AlCl₃, H₂S, H₂SO₄, CO₂, SiO₂, and the ore-forming metals. As a result of extensive experimental and theoretical investigation of departures from ideality, speciation, and the stoichiometric solubilities of minerals in such solutions, the chemical and thermodynamic properties of hydrothermal systems are reasonably well understood. However, because the components of hydrothermal solutions are rarely present in proportions corresponding to those in minerals, and because many silicates react irreversibly and incongruently with aqueous solutions, stoichiometric solubility studies yield little information about the *genesis* of ore deposits. Similarly, owing to technologic limi-

tations and the multivariant nature of hydrothermal systems, experimental attempts to simulate ore-forming processes generally fail to define the chemical controls responsible for simultaneous alteration of host rocks and deposition of sulfides.

It has long been recognized that the association of sulfides with altered wallrocks is a manifestation of the chemical link between the alteration process and the precipitation of ore minerals in hydrothermal veins. Nevertheless, the chemical reactions responsible for the occurrence of one or another sulfide in a given depositional environment are still poorly understood. Similar ambiguities attend determination of the effect of diffusional transport of material from reaction fronts in alteration zones on the chemical consequences of bulk transport in adjoining fractures. Consequently, genetic implications of zonal patterns and the directional distribution of alteration minerals and associated sulfides remain obscure.

Recognition of subtle indicators of favorable environments for ore deposition depends to a large extent on the ability of the geologist to distinguish cause and effect in the geologic record. Mass transfer calculations indicate that precipitation of one or another sulfide may be caused indirectly by seemingly unrelated processes in different parts of the system. For example, the incongruent reaction of a calcium-poor, sulfate-rich solution with plagioclase to produce anhydrite may deplete the solution in SO₄²⁻. As a consequence, the fugacity of oxygen is decreased significantly, which favors sulfide deposition. Similarly, precipitation of hydrothermal biotite, siderite, or chlorite in response to incongruent reaction of an aqueous solution with a wallrock may cause the Cu/Fe ratio in solution to increase sufficiently to precipitate chalcopyrite or bornite. Depending on the presence or absence of other iron-bearing minerals in the system, hydrothermal leaching and more than one generation of a given sulfide may also result from these reactions (Helgeson, 1970). All of the various ramifications and consequences of these and many other much more complicated sets of interdependent reaction couples have yet to be unraveled. Theoretical calculations of equilibrium and mass transfer among minerals and aqueous solutions with the aid of thermodynamics, fluid mechanics, chemical kinetics, transport theory, and computer technology afford a means to this end.

Accelerated interest in hydrothermal transport processes over the past decade has led to a number of different theoretical models of chemical transfer in hydrothermal systems. Most of these incorporate specific mechanisms of transport, such as the diffusional transfer models adopted by Korzhinskii (1970), Fisher (1970, 1973, 1975), Elliot (1973), Fisher and Elliot (1974), Wood (1974), Fletcher and Hofmann (1974), Weare et al., (1976), Frantz and Mao (1976), Joesten (1977), Brady (1977), and others.

Recent developments in the application of chromatographic transport theory to infiltration metasomatism (Korzhinskii, 1959, 1970, 1973; Hofmann, 1972, 1973; Fletcher and Hofmann, 1974; Frantz and Weisbrod, 1973) parallel those in diffusion theory. Other theoretical studies incorporate composite models of fluid flow and heat transfer (Norton, 1972, 1977, 1978, 1979; Norton and Knapp, 1977; Norton and Knight, 1977; Villas and Norton, 1977; Norton and Taylor, 1979; Norton and Cathles, Chapter 12; Cathles, 1976; Brownell et al., 1975; Cheng and Lau, 1974; Donaldson, 1970; Faust and Mercer, 1975; Lasseter and Witherpoon, 1975; Mercer and Pinder, 1974; Mercer et al., 1975; Wolery and Sleep, 1976; Straus and Schubert, 1977), many of which provide quantitatively for simultaneous diffusional flux and bulk transport as a function of space and time.

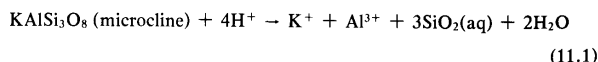
An alternate approach to those cited above, and one that is not restricted to a given mechanism of mass transfer nor explicit with respect to space and time, takes advantage of thermodynamic constraints imposed by local and partial equilibrium to calculate the extent to which components are redistributed among minerals and an aqueous solution as the solution reacts irreversibly with its mineralogic environment (Helgeson, 1967, 1968, 1970, 1972, 1974; Helgeson et al., 1969; Helgeson et al., 1970; Lafon and Mackenzie, 1971; Fritz and Tardy, 1976a, b; Droubi et al., 1976a, b; Sarazan et al., 1976; Fouillac et al., 1977; Wolery, 1978). The concepts involved in these calculations are reviewed below to encourage further application of the approach to the study of ore-forming processes.

CHEMICAL REACTIONS AND MASS TRANSFER

Mass transfer among minerals and aqueous solutions in geochemical processes can be represented by an array of chemical reactions representing reversible and irreversible changes in the distribution of components within or among the phases in a system. Regardless of whether the reactions are homogeneous or heterogeneous, each contributes to progress in the process, which leads ultimately to a state of overall equilibrium in the system; that is, a state of minimal Gibbs free energy at a given temperature and pressure. Of the many reactions that might occur in a given process, some are inhibited or favored kinetically, whereas others are precluded or promoted by thermodynamic constraints operating on or within the system. These constraints include constant temperature and/or pressure and fixed chemical potentials of one or more of the components in the system. The chemical potential of a component may be fixed by the presence of a phase with a composition corresponding to the component, by osmotic equilib-

rium with an external reservoir, or simply by the presence of a large mass of the component in the aqueous solution relative to the mass of the component redistributed among the phases in the process. The paragenesis of reaction products and the relative degree to which components are redistributed among phases depends to a large extent on the relative magnitude of the chemical potentials of the components in the aqueous solution at the beginning of the process. These chemical potentials are determined by the initial solution composition and the distribution of species in the aqueous phase.

Chemical reactions can be viewed as symbolic representations of differential equations describing mass transfer of components or ionic species among phases. For example, the congruent dissolution of microcline in an acid aqueous phase in which no complexing occurs can be described by writing



which expresses the dissolution process in terms of the conservation of mass and charge required by the first law of thermodynamics, that is,

$$\sum_i \nu_{i,j} \frac{dn_{i,j}}{d\xi_j} = 0 \quad (11.2)$$

where $\nu_{i,j}$ refers to the number of moles of the i th element in one mole of the i th solid or aqueous species, $dn_{i,j}$ stands for the change in the number of moles of the species caused by the j th reaction, and ξ_j represents the progress variable for the reaction (De Donder, 1920; De Donder and Van Rysselberghe, 1936; Prigogine and Defay, 1954; Prigogine, 1955). The progress variable, ξ_j , which is a measure of the extent (or degree of advancement) of the j th reaction, is equal to the number of moles of a given reactant that has been converted into products by the reaction, divided by the stoichiometric coefficient of the reactant in the j th reaction. It follows that the differentials in equation (11.2) correspond to the stoichiometric coefficients in reaction (11.1). We can thus replace j by reaction (11.1) and write,

$$\frac{dn_{\text{KAlSi}_3\text{O}_8, (11.1)}}{d\xi_{(11.1)}} = -1 \quad (11.3)$$

$$\frac{dn_{H^+,(11.1)}}{d\xi_{(11.1)}} = -4 \quad (11.4)$$

$$\frac{dn_{K^+,(11.1)}}{d\xi_{(11.1)}} = 1 \quad (11.5)$$

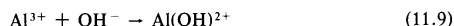
$$\frac{dn_{Al^{3+},(11.1)}}{d\xi_{(11.1)}} = 1 \quad (11.6)$$

$$\frac{dn_{SiO_2,(11.1)}}{d\xi_{(11.1)}} = 3 \quad (11.7)$$

and

$$\frac{dn_{H_2O,(11.1)}}{d\xi_{(11.1)}} = 2 \quad (11.8)$$

The stoichiometric coefficients in reaction (11.1) are constants under all circumstances, but they represent the actual change in the number of moles of the subscripted species only as long as the reaction remains congruent and no significant complexing takes place in the aqueous phase. For example, as reaction (11.1) proceeds and H^+ is consumed, the solution pH must eventually increase. Consequently, at some stage of reaction progress, $Al(OH)^{2+}$ may form to a significant degree. Reaction (11.1) alone is then not adequate to describe the process, but rather some combination of reaction (11.1) and



for which

$$\frac{dn_{Al^{3+},(11.9)}}{d\xi_{(11.9)}} = \frac{dn_{OH^-, (11.9)}}{d\xi_{(11.9)}} = -\frac{dn_{Al(OH)^{2+}, (11.9)}}{d\xi_{(11.9)}} = -1 \quad (11.10)$$

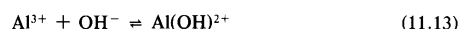
Under these conditions, the extent to which dissolved aluminum derived from the feldspar by the aqueous phase is distributed among Al^{3+} and $Al(OH)^{2+}$ is no longer *a priori* obvious. At each stage of reaction progress, the distribution of aluminum transferred to the solution is determined by $d\xi_{(11.9)}/d\xi_{(11.1)}$. This can be seen by taking advantage of equations (11.6) and (11.10) to describe the net change in the number of moles of Al^{3+} in the aqueous phase ($dn_{Al^{3+}}$), which can be expressed as

$$dn_{Al^{3+}} = dn_{Al^{3+},(11.1)} + dn_{Al^{3+},(11.9)} = d\xi_{(11.1)} - d\xi_{(11.9)} \quad (11.11)$$

Hence,

$$\frac{dn_{Al^{3+}}}{d\xi_{(11.1)}} = 1 - \frac{d\xi_{(11.9)}}{d\xi_{(11.1)}} \quad (11.12)$$

The quotient on the right side of equation (11.12) corresponds to the relative rate of the two reactions. If $d\xi_{(11.9)}/dt$ (where t stands for time) is smaller than $\partial\xi_{(11.1)}/\partial t$, $dn_{Al^{3+}}/\partial\xi_{(11.1)}$ is positive and the bulk of the aluminum transferred to the aqueous solution is present as Al^{3+} . If $d\xi_{(11.9)}/d\xi_{(11.1)}$ is $\ll 1$, $dn_{Al^{3+}}/d\xi_{(11.1)} \approx 1$. The distribution of aluminum in the aqueous phase is thus a function of the kinetics of the homogeneous reaction of Al^{3+} with OH^- to form $Al(OH)^{2+}$, relative to the kinetics of the heterogeneous reaction of microcline with the aqueous solution. Where the latter is slower (which is almost invariably the case), equilibrium among the aqueous species prevails and we can write,



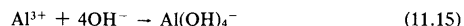
which defines the conservation requirement for reversible mass transfer among $Al(OH)^{2+}$, Al^{3+} , and OH^- in solution.

Although activity coefficients of aqueous species change during the hydrolysis of feldspar in H_2O , the changes are slight and affect negligibly the extent of mass transfer in the process. Accordingly, if temperature and pressure, as well as the activity coefficients of the aqueous species are constant, it follows from the law of mass action (see below) that

$$\frac{d \ln n_{Al(OH)^{2+}}}{d\xi_{(11.1)}} = \frac{d \ln n_{Al^{3+}}}{d\xi_{(11.1)}} + \frac{d \ln n_{OH^-}}{d\xi_{(11.1)}} \quad (11.14)$$

Conservation of mass and the constraint imposed by equation (11.14) specify implicitly the magnitude of $d\xi_{(11.9)}/d\xi_{(11.1)}$ at each stage of reaction progress. Consequently, the entire reaction process can be described in terms of the progress variable for reaction (11.1), which is the rate limiting reaction for the process as long as reaction (11.13) remains reversible.

As reaction (11.1) continues and the pH of the solution increases further, $Al(OH)_4^-$ may begin to form to a significant degree, which can be described by writing



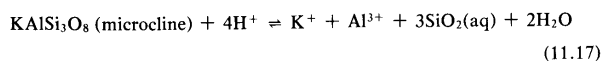
If the rate of this reaction is also faster than that of reaction (11.1) and

equivalent to that of reaction (11.13), the reversible mass transfer constraint imposed by

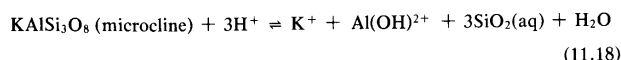
$$\frac{d \ln n_{\text{Al(OH)}_4^-}}{d\xi_{(11.1)}} = \frac{d \ln n_{\text{Al}^{3+}}}{d\xi_{(11.1)}} + 4 \frac{d \ln n_{\text{OH}^-}}{d\xi_{(11.1)}} \quad (11.16)$$

becomes important (see below). Although the absolute rates of reaction (11.13) and the reversible analog of reaction (11.15) may not be strictly equivalent, most homogeneous reactions in an aqueous solution are so much faster than heterogeneous reactions that their rates can be regarded as infinite and equal in the context of geologic time. Equation (11.16) corresponds to the analog of equation (11.14) for the reversible dissociation of Al(OH)_3 . Note that equation (11.16) obviates the need to consider explicitly $d\xi_{(11.15)}/d\xi_{(11.1)}$.

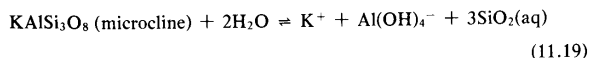
In addition to Al^{3+} , Al(OH)^{2+} , H^+ , OH^- , and Al(OH)_4^- , other aqueous species may become important during the reaction of feldspar with an aqueous phase. The degree to which these various species form determines to a large extent the ultimate equilibrium composition of the solution. If and when overall equilibrium is achieved we can write



or



and



as well as other reversible reactions. Each of these must hold simultaneously at equilibrium, regardless of the presence of other minerals produced by the process. All mass transfer caused by slight perturbations of the equilibrium state is then reversible and the system is in a state of lowest Gibbs free energy characterized by products and ratios of the activities of aqueous species.

Values of $dn_{\text{Al}^{3+}}/d\xi_{(11.1)}$, $dn_{\text{Al(OH)}^{2+}}/d\xi_{(11.1)}$, $dn_{\text{Al(OH)}_4^-}/d\xi_{(11.1)}$ and the corresponding differentials for other aqueous species formed during the

hydrolysis of feldspar can be computed by simultaneous consideration of equations describing reversible mass transfer and conservation of mass in the process. The equations and algorithms used to carry out such calculations are discussed in detail below. However, at this point in the discussion it is of interest to consider the results of such calculations in the context of chemical affinity and the precipitation of incongruent reaction products caused by the hydrolysis of feldspar.

Changes in the concentrations of aqueous species caused by the hydrolysis of microcline in H_2O at 25°C and 1 bar are depicted in Figure 11.1, which was generated from mass-transfer calculations reported elsewhere (Helgeson et al., 1969). The reaction path corresponding to ABCDE in Figure 11.1 is shown on the activity diagram in Figure 11.2. It can be seen in the idealized case represented in Figure 11.1 that the reaction of microcline with the aqueous phase leads to the sequential appearance of gibbsite, kaolinite, and muscovite, which precipitate in response to the changing activities of aqueous species in the hydrolytic process. In other cases, reaction of microcline with aqueous solutions may result in a different sequence of reaction products, which may include metastable phases. Note that the reaction paths labeled A'B'C'D' and A'B'D' in Figure 11.2, which were generated from calculations representing microcline reacting alternately with a static (A'B'C'D') and flowing (A'B'D') solution containing given initial concentrations of HCl and $\text{SiO}_2(\text{aq})$, fail to encounter the muscovite stability field. Higher initial concentrations of $\text{SiO}_2(\text{aq})$ may cause the appearance of kaolinite (instead of gibbsite) as the first phase to precipitate. Incongruent reactions of minerals with solutions having different initial compositions may thus lead to different zonal patterns of reaction products in geochemical processes. The identity and paragenesis of the minerals produced by the reactions depend on the relative changes in the chemical affinities of hydrolysis reactions for all potential reaction products during the process.

CHEMICAL AFFINITY AND REACTION PROGRESS

Chemical affinity can be regarded as a measure of reaction potential. The chemical affinity of the j th reaction among a given set of minerals, gases, and/or aqueous species at constant pressure and temperature (A_j) can be expressed as a function of reaction progress by writing (De Donder, 1920; De Donder and Van Rysselberghe, 1936)

$$A_j = - \left(\frac{\partial G}{\partial \xi_j} \right)_{P,T,\xi_k} = - \sum_i \mu_i \nu_{ij} \quad (11.20)$$

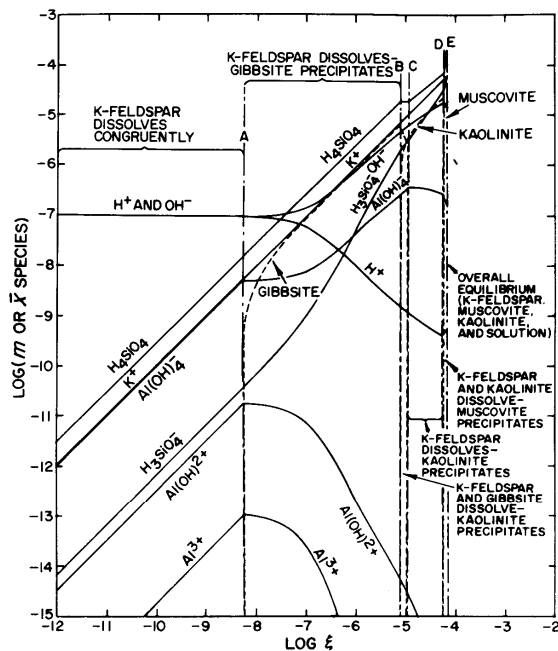


Fig. 11.1 Molalities (m) of species (—) in the aqueous phase and moles of minerals ($\text{kg H}_2\text{O}^{-1}$) produced and destroyed (---) during the hydrolysis of potassium feldspar at 25°C and 1 bar (after Helgeson et al., 1969; Helgeson, 1974, reproduced with permission from Pergamon Press and Manchester University Press). The curves shown in the figure were generated from mass transfer calculations. The letters correspond to points ABCDE on the reaction path in Figure 11.2.

where G stands for the Gibbs free energy of the system, ξ_j again represents the progress variable for the j th reaction, μ_i refers to the chemical potential of the i th species in the system ($i = 1, 2, \dots, i$) and $\hat{n}_{i,j}$ corresponds to the stoichiometric reaction coefficient of the species in the reaction, which is positive for products and negative for reactants. The stoichiometric reaction coefficient can be expressed as

$$\hat{n}_{i,j} \equiv \frac{dn_{i,j}}{d\xi_j} \quad (11.21)$$

where $dn_{i,j}$ refers to the change in the number of moles of the i th species caused by the j th reaction. In contrast to ξ_j , which has units of moles, $\hat{n}_{i,j}$ is dimensionless. Note that equations (11.3)–(11.8) are specific statements of equation (11.21) for reaction (11.1). As emphasized above, stoichiometric reaction coefficients are constants determined solely by constraints imposed by equation (11.2), which can now be written as

$$\sum_i \nu_{e,i} \hat{n}_{i,j} = 0 \quad (11.22)$$

where $\nu_{e,i}$ again stands for the number of moles of the e th element in one mole of the i th species. Note that the subscript j in equation (11.20) refers

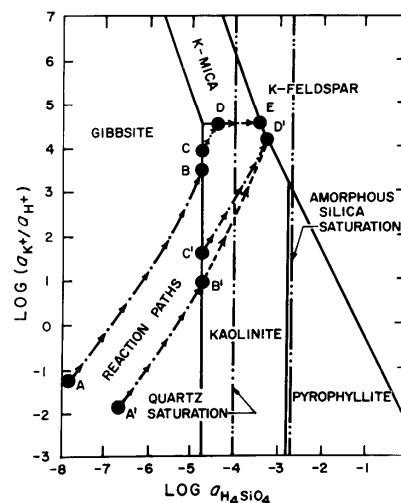


Fig. 11.2 Equilibrium activity diagram for the system $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 25°C and 1 bar (after Helgeson, 1974 and reproduced with permission from Manchester University Press). Reaction path ABCDE corresponds to that generated by the reaction represented in Figure 11.1.

only to reactions for which $\hat{n}_{i,j}$ can be assessed unambiguously with the aid of equation (11.22). All others are composites of these reactions.

The chemical affinity of the j th reaction can also be expressed as a function of activity by taking account of

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (11.23)$$

where a_i stands for the activity of the i th species in the system. Multiplying equation (11.23) by $\hat{n}_{i,j}$ and summing across all values of i permits equation (11.20) to be written as

$$A_j = - \sum_i \mu_i^0 \hat{n}_{i,j} - RT \sum_i \hat{n}_{i,j} \ln a_i \quad (11.24)$$

which can be combined with

$$\sum_i \mu_i^0 \hat{n}_{i,j} = \Delta G_{r,j}^0 = -RT \ln K_j \quad (11.25)$$

and

$$Q_j = \prod_i a_i^{\hat{n}_{i,j}} \quad (11.26)$$

to give

$$A_j = RT \ln(K_j/Q_j) \quad (11.27)$$

where μ_i^0 stands for the chemical potential of the i th species in its standard state, $\Delta G_{r,j}^0$ refers to the standard molal Gibbs free energy of the j th reaction, and K_j and Q_j represent the equilibrium constant and activity product for the reaction, respectively. The derivative of equation (11.27) with respect to ξ_j appears as

$$\frac{dA_j}{d\xi_j} = -RT \frac{d \ln Q_j}{d\xi_j} = -RT \sum_i \hat{n}_{i,j} \frac{d \ln a_i}{d\xi_j} \quad (11.28)$$

As equilibrium is approached, $Q_j \rightarrow K_j$ and $A_j \rightarrow dA_j/d\xi_j \rightarrow 0$. When the j th reaction becomes reversible,

$$A_j = \frac{dA_j}{d\xi_j} = 0 \quad (11.29)$$

Partial and/or local equilibrium (see below) requires equation (11.29) to hold for one or more of the simultaneous reactions occurring in a given geochemical process, but overall equilibrium is achieved only when $A_j = 0$ for all such reactions. Note that the second identity in equation (11.29) is not in itself a sufficient criterion for equilibrium. For example, chemical potential constraints or changes in solution composition and the distribution of species in the aqueous phase arising from precipitation or dissolution of minerals in geochemical processes may cause the derivatives of the chemical affinities of reactions involving other minerals to approach zero at an intermediate stage of reaction progress. Nevertheless, the affinities of these reactions may be much greater than zero. A case in which this behavior occurs is shown in Figure 11.3, where it can be seen that $dA_j/d\xi_j$ for the hydrolysis of high sanidine during reaction of a granitic rock with a hydrothermal solution abruptly changes to \sim zero after the appearance of calcite as a reaction product, despite the fact that A_j for the hydrolysis of high sanidine is >0 . It is thus necessary, but not sufficient that $dA_j/d\xi_j = 0$ at equilibrium, but both necessary and sufficient that $A_j = 0$ for all values of j at equilibrium.

Chemical affinity is commonly used in geochemistry as a measure of the relative extent to which one or another mineral is out of equilibrium with a given aqueous solution. However, ranking minerals according to the

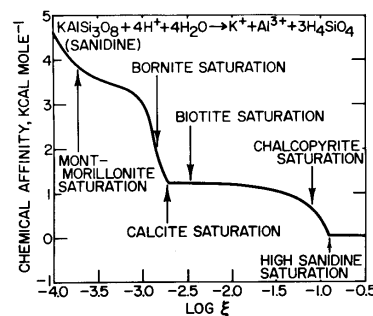


Fig. 11.3 Chemical affinity of the reaction shown above as a function of progress in the irreversible reaction of a granitic rock with a hydrothermal solution at 200°C and 15 bars. The curve was generated from calculations of the kind reported by Helgeson (1970) using thermodynamic data taken from Helgeson (1969).

chemical affinities of their hydrolysis reactions affords little indication of the order in which they will equilibrate with the aqueous phase. The relative magnitude of these chemical affinities takes no account of the differential influence of homogeneous and heterogeneous reaction coupling on the extent to which they change as a function of reaction progress. Reaction coupling arises from ion association and the appearance of intermediate reaction products, which affect the change in the chemical affinities of the hydrolysis reactions for all other potential reaction products. This can be deduced by combining two statements of equation (11.28) for $j = 1$ and $j = 2$ representing two simultaneous heterogeneous reactions to give

$$\frac{dA_1}{dA_2} = \frac{d \ln Q_1}{d \ln Q_2} = \frac{\sum_i \bar{n}_{i,1} \frac{d \ln a_i}{d \xi_1}}{\sum_i \bar{n}_{i,2} \frac{d \ln a_i}{d \xi_2}} \quad (11.30)$$

Because all of the species in the two reactions represented by $j = 1$ and $j = 2$ in equation (11.30) are not necessarily the same, and because changes in the activities of the species depend differentially on homogeneous reactions taking place in the process, the order of relative change in the chemical affinities of the reactions may be drastically different from the order of relative affinities at any given stage of the process. This dependence is manifested in part by the curves representing chemical affinities in Figure 11.4. Note that in the early stages of the reaction of microcline with the aqueous solution, the order of increasing chemical affinity of the hydrolysis reactions for the minerals corresponds to gibbsite, amorphous silica, kaolinite, microcline, potassium montmorillonite, muscovite. In contrast, the order at $\log \xi = -8$ is amorphous silica, kaolinite, potassium montmorillonite, muscovite, microcline. However, it can be seen that only two of these minerals actually appear as reaction products (gibbsite and kaolinite) before microcline equilibrates with the aqueous phase.

Although De Donder (1920) assigned a separate progress variable to each reaction that takes place in a given system, it is advantageous to introduce the concept of an overall progress variable (ξ) for a geochemical process. The overall progress variable refers to the rate-limiting reaction in the process, which in most cases corresponds to the irreversible reaction of the aqueous phase with one of the minerals in the reactant mineral assemblage. The rates at which the other minerals in the assemblage react can be expressed in terms of ξ by defining relative reaction rates for the minerals (see below). Similarly, all reversible mass transfer can be described as a function of the overall progress variable by taking advantage of

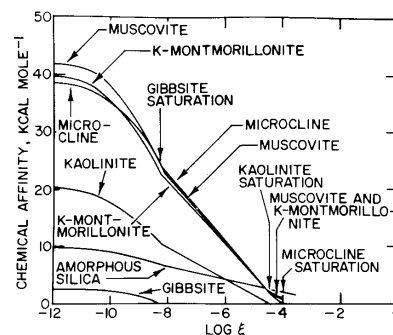


Fig. 11.4 Chemical affinities of hydrolysis reactions for the minerals shown above as a function of progress in the reaction of potassium feldspar with an aqueous phase at 25°C and 1 bar. The curves were generated using thermodynamic data taken from Helgeson (1969).

thermodynamic constraints imposed by partial and local equilibrium states established in the process.

The change in the Gibbs free energy of a system caused by a set of simultaneous reactions can be expressed in terms of the overall progress variable (ξ) by writing

$$A = - \left(\frac{\partial G}{\partial \xi} \right)_{p,T} = - \sum_i \mu_i \bar{n}_i \quad (11.31)$$

where A stands for the total chemical affinity of the process and \bar{n}_i represents the net change in the number of moles of the i th species caused by all of the reactions taking place in the system; that is,

$$\bar{n}_i = \frac{dn_i}{d\xi} \quad (11.32)$$

Note that in contrast to $\bar{n}_{i,j}$, \bar{n}_i is not necessarily a constant.

Equation (11.31) can also be expressed in terms of the chemical affinities of the reactions involved in a geochemical process by taking account of

$$\bar{n}_i = \sum_j \bar{n}_{i,j} \frac{d\xi_j}{d\xi} \quad (11.33)$$

which can be combined with equations (11.20) and (11.31) to give

$$A = - \sum_i \sum_j \mu_i \tilde{n}_{ij} \frac{d\xi_j}{d\xi} = \sum_j A_j \frac{d\xi_j}{d\xi} \quad (11.34)$$

Similarly, the change in Gibbs free energy of the system caused by the j th reaction can be expressed as a function of the overall progress variable by first defining

$$A_j^* = A_j \frac{d\xi_j}{d\xi} \quad (11.35)$$

which permits equation (11.34) to be written as

$$A = \sum_j A_j^* \quad (11.36)$$

We can now write a combined statement of equations (11.23), (11.31), and (11.36) as

$$A_j^* = - \sum_i \mu_i^0 \tilde{n}_{ij} - RT \sum_i \tilde{n}_{ij} \ln a_i \quad (11.37)$$

where \tilde{n}_{ij} refers to the change in the number of moles of the i th species caused by the j th reaction, relative to the overall progress variable, ξ ; that is,

$$\tilde{n}_{ij} \equiv \frac{dn_{ij}}{d\xi} = \tilde{n}_{ij} \frac{d\xi_j}{d\xi} \quad (11.38)$$

It then follows from equations (11.25)–(11.27), (11.31), and (11.37) that

$$\begin{aligned} A_j^* &= A_j - \sum_i (\tilde{n}_{ij} - \hat{n}_{ij}) \mu_i \\ &= RT \ln (K_j/Q_j) - RT \sum_i (\tilde{n}_{ij} - \hat{n}_{ij}) \mu_i^0 \\ &\quad - RT \sum_i (\tilde{n}_{ij} - \hat{n}_{ij}) \ln a_i \end{aligned} \quad (11.39)$$

Although equation (11.39) cannot be evaluated *a priori* for a given reaction in a geochemical process, it provides a measure of the extent to which the Gibbs free energy of the system is affected by the j th reaction, relative to the progress variable for the rate-limiting step in the process.

PARTIAL AND LOCAL EQUILIBRIUM

Systems involved in geochemical processes are almost invariably in a state of partial equilibrium; that is, the system is in equilibrium with respect to at least one process (which can be described by a reversible chemical reaction) but out of equilibrium with respect to others. For example, as indicated above, the rates of homogeneous reactions in an aqueous phase generally exceed by many orders of magnitude those of heterogeneous reactions. Consequently, most dissociational reactions in a hydrothermal solution reacting with its mineralogic environment can be regarded as reversible reactions, all of which contribute to the partial equilibrium state of the system.

In contrast to partial equilibrium, local equilibrium (Thompson, 1959; Fitts, 1962) carries a spatial connotation. Local equilibrium occurs in a system when phases in contact with one another react reversibly in response to changes in chemical potential, temperature, or pressure. Local equilibrium may be established along grain boundaries or manifested by a zonal distribution of reaction products in a hydrothermal system. If, as a consequence of the reaction of a mineral assemblage with an aqueous solution, the solution becomes saturated with one or another potential reaction product, further progress in the overall reaction may or may not lead to precipitation of the mineral. For the product mineral to precipitate, the solution must be supersaturated with respect to the mineral. However, the degree of supersaturation required for precipitation depends on kinetic constraints, such as the nucleation energy required to crystallize the phase. In certain cases (such as quartz at 25°C), the kinetic barriers are so great that the potential product mineral fails to precipitate, even from highly supersaturated solutions. In others, the degree of supersaturation required to cause precipitation is negligible compared to the total mass transfer among the phases in the system. Under these circumstances, precipitation of a reaction product can be viewed as a reversible process in the context of geologic time. Ample evidence suggests that such reactions predominate in geochemical processes, which permits us to consider a mineral produced by the incongruent reaction of a hydrothermal solution with its mineralogic environment to be in local equilibrium with the solution from which it forms. The validity of this assumption is unaffected by the fact that the mass of the mineral in the system is changing as a function of progress in the overall irreversible reaction. If homogeneous equilibrium is maintained, and supersaturation with respect to all reaction products is negligible, then the rate-limiting step in the process corresponds to the irreversible reaction of the solution with the slowest mineral to react in the reactant mineral assemblage.

Reversible mass transfer from an aqueous solution to a solid reaction product in response to changes in solution composition caused by reaction of the solution with its mineralogic environment restricts relative changes in the activities of aqueous species to those compatible with $A_j = 0$ for the reversible reaction. Constraints imposed on the distribution of species in the aqueous phase by a local equilibrium state of this kind are depicted schematically in Figure 11.5. The curves in the figure represent changes in the activities of the species involved in a reversible reaction with a given mineral for which $Q_j = K_j$ at all stages of progress in an irreversible reaction of an aqueous phase with other minerals. If in the actual process, the aqueous phase is supersaturated with respect to the mineral so that $Q > K$, the chemical affinity for the reaction is negative. However, if the absolute value of the affinity of the j th reaction is small compared to the total chemical affinity of the process (which is generally the case), the departure from local equilibrium has a negligible effect on the total mass transfer among the phases in the system. Accordingly, in a geologic context, comparative discrepancies in the results of mass-transfer calculations and field observations caused by departures in nature from local equilibrium constraints should be slight compared to other uncertainties involved in such calculations. A constant state of supersaturation with respect to a given product mineral constitutes a metastable state of local equilibrium, which can also be taken into account in mass transfer calculations.

All partial and local equilibrium states in a geochemical process can be represented by differential equations corresponding to the derivatives of the law of mass action. For the j th reversible reaction involving only stoichiometric

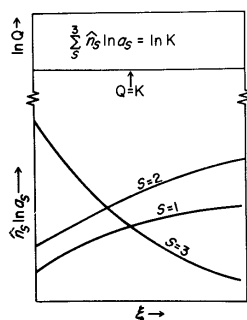


Fig. 11.5 Schematic illustrations of the relative change in the activities of three aqueous species (designated by the subscript s) permitted by constraints imposed by local equilibrium among the species and a reaction product during irreversible reaction of a hydrothermal solution with its mineralogic environment. The upper (horizontal) curve represents the activity product for the reaction (see text).

metric minerals and/or aqueous species (designated by the subscripts ψ and s , respectively), the law of mass action can be written as

$$\sum_s \hat{n}_{s,j} \ln a_s = \sum_s \hat{n}_{s,j} \ln m_s + \sum_s \hat{n}_{s,j} \ln \gamma_s = \ln K_j \quad (11.40)$$

where $\hat{n}_{s,j}$ corresponds to the stoichiometric coefficient of the s th aqueous species in the j th reversible reaction and a_s , m_s , and γ_s represent the activity, molality, and activity coefficient of the subscripted aqueous species. Before differentiating equation (11.40) let us relate explicitly, $dn_s/d\xi$ to $dm_s/d\xi$, which can be accomplished by dividing an appropriate statement of equation (11.32) by the number of kilograms of H_2O in the system (W_{H_2O}), which leads to

$$\bar{n}_s = \frac{\hat{n}_s}{W_{H_2O}} = \frac{dm_s}{d\xi} = \frac{1}{W_{H_2O}} \frac{dn_s}{d\xi} \quad (11.41)$$

and (by analogy)

$$\bar{n}_\psi = \frac{\hat{n}_\psi}{W_{H_2O}} = \frac{d\bar{x}_\psi}{d\xi} = \frac{1}{W_{H_2O}} \frac{dn_\psi}{d\xi} \quad (11.42)$$

where \bar{n}_s and \bar{n}_ψ correspond to the change in the number of moles of the subscripted species relative to a kilogram of H_2O , and \bar{x}_ψ designates the number of moles of the ψ th mineral ($kg H_2O$)⁻¹ in the system. Note that equations (11.41) and (11.42) specify the same concentration scale for both minerals and aqueous species.

The equilibrium state represented in Figure 11.5 can now be described by differentiating equation (11.40) with respect to ξ , the progress variable for the overall irreversible process responsible for changing the solution composition, to give

$$\begin{aligned} \sum_s \hat{n}_{s,j} \frac{d \ln a_s}{d\xi} &= \sum_s \hat{n}_{s,j} \left(\frac{\partial \ln m_s}{d\xi} + \frac{\partial \ln \gamma_s}{d\xi} \right) \\ &= \sum_s \left(\frac{\hat{n}_{s,j}}{m_s} \frac{dm_s}{d\xi} + \hat{n}_{s,j} \frac{d \ln \gamma_s}{d\xi} \right) \\ &= \sum_s \left(\frac{\hat{n}_{s,j} \bar{n}_s}{m_s} + \hat{n}_{s,j} \frac{d \ln \gamma_s}{d\xi} \right) = \frac{d \ln K_j}{d\xi} \quad (11.43) \end{aligned}$$

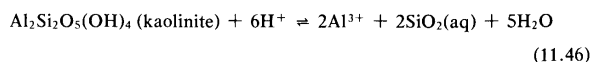
Differentiating equation (11.43) permits us to write

$$\sum_s \left(\frac{\bar{n}_{s,j} \bar{n}_s'}{m_s} + \bar{n}_{s,j} \frac{d^2 \ln \gamma_s}{d\xi^2} \right) = \frac{d^2 \ln K_j}{d\xi^2} + \sum_s \frac{\bar{n}_{s,j} \bar{n}_s'^2}{m_s^2} \quad (11.44)$$

where \bar{n}_s' stands for the first derivative of \bar{n}_s ; that is,

$$\bar{n}_s' = \frac{d\bar{n}_s}{d\xi} = \frac{d^2 m_s}{d\xi^2} \quad (11.45)$$

Equations (11.43) and (11.44) represent explicitly constraints on reversible mass transfer imposed by partial and/or local equilibrium states in geochemical processes. They refer to any reversible reaction involving stoichiometric species such as



or



Including provision in equations (11.43) and (11.44) for solid solution among reaction products is discussed elsewhere (Helgeson et al., 1970).

The logarithmic derivatives of the activity coefficients in equations (11.43) and (11.44) can be expressed as functions of ξ , pressure P , and temperature T . It thus follows that

$$\begin{aligned} \frac{d \ln \gamma_s}{d\xi} &= \left(\frac{\partial \ln \gamma_s}{\partial \xi} \right)_{P,T} + \left(\frac{\partial \ln \gamma_s}{\partial P} \right)_{T,\xi} \frac{dP}{d\xi} + \left(\frac{\partial \ln \gamma_s}{\partial T} \right)_{P,\xi} \frac{dT}{d\xi} \\ &= \left(\frac{\partial \ln \gamma_s}{\partial \xi} \right)_{P,T} + \frac{(\bar{V}_s - \bar{V}_s^0)}{RT} \frac{dP}{d\xi} - \frac{(\bar{H}_s - \bar{H}_s^0)}{RT^2} \frac{dT}{d\xi} \end{aligned} \quad (11.48)$$

where $(\bar{V}_s - \bar{V}_s^0)$ and $(\bar{H}_s - \bar{H}_s^0)$ stand for the relative partial molal volume and enthalpy of the s th aqueous species. In contrast, the equilibrium constant is independent of ξ . Hence, for an unrestricted standard state with respect to temperature and pressure we can write,

$$\begin{aligned} \frac{d \ln K_j}{d\xi} &= \left(\frac{\partial \ln K_j}{\partial P} \right)_T \frac{dP}{d\xi} + \left(\frac{\partial \ln K_j}{\partial T} \right)_P \frac{dT}{d\xi} \\ &= - \frac{\Delta V_{r,j}^0}{RT} \frac{dP}{d\xi} + \frac{\Delta H_{r,j}^0}{RT^2} \frac{dT}{d\xi} \end{aligned} \quad (11.49)$$

where $\Delta V_{r,j}^0$ and $\Delta H_{r,j}^0$ refer to the standard molal volume and enthalpy of the j th reaction. Equations similar to, but more complicated than equations (11.48) and (11.49) can be derived for $d^2 \ln \gamma_s/d\xi^2$ and $d^2 \ln K_j/d\xi^2$. Note that for isobaric/isothermal processes, equations (11.48) and (11.49) reduce to

$$\frac{d \ln \gamma_s}{d\xi} = \left(\frac{\partial \ln \gamma_s}{\partial \xi} \right)_{P,T} \quad (11.50)$$

and

$$\frac{d \ln K_j}{d\xi} = 0 \quad (11.51)$$

CONSERVATION OF MASS AND CHARGE

A geochemical process in a closed system takes place with no exchange of matter between the system and its surroundings. Consequently, the extent to which components are redistributed among the phases is constrained by

$$\sum_{\psi} \nu_{e,\psi} \bar{n}_{\psi} + \sum_s \nu_{e,s} \bar{n}_s = 0 \quad (11.52)$$

and

$$\sum_s Z_s \bar{n}_s = 0 \quad (11.53)$$

where \bar{n}_{ψ} and \bar{n}_s are defined by equations (11.41) and (11.42), $\nu_{e,\psi}$ and $\nu_{e,s}$ refer to the number of moles of the e th element in 1 mole of the subscripted species, and Z_s designates the charge on the s th aqueous species. Note that differentiation of these equations leads to

$$\sum_{\psi} \nu_{e,\psi} \bar{n}_{\psi}' + \sum_s \nu_{e,s} \bar{n}_s' = 0 \quad (11.54)$$

and

$$\sum_s Z_s \bar{n}_s' = 0 \quad (11.55)$$

The rate at which a given mineral reacts with an aqueous phase compared to the corresponding reaction rate for some other mineral is referred to as the relative reaction rate for the two minerals. If we designate this quantity for the r th reactant mineral ($r = 1, 2, \dots, \bar{r}$) relative to that of the \bar{r} th as $\theta_{r/\bar{r}}$ we can write,

$$\theta_{r/\bar{r}} = \frac{\bar{n}_r}{\bar{n}_{\bar{r}}} \quad (11.56)$$

Relative reaction rates depend on differences in the total surface area of the minerals as well as differences in their reaction rates (cm^2 of surface area) $^{-1}$. The magnitude of $\theta_{r/\bar{r}}$ is thus a function of both the relative abundance of the minerals in the rock and the relative extent to which each reaction is controlled by chemical kinetics at the reactant surface or diffusional transfer of material through the aqueous phase.

The rate-limiting step in the hydrolysis of feldspar has been the subject of considerable discussion and controversy (Lagache, 1965, 1976; Wollast, 1967; Helgeson, 1971, 1972; Paces, 1973; Busenberg and Clemency, 1976; Petrovic, 1976), but mounting evidence suggests that surface control of reaction rates probably predominates in geochemical processes (Lagache, 1965, 1976; Petrovich, 1976; Berner, 1978; Grandstaff, 1978; Aagaard and Helgeson, 1977, 1979). Regardless of whether the rate-limiting step is controlled by diffusion or surface kinetics, the total number of moles of a given element ($\text{kg H}_2\text{O}$) $^{-1}$ transferred by reaction of a rock with a solution

$$\bar{n}_{t,e} = \sum_r \nu_{e,r} \theta_{r/\bar{r}} \bar{n}_{\bar{r}} \quad (11.57)$$

and (for constant relative reaction rates)

$$\bar{n}_{t,e}' = \sum_i \nu_{e,i} \theta_{i/\bar{r}} \bar{n}_{\bar{r}}' \quad (11.58)$$

If we now designate product minerals with the subscript ϕ ($\phi = 1, 2, \dots, \Phi$) and reactant minerals with the index r (as above), we can write equations (11.52) and (11.54) as

$$\sum_{\phi} \nu_{e,\phi} \bar{n}_{\phi} + \sum_s \nu_{e,s} \bar{n}_s = - \sum_r \nu_{e,r} \theta_{r/\bar{r}} \bar{n}_{\bar{r}} \quad (11.59)$$

and

$$\sum_{\phi} \nu_{e,\phi} \bar{n}_{\phi}' + \sum_s \nu_{e,s} \bar{n}_s' = - \sum_r \nu_{e,r} \theta_{r/\bar{r}} \bar{n}_{\bar{r}}' \quad (11.60)$$

If both the relative rate of reaction and \bar{n}_r are constant, equation (11.60) reduces to zero.

Although H_2O is almost invariably consumed or produced during reaction of an aqueous solution with a silicate mineral assemblage, in a closed system the change is usually negligible compared to the total number of moles of H_2O in the solution. However, conservation of mass in a system open to H_2O requires modification of the equations given above to include provision for the changing mass of H_2O as well as the effect of the change on the molalities of the aqueous species in solution. This can be accomplished by combining the first identities in equations (11.41) and (11.42) with the mass transfer equations summarized above. In addition, if a given component other than H_2O is abstracted from or added to the system (such as CO_2 boiling off from a hydrothermal solution), equation (11.59) must be amended to

$$\sum_{\phi} \nu_{e,\phi} \bar{n}_{\phi} + \sum_s \nu_{e,s} \bar{n}_s = - \sum_r \nu_{e,r} \theta_{r/\bar{r}} \bar{n}_{\bar{r}} - \sum_f \nu_{e,f} \bar{n}_f \quad (11.61)$$

where $\nu_{e,f}$ stands for the number of moles of the e th element in one mole of the f th fugitive component and \bar{n}_f represents the change in the molality of the component in the aqueous phase defined by

$$\bar{n}_f \equiv \frac{dm_f}{d\xi} \quad (11.62)$$

CALCULATION OF MASS TRANSFER

For the sake of clarity, a large number of variables were omitted in deriving the equations summarized above to promote conceptual appreciation for the thermodynamic constraints imposed by partial and local equilibrium on mass transfer among minerals and aqueous solutions in geochemical processes. These omissions include explicit provision for changes in the activity of H_2O , solid solution, oxidation/reduction reactions, fluid flow, fixed chemical potentials of components, departures from local equilibrium, calculation of changes in activity coefficients, and evaluation of the pressure and temperature dependence of equilibrium constants. The modifications required to provide for a number of these have

been summarized in detail elsewhere, together with the grand matrix equation for the general case of an aqueous solution reacting with its mineralogic environment (Helgeson et al. 1970). The grand matrix equation is composed of linear differential equations representing reversible mass transfer and conservation of mass and charge like those for the simple case derived above. However, it can be condensed by substituting the differential equations representing reversible mass transfer into those describing conservation of mass, which simplifies the computational procedure by eliminating \bar{n}_s for aqueous complexes from the unknown coefficient column vector. In either case, the matrix equation can be represented by

$$\bar{\beta} = \bar{\Gamma}^{-1}\bar{\lambda} \quad (11.63)$$

where $\bar{\Gamma}$ denotes the matrix, $\bar{\beta}$ refers to the column vector of unknown reaction coefficients, and $\bar{\lambda}$ stands for the reactant mineral (or known coefficient) column vector. Evaluation of this equation for a solution of a given composition can be carried out quickly with the aid of a computer by first calculating the distribution of species in the solution at the outset of the reaction. Evaluation of the matrix equation then yields values of \bar{n}_s and \bar{n}_s' at the beginning of the process. The numerical values of these derivatives depend on the composition of, and the distribution of species in the aqueous phase. They are thus path-dependent variables that cannot be described by exact differentials. However, their integrals can be represented by Taylor's expansions of the form

$$m_s = m_s^0 + \bar{n}_s \Delta\xi + \frac{\bar{n}_s'(\Delta\xi)^2}{2!} + \dots \quad (11.64)$$

and (after the appearance of the ϕ th product mineral),

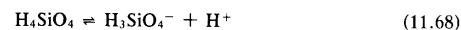
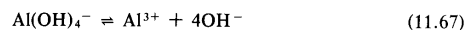
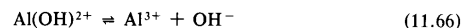
$$\bar{x}_\phi = \bar{x}_\phi^0 + \bar{n}_\phi \Delta\xi + \frac{\bar{n}_\phi'(\Delta\xi)^2}{2!} + \dots \quad (11.65)$$

where m_s^0 and \bar{x}_ϕ^0 stand for the molality of the s th aqueous species and the number of moles of the ϕ th mineral ($\text{kg H}_2\text{O}^{-1}$) in the system at the current stage of reaction progress, and m_s and \bar{x}_ϕ refer to these variables after a small increment of reaction progress represented by $\Delta\xi$. The values of m_s computed from equation (11.64) after the first increment of reaction progress permit a new matrix equation to be evaluated, which yields new values of \bar{n}_s and \bar{n}_s' . These values can then be used to compute from equation (11.64) the molalities of aqueous species and the number of moles of the

ϕ th mineral in the system after the second increment of reaction progress. Repetition of this procedure allows calculation of the changes in solution composition and distribution of species in the aqueous phase for the entire reaction process. If no minerals are in equilibrium with the aqueous solution at the outset of the process, $\bar{n}_\phi = \bar{n}_\phi' = \bar{x}_\phi = 0$ at $\xi = 0$. However, the changes in solution composition caused by irreversible reaction of the aqueous phase with the mineral assemblage may cause the solution to become saturated with one or another mineral in the system. Provision for reversible precipitation of the product mineral is then incorporated in the calculations. Detection of the stage of reaction progress where the chemical affinity of the hydrolysis reaction for a given mineral equals zero can be accomplished by calculating chemical affinities of hydrolysis reactions for all potential reaction products at each stage of reaction progress. After finding the value of ξ at which the solution becomes saturated with one of them, the matrix equation is enlarged to accommodate \bar{n}_ϕ and the reversible mass transfer equation for the mineral. This procedure provides automatically for the possibility that the mineral will dissolve at some later stage of reaction progress.

A Numerical Example—The Hydrolysis of Feldspar

To illustrate construction of the matrix equation for an actual process, let us consider the reaction of 1 mole of pure microcline with a solution containing 1000 g of H_2O and an initial concentration of 10^{-3} mole $\text{HCl} (\text{kg H}_2\text{O})^{-1}$ at 25°C and 1 bar. The system is closed and composed of five elements (potassium, aluminum, silicon, oxygen, and hydrogen) in addition to chlorine, which does not participate in the reaction. We can thus write five statements of equation (11.59) to describe conservation of mass among the species involved in the reaction process. For purposes of illustration, let us assume that only five aqueous complexes form to significant degrees during the reaction, that is, $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_4^-$, H_4SiO_4 , H_3SiO_4^- , and H_2O . We can now write four statements of equation (11.40) to describe homogeneous equilibrium in the aqueous phase. The dissociational reactions appear as



for which

$$\frac{a_{\text{Al}^{3+}} a_{\text{OH}^-}}{a_{\text{Al(OH)}^{2+}}} = \frac{m_{\text{Al}^{3+}} \gamma_{\text{Al}^{3+}} m_{\text{OH}^-} \gamma_{\text{OH}^-}}{m_{\text{Al(OH)}^{2+}} \gamma_{\text{Al(OH)}^{2+}}} = K_{\text{Al(OH)}^{2+}}, \quad (11.70)$$

$$\frac{a_{\text{Al}^{3+}} a_{\text{OH}^-}^4}{a_{\text{Al(OH)}_4^-}} = \frac{m_{\text{Al}^{3+}} \gamma_{\text{Al}^{3+}} m_{\text{OH}^-}^4 \gamma_{\text{OH}^-}^4}{m_{\text{Al(OH)}_4^-} \gamma_{\text{Al(OH)}_4^-}} = \beta_{\text{Al(OH)}_4^-}, \quad (11.71)$$

$$\frac{a_{\text{H}^+} a_{\text{H}_4\text{SiO}_4}}{a_{\text{H}_2\text{SiO}_3}} = \frac{m_{\text{H}^+} \gamma_{\text{H}^+} m_{\text{H}_4\text{SiO}_4} \gamma_{\text{H}_4\text{SiO}_4}}{m_{\text{H}_2\text{SiO}_3} \gamma_{\text{H}_2\text{SiO}_3}} = K_{\text{H}_2\text{SiO}_3}, \quad (11.72)$$

and

$$a_{\text{H}^+} a_{\text{OH}^-} = m_{\text{H}^+} \gamma_{\text{H}^+} m_{\text{OH}^-} \gamma_{\text{OH}^-} = K_{\text{H}_2\text{O}} \quad (11.73)$$

where $K_{\text{Al(OH)}^{2+}}$ and $K_{\text{H}_2\text{SiO}_3}$ stand for the stepwise dissociation constants for the subscripted species, $\beta_{\text{Al(OH)}_4^-}$ represents the overall dissociation constant for Al(OH)_4^- , and $K_{\text{H}_2\text{O}}$ refers to the activity product constant for H_2O . The total number of differential equations we can write to describe conservation of mass and reversible mass transfer in the reaction process is thus nine, which is equal to the total number of unknown values of \bar{n}_i for the species in the aqueous phase (Al^{3+} , Al(OH)^{2+} , Al(OH)_4^- , H_4SiO_4 , H_2SiO_3 , H_2O , K^+ , H^+ , and OH^-). Of the species considered in the present calculation, only K^+ and Cl^- fail to form complexes to a significant degree at 25°C and 1 bar.

Calculation of the distribution of species in the solution at the outset of the reaction requires evaluation of mass balance equations for aluminum and silicon in the aqueous phase, which can be written as

$$m_{\text{t,Al}} = m_{\text{Al}^{3+}} + m_{\text{Al(OH)}^{2+}} + m_{\text{Al(OH)}_4^-} \quad (11.74)$$

and

$$m_{\text{t,Si}} = m_{\text{H}_4\text{SiO}_4} + m_{\text{H}_2\text{SiO}_3} \quad (11.75)$$

where $m_{\text{t,Al}}$ and $m_{\text{t,Si}}$ stand for the total molalities of the subscripted elements in solution. Taking account of equations (11.70)–(11.72) we can thus write,

$$m_{\text{t,Al}} = m_{\text{Al}^{3+}} \left(1 + \frac{\gamma_{\text{Al}^{2+}} m_{\text{OH}^-} \gamma_{\text{OH}^-}}{K_{\text{Al(OH)}^{2+}} \gamma_{\text{Al(OH)}^{2+}}} + \frac{\gamma_{\text{Al}^{3+}} m_{\text{OH}^-}^4 \gamma_{\text{OH}^-}^4}{K_{\text{Al(OH)}_4^-} \gamma_{\text{Al(OH)}_4^-}} \right) \quad (11.76)$$

and

$$m_{\text{t,Si}} = m_{\text{H}_4\text{SiO}_4} \left(1 + \frac{K_{\text{H}_2\text{SiO}_3} \gamma_{\text{H}_2\text{SiO}_3}}{m_{\text{H}^+} \gamma_{\text{H}^+} \gamma_{\text{H}_2\text{SiO}_3}} \right) \quad (11.77)$$

which define the total concentrations of aluminum and silicon in the solution in terms of the molalities and activity coefficients of four species: Al^{3+} , H_4SiO_4 , OH^- , and H^+ .

Activity coefficients and dissociation constants for aqueous species can be computed from thermodynamic data and equations. Employing data and equations summarized by Helgeson (1969) for this purpose, let us compute the distribution of species in the solution at the outset of the reaction process. Because the solution is so acid, we can write as a close approximation,

$$m_{\text{H}^+} \approx m_{\text{t,HCl}} = 10^{-3} \quad (11.78)$$

and thus

$$m_{\text{OH}^-} \approx \frac{K_{\text{H}_2\text{O}}}{10^{-3}} = \frac{10^{-14}}{10^{-3}} = 10^{-11} \quad (11.79)$$

which follows from equation (11.73) for dilute solutions in which activity coefficients can be regarded as unity without introducing unacceptable uncertainties in the calculation. Aside from H_2O and Cl^- (which does not participate in the reaction process), no other species are present in significant concentrations in the aqueous phase prior to reaction of the solution with microcline. However, after an infinitesimal amount of microcline dissolves congruently in the solution, say 10^{-10} moles, we can evaluate equations (11.76) and (11.77) to define $m_{\text{Al}^{3+}}$ and $m_{\text{H}_4\text{SiO}_4}$. The ionic strength of the solution is affected negligibly by the dissolution of 10^{-10} moles of microcline, which permits us to again regard all activity coefficients as unity. Because the initial solution is so acid, essentially all of the dissolved aluminum and silicon in solution after reaction of 10^{-10} moles of microcline is present as Al^{3+} and H_4SiO_4 , respectively. This can be demonstrated by rearranging equations (11.76) and (11.77) and combining the resulting expressions with the values of m_{H^+} and m_{OH^-} computed above and the dissociation constants for Al(OH)^{2+} and Al(OH)_4^- , which leads (for $m_{\text{t,Al}} = 10^{-10}$) to

$$m_{\text{Al}^{3+}} = \frac{10^{-10}}{1 + \frac{10^{-11}}{10^{-9.3}} + \frac{10^{-44}}{10^{-32.7}}} = \frac{10^{-10}}{1 + 10^{-1.7} + 10^{-11.3}} = 10^{-10} \quad (11.80)$$

and (because it follows from the stoichiometry of microcline that $m_{\text{t, Si}} = 3m_{\text{t, Al}} = 3 \times 10^{-10} = 10^{-9.5}$),

$$m_{\text{H}_2\text{SiO}_4} = \frac{10^{-9.5}}{1 + \frac{10^{-9.6}}{10^{-3}}} = \frac{10^{-9.5}}{1 + 10^{-6.6}} = 10^{-9.5} \quad (11.81)$$

We can now evaluate equations (11.70)–(11.72) to obtain the molalities of the other species in solution after dissolution of 10^{-10} moles of microcline, which leads to

$$m_{\text{Al(OH)}^{2+}} = \frac{10^{-10} 10^{-11}}{10^{-9.3}} = 10^{-11.7} \quad (11.82)$$

$$m_{\text{Al(OH)}_4^-} = \frac{10^{-10} 10^{-44}}{10^{-32.7}} = 10^{-21.3} \quad (11.83)$$

and

$$m_{\text{H}_2\text{SiO}_4^-} = \frac{10^{-9.5} 10^{-9.6}}{10^{-3}} = 10^{-16.1} \quad (11.84)$$

Because the potassium ion does not associate appreciably at 25°C and 1 bar in the solution under consideration, $m_{\text{K}^+} = m_{\text{t, K}} = 10^{-10}$.

We now have all the information necessary to construct the matrix equation for the "initial" state of the system; that is, after an infinitesimal amount of reaction has taken place, which is defined in this case as 10^{-10} mole microcline dissolved in a solution containing 1000 g of H_2O and 10^{-3} mole HCl. For a small increment of progress in the reaction of microcline with this solution, we can write as a close approximation,

$$\frac{d \ln \gamma_s}{d\xi} \approx 0 \quad (11.85)$$

and because temperature and pressure are constant, equation (11.51) applies to the process. Hence, equation (11.43) can be written for the four dissociational reactions [reactions (11.66)–(11.69)] as

$$\frac{\bar{n}_{\text{Al}^{3+}}}{m_{\text{Al}^{3+}}} + \frac{\bar{n}_{\text{OH}^-}}{m_{\text{OH}^-}} - \frac{\bar{n}_{\text{Al(OH)}^{2+}}}{m_{\text{Al(OH)}^{2+}}} = \frac{\bar{n}_{\text{Al}^{3+}}}{10^{-10}} + \frac{\bar{n}_{\text{OH}^-}}{10^{-11}} - \frac{\bar{n}_{\text{Al(OH)}^{2+}}}{10^{-11.7}} = 0 \quad (11.86)$$

$$\frac{\bar{n}_{\text{Al}^{3+}}}{m_{\text{Al}^{3+}}} + \frac{4\bar{n}_{\text{OH}^-}}{m_{\text{OH}^-}} - \frac{\bar{n}_{\text{Al(OH)}_4^-}}{m_{\text{Al(OH)}_4^-}} = \frac{\bar{n}_{\text{Al}^{3+}}}{10^{-10}} + \frac{4\bar{n}_{\text{OH}^-}}{10^{-11}} - \frac{\bar{n}_{\text{Al(OH)}_4^-}}{10^{-21.3}} = 0 \quad (11.87)$$

$$\frac{\bar{n}_{\text{H}^+}}{m_{\text{H}^+}} + \frac{\bar{n}_{\text{H}_2\text{SiO}_4^-}}{m_{\text{H}_2\text{SiO}_4^-}} - \frac{\bar{n}_{\text{H}_2\text{SiO}_4}}{m_{\text{H}_2\text{SiO}_4}} = \frac{\bar{n}_{\text{H}^+}}{10^{-3}} + \frac{\bar{n}_{\text{H}_2\text{SiO}_4^-}}{10^{-16.1}} - \frac{\bar{n}_{\text{H}_2\text{SiO}_4}}{10^{-9.5}} = 0 \quad (11.88)$$

and

$$\frac{\bar{n}_{\text{H}^+}}{m_{\text{H}^+}} + \frac{\bar{n}_{\text{OH}^-}}{m_{\text{OH}^-}} = \frac{\bar{n}_{\text{H}^+}}{10^{-3}} + \frac{\bar{n}_{\text{OH}^-}}{10^{-11}} = 0 \quad (11.89)$$

Statements of equation (11.59) for the five elements involved in the reaction process appear (in the order, aluminum, silicon, oxygen, hydrogen, and potassium) as

$$\bar{n}_{\text{Al}^{3+}} + \bar{n}_{\text{Al(OH)}^{2+}} + \bar{n}_{\text{Al(OH)}_4^-} = -\bar{n}_{\text{KAlSi}_3\text{O}_8} \quad (11.90)$$

$$\bar{n}_{\text{H}_2\text{SiO}_4} + \bar{n}_{\text{H}_2\text{SiO}_4^-} = -3\bar{n}_{\text{KAlSi}_3\text{O}_8} \quad (11.91)$$

$$\bar{n}_{\text{Al(OH)}^{2+}} + 4\bar{n}_{\text{Al(OH)}_4^-} + 4\bar{n}_{\text{H}_2\text{SiO}_4} + 4\bar{n}_{\text{H}_2\text{SiO}_4^-} + \bar{n}_{\text{H}_2\text{O}} + \bar{n}_{\text{OH}^-} = -8\bar{n}_{\text{KAlSi}_3\text{O}_8} \quad (11.92)$$

$$\bar{n}_{\text{Al(OH)}^{2+}} + 4\bar{n}_{\text{Al(OH)}_4^-} + 4\bar{n}_{\text{H}_2\text{SiO}_4} + 3\bar{n}_{\text{H}_2\text{SiO}_4^-} + 2\bar{n}_{\text{H}_2\text{O}} + \bar{n}_{\text{H}^+} + \bar{n}_{\text{OH}^-} = 0 \quad (11.93)$$

and

$$\bar{n}_{\text{K}^+} = -\bar{n}_{\text{KAlSi}_3\text{O}_8} \quad (11.94)$$

which can be combined for $\bar{n}_{\text{KAlSi}_3\text{O}_8} = -1$ with equations (11.86)–(11.89) to give equation (11.95), which is shown in Table 11.1. Successive differentiation of this equation yields matrices identical to that in equation (11.95), but the upper part of the reactant column vector reduces to zero and the lower (reversible mass transfer) part takes on numerical entries equal (in the case of the first derivative) to the right side of equation (11.44). In each derivative of equation (11.95), the reactant coefficient column vector contains the appropriate values of \bar{n}_s or its derivatives.

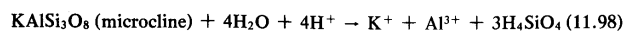
As indicated above, equation (11.95) can be simplified by first combining equations (11.86)–(11.93) to eliminate $\bar{n}_{\text{Al}(\text{OH})_2^+}$, $\bar{n}_{\text{Al}(\text{OH})_4^-}$, $\bar{n}_{\text{H}_2\text{SiO}_4}$, and $\bar{n}_{\text{H}_2\text{O}}$. For example, substituting equations (11.86) and (11.87) into equation (11.90) results in

$$\begin{aligned} & \bar{n}_{\text{Al}^{3+}} \left(1 + \frac{m_{\text{Al}(\text{OH})_2^+} + m_{\text{Al}(\text{OH})_4^-}}{m_{\text{Al}^{3+}}} \right) \\ & + \bar{n}_{\text{OH}^-} \left(\frac{m_{\text{Al}(\text{OH})_2^+} + 4m_{\text{Al}(\text{OH})_4^-}}{m_{\text{OH}^-}} \right) = -\bar{n}_{\text{KAlSi}_3\text{O}_8} \\ & = (1 + 10^{-1.7}) \bar{n}_{\text{Al}^{3+}} + 10^{-0.7} \bar{n}_{\text{OH}^-} = 1 \end{aligned} \quad (11.96)$$

Similarly, equations (11.88) and (11.91) can be combined to give

$$\begin{aligned} & \bar{n}_{\text{H}_2\text{SiO}_4} \left(1 + \frac{m_{\text{H}_2\text{SiO}_4}}{m_{\text{H}_2\text{SiO}_4}} \right) - \frac{m_{\text{H}_2\text{SiO}_4} \bar{n}_{\text{H}^+}}{m_{\text{H}^+}} = -3\bar{n}_{\text{KAlSi}_3\text{O}_8} \\ & = (1 + 10^{-16.6}) \bar{n}_{\text{H}_2\text{SiO}_4} - 10^{-13.1} \bar{n}_{\text{H}^+} = 3 \end{aligned} \quad (11.97)$$

Rather than solving equation (11.95) or evaluating simultaneously a set of equations like equations (11.96) and (11.97), it will suffice for the purpose of illustrating the procedure involved in calculating the molalities of aqueous species after a small increment of reaction progress if we compute by inspection approximate values of \bar{n}_s at the outset of the reaction. Because essentially all of the aluminum and silica in solution during the early stages of the reaction is present as Al^{3+} and H_4SiO_4 , it follows from the stoichiometry of microcline and equations (11.96) and (11.97) that $\bar{n}_{\text{Al}^{3+}} \approx \bar{n}_{\text{Al}}$ = 1 and $\bar{n}_{\text{H}_2\text{SiO}_4} \approx \bar{n}_{\text{Si}} = 3$. Maintenance of charge balance in the process thus requires the reaction to proceed as



so $\bar{n}_{\text{H}^+} = \bar{n}_{\text{H}^+ (11.98)} = -4$ and \bar{n}_{OH^-} is given by [from equation (11.89)]

Table 11.1 Equation (11.95)

Conservation of mass	Al^{3+}	$\text{Al}(\text{OH})_2^+$	$\text{Al}(\text{OH})_4^-$	H_4SiO_4	H_2SiO_4^-	H_2O	K^+	H^+	OH^-	Reaction coefficient column vector	Reactant column vector
Al	1	0	0	0	0	0	0	0	0	$-\bar{n}_{\text{Al}^{3+}}$	1
Si	0	0	0	1	1	0	0	0	0	$-\bar{n}_{\text{Al}(\text{OH})_2^+}$	3
O	0	0	4	4	4	1	0	0	1	$-\bar{n}_{\text{Al}(\text{OH})_4^-}$	8
H	0	1	4	4	3	2	0	1	0	$-\bar{n}_{\text{H}_2\text{SiO}_4}$	0
K	0	0	0	0	0	0	1	0	0	$-\bar{n}_{\text{H}_2\text{SiO}_4^-}$	1
Reversible mass transfer	10^{-10}	$10^{-11.7}$	0	0	0	0	0	0	10^{-11}	$-\bar{n}_{\text{H}_2\text{O}}$	0
$\text{Al}(\text{OH})_2^+$	10^{-10}	0	$10^{-21.3}$	0	0	0	0	0	$10^{-11.6}$	$-\bar{n}_{\text{H}^+}$	0
$\text{Al}(\text{OH})_4^-$	0	0	0	$10^{-9.5}$	0	0	0	10^{-3}	0	$-\bar{n}_{\text{OH}^-}$	0
H_4SiO_4	0	0	0	0	$10^{-16.1}$	0	0	10^{-3}	10^{-11}		0
H_2O	0	0	0	0	0	0	0	0	0		0

$$\bar{n}_{\text{OH}^-} = \frac{10^{0.60} 10^{-11}}{10^{-3}} = 10^{-7.4} \quad (11.99)$$

Similarly (from equations 11.86 through 11.88),

$$\bar{n}_{\text{Al(OH)}^{2+}} = 10^{-11.7} \left(\frac{1}{10^{-10}} + \frac{10^{-7.4}}{10^{-11}} \right) = 10^{-1.7} \quad (11.100)$$

$$\bar{n}_{\text{Al(OH)}_4^-} = 10^{-21.3} \left(\frac{1}{10^{-10}} + \frac{10^{0.6} 10^{-7.4}}{10^{-11}} \right) = 10^{-11.3} \quad (11.101)$$

and

$$\bar{n}_{\text{H}_4\text{SiO}_4} = 10^{-16.1} \left(\frac{10^{0.5}}{10^{-9.5}} + \frac{10^{0.6}}{10^{-3}} \right) = 10^{-6.1} \quad (11.102)$$

If we omit the second and higher order derivatives, these calculations permit evaluation of equation (11.64) to compute values of m_i for the various species after the first increment of reaction progress. For example, if we let $\Delta\xi$ be 10^{-9} , the molality of Al(OH)^{2+} after the first increment is given by

$$m_{\text{Al(OH)}^{2+}} = 10^{-11.7} + 10^{-1.7} \times 10^{-9} = 10^{-10.8} \quad (11.103)$$

Similar calculations for the other aqueous species provide all of the input data necessary to evaluate equation (11.95) or its condensed analog for the next increment of reaction progress.

Although at the outset of the reaction, the pH of the solution considered above is low and Al(OH)^{2+} , Al(OH)_4^- , and H_4SiO_4 contribute negligibly to the hydrolytic process, with continued reaction the solution pH increases and these species become important. The approximations represented by setting $\bar{n}_{\text{Al}^{3+}} = 1$ and $\bar{n}_{\text{H}_4\text{SiO}_4} = 3$ are then invalid and the matrix equation must be solved to compute accurate values of \bar{n}_i . Similarly, in most cases the assumption that $\gamma_i = 1$ and the approximation represented by equation (11.85) are not warranted. Matrix equations incorporating provision for changing ionic strength, activity coefficients, solid solution, oxidation/reduction reactions, and changing activity of H_2O can be solved quickly for a given increment of reaction progress with the aid of a computer and any one of several standard algorithms (Helgeson et al., 1970; Wolery, 1978).

Undesirable consequences of ill-conditioned matrices in mass transfer equations can be avoided by invoking predictor/corrector methods and

curve crawling techniques in the evaluation algorithms, subdividing the matrix, or solving integrals of the differential equations (Crerar, 1975; Wolery, 1978). For example, Karpov et al. (1973), Wood (1974), Crerar (1975), and others avoid differential equations by employing finite difference methods and optimal programming techniques to determine the distribution of components corresponding to the minimum Gibbs free energy of the system at each stage of reaction progress. Although this approach can be used to evaluate simultaneously a set of material balance and law of mass action equations representing conservation of mass and local and partial equilibrium states in the system, the set of equations is nonlinear. In contrast, the corresponding set of differential equations summarized above is linear, which simplifies considerably the computation of mass transfer in multicomponent systems.

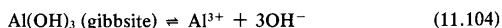
Calculation of \bar{n}_i , \bar{n}_o , and their derivatives permit evaluation of the Taylor's expansion represented by equation (11.64) for all of the species in the system. The distribution of species in the aqueous phase is calculated after each increment of reaction progress represented by a small but finite change in ξ from ξ to $\xi + \Delta\xi$. The new molalities of Al^{3+} , Al(OH)^{2+} , Al(OH)_4^- , H_4SiO_4 , H_3SiO_4^- , K^+ , H^+ , and OH^- in solution can then be used to compute the solution composition, ionic strength, and activity coefficients of the species after the increment of progress represented by $\Delta\xi$. This permits evaluation of new matrix equations to compute values of \bar{n}_i and its derivatives for $\xi + \Delta\xi$, which in turn permits calculation of the distribution of species and solution composition after another increment of reaction progress ($\xi + 2\Delta\xi$).

Candidates for reaction products resulting from the hydrolysis of microcline in the example considered above include

hydrogen-feldspar	$\text{H}_x\text{K}_{(1-x)}\text{AlSi}_3\text{O}_8$
illite	$\left\{ \begin{array}{l} \text{K}_x\text{Al}_2(\text{Al}_x\text{Si}_{(4-x)}\text{O}_{10})(\text{OH})_2 \\ \text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2 \end{array} \right.$
montmorillonite	
muscovite	
kaolinite	$\left\{ \begin{array}{l} \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \end{array} \right.$
halloysite	
dickite	
gibbsite	Al(OH)_3
boehmite	$\left\{ \begin{array}{l} \text{AlO(OH)} \end{array} \right.$
diaspore	
quartz	$\left\{ \begin{array}{l} \text{SiO}_2 \end{array} \right.$
amorphous silica	

and others, some of which are metastable at 25°C and 1 bar. By computing the chemical affinities of hydrolysis reactions for all of these minerals

after each increment of reaction progress, we can determine the exact stage at which the solution becomes saturated with respect to one or more of the phases. If the reaction product precipitates reversibly as microcline continues to dissolve (i.e., negligible supersaturation occurs so that the solution essentially maintains equilibrium with the reaction product), the matrix must be enlarged by one row and one column. For example, if the reaction remains congruent until the solution becomes saturated with respect to gibbsite, a column would be added to the matrix in equation (11.95) for $\bar{n}_{\text{gibbsite}}$, and a row would be inserted for the differential equation derived from the law of mass action for the reaction describing equilibrium between gibbsite and the aqueous phase; that is,



for which

$$a_{\text{Al}^{3+}} a_{\text{OH}^-}^3 = K \quad (11.105)$$

Differentiating equation (11.105) with respect to ξ at constant pressure and temperature leads to

$$\frac{\bar{n}_{\text{Al}^{3+}}}{m_{\text{Al}^{3+}}} + \frac{3\bar{n}_{\text{OH}^-}}{m_{\text{OH}^-}} + \frac{d \ln \gamma_{\text{Al}^{3+}}}{d\xi} + 3 \frac{d \ln \gamma_{\text{OH}^-}}{d\xi} = 0 \quad (11.106)$$

which imposes the constraint of reversible mass transfer between the aqueous solution and gibbsite on further reaction progress.

DISCUSSION

Provision for precipitation of metastable phases can be made in mass transfer calculations by suppressing the appearance of stable polymorphs in the computer routine used to detect local equilibrium states. Similarly, supersaturation states and specific kinetic constraints can be incorporated by allowing selected reactions to have negative chemical affinities, which may or may not be expressed as functions of ξ . The consequences of fluid flow and open-space filling can be taken into account by precluding destruction of reaction products in the calculations. Otherwise, the simultaneous dissolution and precipitation of different reaction products corresponds to replacement of one mineral by another.

Observations of the relative extent to which minerals in a rock have been destroyed by interaction of the minerals with an aqueous solution are not

necessarily indicative of the relative rate at which the minerals reacted with the aqueous phase. Even though a given mineral may react more slowly, it may also equilibrate with the aqueous phase before the other minerals in the rock. Mass transfer calculations indicate that this is the primary reason why potassium feldspar commonly survives the weathering process at the expense of plagioclase. Results of such calculations for the reaction of potassium feldspar and coexisting albite with H_2O at 25°C and 1 bar are shown in Figure 11.6. The calculations indicate that reaction of the two minerals with $\theta_{r/p} = 1$ leads to the sequential appearance of gibbsite, kaolinite, muscovite, sodium montmorillonite, and potassium feldspar. It can be seen that the potassium feldspar in the reactant mineral assemblage equilibrates long before albite, despite the fact that $\theta_{r/p}$ was set to unity in the calculations. Note that the overall process leads to dissolution and precipitation of $>0.3 \text{ g/kg H}_2\text{O}$ of reaction products during the process.

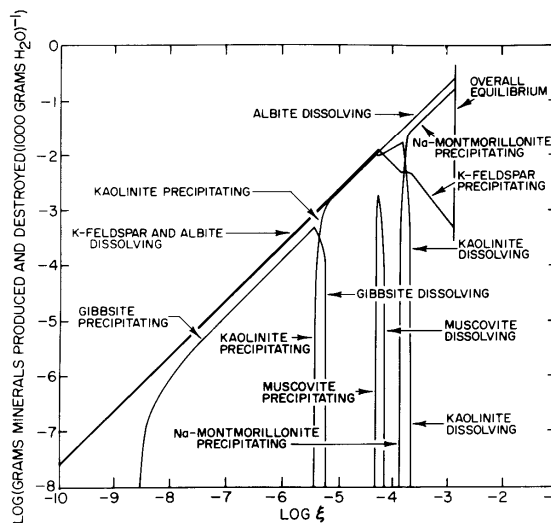


Fig. 11.6 Mass of minerals produced and destroyed ($\text{kg H}_2\text{O}^{-1}$) during reaction of albite and coexisting potassium feldspar with an aqueous phase at 25°C and 1 bar. The curves were computed for a relative reaction rate ($\theta_{r/p}$) equal to 1.0 using thermodynamic data taken from Helgeson (1969).

Little is known of the difference in the rates/cm² of surface area at which various silicates react with aqueous solutions. However, it seems likely that the rates are controlled by surface reactions and are comparable for minerals in a given structural class. This certainly seems to be true in the case of feldspars. Experimental data reported by Busenberg and Clemency (1976) leave little doubt that the dissolution of the reactant mineral is the primary rate-limiting step in the incongruent hydrolysis of feldspar. Their data also indicate that albite reacts only 1.5 times faster/cm² of surface area than potassium feldspar at 25°C and 1 bar, and that the relative reaction rate varies insignificantly with reaction progress.

The choice of relative reaction rates to be used in mass-transfer calculations is usually based on trial and error evaluation of the consequences of selecting different rates, or notions of relative rates based on relative abundances of minerals in geologic systems. For example, a trial calculation can be carried out with $\theta_{r/s}$ set equal to the relative surface area of the reactant minerals in the rock, which means that all reaction rates/cm² of surface area are taken to be equal. If the results of the calculation fail to agree quantitatively with field or laboratory data, the value of $\theta_{r/s}$ can be adjusted and the calculation repeated, which permits another comparison with observational data. Repetition of this procedure leads to convergence of the values of $\theta_{r/s}$ with field or laboratory observations. The same approach can be used to refine ambiguities in choosing the initial composition of an aqueous solution corresponding to the composition of the actual aqueous phase responsible for a given geochemical process. The compositions of fluid inclusions, geothermal waters, and interstitial fluids in rocks afford a basis for selecting a trial solution composition. The results of calculations for this solution composition can then be compared quantitatively with observations, which affords a basis for refining the initial composition of the aqueous phase used in subsequent mass-transfer calculations.

Results of isobaric/isothermal mass transfer calculations for two hydrothermal systems are shown in Figures 11.7 and 11.8, which depict the computed mass of minerals produced and destroyed during reaction of "typical" ore-forming solutions with granitic rocks. The sequence and relative abundance of the alteration products and sulfides resulting from these calculations closely approximate those in hydrothermal ore deposits. It can be seen in Figure 11.8 that the reaction leads to two generations of pyrite, which result from intricate changes in the oxidation state of the system as the reaction proceeds.

In principle, mass transfer calculations can be carried out for a wide variety of geochemical processes, including those in which temperature and pressure are variables. As in the isothermal/isobaric case, the first partial derivative on the right side of equation (11.48) can be represented in the

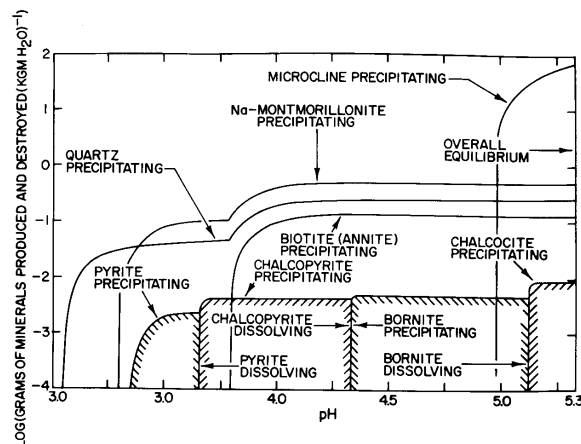


Fig. 11.7 Mass of minerals produced and destroyed (kg H₂O)⁻¹ as a function of solution pH during reaction of a granitic rock with a potential ore-forming solution at 200°C and 15 bars (modified after Helgeson, 1970 and reproduced with permission from the Mineralogical Society of America).

calculations by equations derived from extended Debye-Hückel theory (Helgeson et al., 1970; Helgeson and Kirkham, 1974b; Helgeson, Kirkham, and Flowers, 1979). The remaining terms in equation (11.48) and those in equation (11.49) can be expressed in terms of equations of state and thermodynamic data summarized elsewhere (Helgeson and Kirkham, 1974a, 1976; Walther and Helgeson, 1977; Helgeson et al., 1978; Helgeson, Kirkham, and Flowers, 1979). However, the extent to which changes in pressure and temperature are coupled to reaction progress must be specified in the calculations. If pressure and temperature are constant, the calculations can be carried out in the manner described above. If not, mass transfer among minerals and aqueous solutions caused by changes in pressure and temperature can be expressed by specifying a geothermal gradient characteristic of a given cooling process, such as reversible or irreversible adiabatic expansion of hydrothermal fluids. In the simplest case, cooling occurs along a geothermal profile represented by

$$P = a + bT \quad (11.107)$$

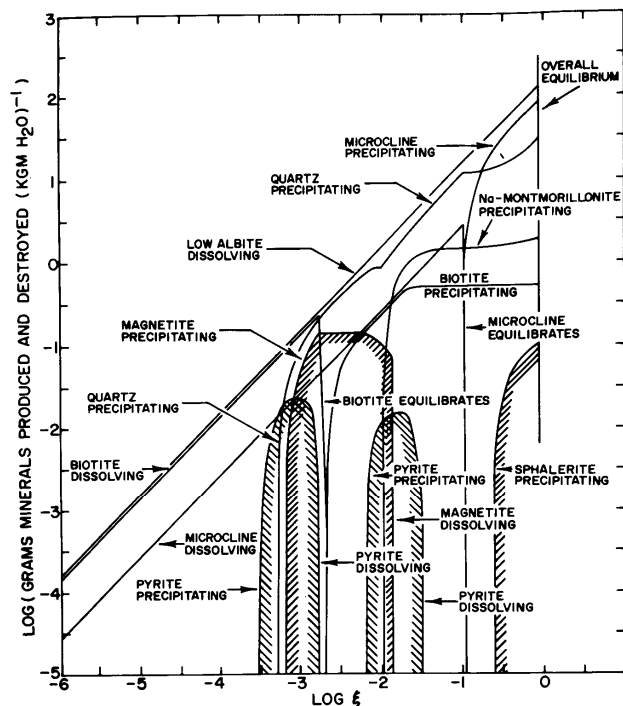


Fig. 11.8 Mass of minerals produced and destroyed $(\text{kg H}_2\text{O})^{-1}$ as a function of progress in the reaction of a granitic rock with a potential ore-forming solution at 300°C and 85 bars (modified after Helgeson, 1970 and reproduced with permission from the Mineralogical Society of America).

where a and b are constants. Hence

$$\frac{dP}{d\xi} = b \frac{dT}{d\xi} \quad (11.108)$$

After carrying out an isothermal/isobaric mass-transfer calculation to characterize the overall equilibrium state resulting from the irreversible reaction of a hydrothermal solution with its mineralogic environment at a given pressure and temperature, we can then let $dT/d\xi = 1$ and examine the consequences of cooling along the geothermal profile represented by equation (11.107).

The consequences of various thermodynamic constraints such as constant enthalpy, entropy, or volume on reactions among minerals and hydrothermal solutions can also be assessed quantitatively with the aid of mass-transfer calculations. For example, if a given hydrothermal process is constrained to take place at constant enthalpy, $dT/d\xi$ becomes an unknown. However, it can be calculated by enlarging the matrix by one row and column to accommodate $dT/d\xi$ and a heat conservation equation for the process. The extent to which thermodynamic components are redistributed among phases in irreversible adiabatic processes can then be evaluated.

CONCLUDING REMARKS

Reaction paths on activity or chemical potential diagrams are vector quantities that can be described in terms of linear algebra. Work is currently in progress to determine the vector properties of various reaction paths and their implications with respect to chemical affinity and its change as a function of reaction progress. Nonequilibrium phase relations in hydrothermal systems can be represented quantitatively on chemical affinity diagrams, which afford a convenient frame of reference for evaluating the thermodynamic consequences of different reaction paths. Other efforts are being directed toward a better understanding of the relation between reaction kinetics and the chemical affinities of hydrolysis reactions. The rates of many of these reactions in nature are probably controlled to a large extent by the thermodynamic properties of the reactant minerals and the aqueous species involved in the reaction process. In some instances rate control may be exercised by the chemical affinity of the reaction. For example, in the case of a reaction near equilibrium, the rate (\dot{f}) can be expressed as (Prigogine, 1967)

$$\dot{f} = \frac{d\xi}{dt} = \frac{kA}{RT} \quad (11.109)$$

where A refers to the chemical affinity of the reaction, t denotes time, and k stands for the rate constant given by

$$k = \hat{A}e^{-\Delta E^{\ddagger}/RT} \quad (11.110)$$

where \hat{A} designates the pre-exponential factor and ΔE^{\ddagger} corresponds to the activation energy for the reaction.

Mass-transfer calculations combined with field and laboratory observations afford a better understanding of the chemistry of processes responsible for hydrothermal phase relations. Each mass-transfer calculation is a computer experiment, which produces quantitative results. Comparison of these results with fluid inclusion analyses and the relative abundances of minerals in hydrothermal systems offers the means to integrate theoretical geochemistry with geologic reality.

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