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DESCRIPTION AND INTERPRETATION OF PHASE RELATIONS IN GEOCHEMICAL PROCESSES INVOLVING AQUEOUS SOLUTIONS

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ABSTRACT. Sets of thermodynamic components consisting solely of oxide and/or sulfide formula units are not adequate to describe compatibilities and reactions among minerals in geologic systems involving natural aqueous solutions. Consideration of the compositional characteristics of such solutions and the extent to which they interact with rocks suggests that the chemical potentials of chloride components such as NaCl are commonly fixed by the composition of the aqueous phase. Under such conditions the chemical potentials of the corresponding oxide components are not independent variables but are controlled by the activity of the hydrogen ion. Recognition of the compositional constraints imposed by the aqueous phase on chemical reactions and equilibrium among phases in geologic systems leads to an integrated thermodynamic frame of reference for description and interpretation of phase relations, and prediction of mass transfer among silicates, sulfides, oxides, carbonates, sulfates, and aqueous solutions.

INTRODUCTION

Mineral compositions and compatibilities in rocks are commonly reported in terms of oxide components which may be used in the phase rule to compute the number of degrees of freedom in the geochemical process responsible for an observed equilibrium mineral assemblage. Any set of independently variable thermodynamic components is suitable for this purpose, but the actual identities of components with fixed chemical potentials corresponding to degrees of freedom in real processes must be deduced on empirical grounds. Geologic systems are seldom viewed by the petrologist in terms of alternate sets of components, and the composition of the aqueous phase is rarely taken into consideration when deductions are made from the phase rule. As a consequence, thermodynamic constraints operative in geochemical processes may be identified incorrectly, and important chemical reactions responsible for observed mineral assemblages may be overlooked. Under these circumstances, phase rule interpretation of mineral assemblages leaves much to be desired as a tool of geochemical investigation.

The aqueous phase involved in such geologic processes as weathering, sedimentation, diagenesis, metamorphism, hydrothermal metasomatism, ore deposition, volcanism, and igneous intrusion is almost invariably an electrolyte solution, commonly containing relatively high concentrations of alkali and/or alkaline earth chlorides (compare, White, 1957a and b, 1965; White, Hem, and Waring, 1963; Burnham, 1967; Roedder, 1967; Garrels and Mackenzie, 1967; Ellis, 1969; Helgeson, 1964, 1967a, 1968a). Solutions of this kind are ubiquitous in the Earth's crust, and their compositions reflect complicated histories of chemical interaction with rocks. Unless provision is included for the composition of these solutions in the set of components chosen to describe equilibrium phase

relations and mass transfer among phases in geochemical processes, quantitative interpretation of phase relations in rocks is subject to considerable error. Acid components such as HCl in natural electrolyte solutions are not present in rocks, yet these components should be included in the set of components chosen to describe the composition and thermodynamic state of many geologic systems.

It is not unusual for CO_2 and H_2O to be regarded as components with fixed chemical potentials in geochemical processes, while those of components such as O, S, Na_2O, K_2O, CaO, MgO, FeO, or Cu, Zn, Fe, Pb, and Ag are commonly considered to be independent variables. The purpose of the present communication is to demonstrate that many of these designations are unrealistic where an aqueous phase is involved, and that description and interpretation of mineral relations solely in terms of oxide and/or elemental components commonly misleads the geologist concerned with interpretation of real systems. Realistic thermodynamic interpretation of mineral assemblages requires consideration of the roles played by the chemical potentials of chloride components in geochemical processes. This can be done within the framework of conventional chemical petrology by taking into account thermodynamic relations among the chemical potentials of corresponding components in alternate sets of components chosen to describe geologic systems.

THERMODYNAMIC COMPONENTS

Thompson (1959), in his study of equilibrium in metasomatic processes, defined and classified various types of thermodynamic components and examined the consequences of choosing one or another of these with respect to equilibrium and the phase rule. Any chemical formula unit of atoms or molecules may be designated as a thermodynamic component provided the number of such units required to describe the composition of the phases in the system corresponds to the minimum number of possible components that could be selected. A thermodynamic component has an unspecified physical state but a definite chemical composition. An *actual* component of a phase is one that can be independently added to or subtracted from the phase without destroying its homogeneity, but an *actual* component of an assemblage of coexisting phases is one that may be added to or subtracted from the system without adding an extra phase to the assemblage. A set of *ultimate* components consists of formula units that can be used to describe the composition of all *actual* components of the phases in a *sequence* of mineral assemblages. Any set of components chosen to describe a system consists of independent components when the composition of each cannot be expressed in terms of the other components in the set.

Various advantages and disadvantages attend selection of one or another set of components to represent a given system or geochemical process. For example, one set of components may be better than others for diagrammatic description of mineral compositions and compatibilities, while another may facilitate interpretation of the chemical environ-

ment in geologic systems. Any set of independently variable components may be used to evaluate the phase rule, but degrees of freedom other than temperature and pressure do not necessarily correspond in the actual geologic system to constant chemical potentials of components in the particular set chosen to describe its composition. Oxides are commonly employed as components in chemical petrology, but it will be shown below that where aqueous chloride solutions are involved, degrees of freedom other than temperature and pressure more often than not refer to constant chemical potentials of chloride components in geochemical processes.

Chloride components are not suitable for diagrammatic description of the composition of geologic systems, because they are not *actual* components of the solid phases. Accordingly, they must be subtracted as well as added to describe the composition of the minerals in the system. For example, the composition of albite in equilibrium with an aqueous chloride solution can be described in terms of the components NaCl–Al_2O_3–SiO_2–H_2O–HCl, but only by NaCl + $\frac{1}{2}Al_2O_3$ + $3SiO_2$ + $\frac{1}{2}H_2O$ – HCl. To plot the composition of albite in terms of these components would require negative dimensions.

In most instances, the sets of components chosen to represent geochemical processes involving an aqueous phase should include provision for the presence of alkali and alkaline earth chlorides in solution. Equilibrium relations and mass transfer among the phases in the system can then be described conveniently in terms approaching geologic reality; that is, in terms of the actual variables involved in geochemical processes. The identity of these variables and their relation to the chemical potentials of various components are discussed below.

Silicate systems—Among the many thermodynamic components that may be chosen to describe geochemical processes involving silicates and aqueous chloride solutions, let us consider three alternate sets of components describing the same system; that is,

Na_2O	NaOH	NaCl
K_2O	KOH	KCl
CaO	$Ca(OH)_2$	$CaCl_2$
MgO	$Mg(OH)_2$	$MgCl_2$
FeO	$Fe(OH)_2$	$FeCl_2$
Fe_2O_3	$Fe(OH)_3$	$FeCl_3$
Al_2O_3	$Al(OH)_3$	$AlCl_3$
SiO_2	SiO_2	SiO_2
H_2O	H_2O	H_2O
HCl	HCl	HCl

The composition of a given phase assemblage (that includes an aqueous chloride solution) described by components in any one of these sets can be represented in terms of corresponding components in either of the other sets, and the required number in each will always be the same and equal to the minimum number required to describe the composition of

the aqueous phase. Each component in each set is an independent *actual* component of the aqueous phase, but each is not necessarily an *actual* component of the system.

A given oxide component can be represented in terms of the corresponding components in the other two sets listed above by writing

$$M\nu_+O\nu_- + \frac{\nu_+Z_+}{2} H_2O \rightleftarrows \nu_+M(OH)_{Z_+} \tag{1}$$

and

$$M\nu_+O\nu_- + \nu_+Z_+HCl \rightleftarrows \nu_+MCl_{Z_+} + \frac{\nu_+Z_+}{2}H_2O \tag{2}$$

for which

$$\frac{a_{M(OH)_{Z_+}}^{\nu_+}}{a_{M_{\nu_+}O_{\nu_-}} a_{H_2O}^{\nu_+Z_+/2}} = K_1 \tag{3}$$

and

$$\frac{a_{MCl_{Z_+}}^{\nu_+} a_{H_2O}^{\nu_+Z_+/2}}{a_{M_{\nu_+}O_{\nu_-}} a_{HCl}^{\nu_+Z_+}} = K_2, \tag{4}$$

where M denotes a cation (other than the hydrogen ion) common to the ovide, hydroxide, and chloride components designated by $M\nu_+O\nu_-$, $M(OH)_{Z_+}$, and MCl_{Z_+}, respectively, ν_+ and ν_- refer to the number of moles of the cation and anion in one mole of the *oxide* component, Z_+ is the charge on the cation, a_{HCl} represents the activity of the subscripted component, and K_1 and K_2 are the equilibrium constants for reactions (1) and (2), respectively.

The chemical potential of the ith component ($i = 1, 2, 3, \ldots, j$) is related to its activity by

$$\mu_i = \mu^\circ_i + RT \ln a_i \tag{5}$$

and thus for a given temperature and pressure

$$\frac{d\mu_i}{d\xi} = \frac{RT\ d \ln a_i}{d\xi}, \tag{6}$$

where μ_i and μ°_i represent the chemical potential of the ith component in the state of interest and the standard state, respectively, R stands for the gas constant, T for the absolute temperature, and ξ is the progress variable for a reaction process (De Donder, 1920; Helgeson, 1967a, 1968b). If we now assume constant activity of H_2O (which we can do by choosing an appropriate standard state; Helgeson, 1967a, 1968b) and combine ap-

propriate statements of equation (6) with the logarithmic derivatives of equations (3) and (4) we can write (for isothermal-isobaric processes)

$$\frac{d\mu_{M_{\nu_+}O_{\nu_-}}}{d\mu_{M(OH)_{Z_+}}} = \frac{d \ln a_{M_{\nu_+}O_{\nu_-}}}{d \ln a_{M(OH)_{Z_+}}} = \nu_+ \tag{7}$$

and

$$\frac{d\mu_{M_{\nu_+}O_{\nu_-}}}{d\mu_{MCl_{Z_+}}} = \frac{d \ln a_{M_{\nu_+}O_{\nu_-}}}{d \ln a_{MCl_{Z_+}}} = \nu_+ - \nu_+ Z_+ \left(\frac{d \ln a_{HCl}}{d \ln a_{MCl_{Z_+}}}\right) . \tag{8}$$

It can be deduced from equation (7) that the chemical potential and the logarithm of the activity of an oxide component are linearly related, respectively, to the chemical potential and logarithm of the activity of the corresponding hydroxide component. Accordingly, when the chemical potential of an oxide component is constant, the chemical potential of the corresponding hydroxide component is also fixed. In contrast, equation (8) indicates that when the chemical potential of a chloride component other than HCl is constant, the chemical potential of the corresponding oxide component is not fixed unless μ_{HCl} is also constant. When the chemical potential of a chloride component other than HCl is constant, we can write equation (4) (for the corresponding oxide component) as

$$a_{M_{\nu_+}O_{\nu_-}} \, a_{HCl}^{\nu_+ Z_+} = \hat{K} \tag{9}$$

where $\hat{K}$ is a constant defined as

$$\hat{K} = \frac{a_{MCl_{Z_+}}^{\nu_+} \, a_{H_2O}^{\nu_+ Z_+/2}}{K_2} . \tag{10}$$

It then follows from equations (6) and (9) that

$$\frac{d\mu_{M_{\nu_+}O_{\nu_-}}}{d\mu_{HCl}} = \frac{d \ln a_{M_{\nu_+}O_{\nu_-}}}{d \ln a_{HCl}} = -\nu_+ Z_+ . \tag{11}$$

Under the conditions represented by equation (11), a change in the chemical potential of an oxide component is proportional to the change in the chemical potential of the component HCl, and the product of the activity of the oxide component and the activity of HCl raised to the $\nu_+ Z_+$ is fixed. Before considering the implications of these relations with respect to geochemical processes, let us first examine alternate choices of thermodynamic components for describing sulfide systems.

Sulfide systems.—Phase relations in sulfide systems are commonly described in terms of elemental thermodynamic components such as Cu, Fe, Pb, Zn, Ag, S, and O. These components permit simple diagrammatic description of mineral compositions and compatibilities in ore deposits. Apparently because of this, the fugacities of elemental components or their polymers have been widely used to describe phase relations in hydro-

thermal systems (for example, Gustafson, 1963; Holland, 1965). Although this approach can be used to advantage for "dry" systems, it does not afford convenient representation of physical reality in hydrothermal systems. The geologist concerned with the actual chemical environment of hydrothermal ore deposition cannot readily interpret the fugacities of elemental components in terms of mineral solubilities, nor can he reconcile simply in a unified frame of reference the fugacities of elemental components of sulfides with the chemical potentials of oxide components in hydrothermal silicates associated with sulfide mineralization. The fugacities of S_2 and O_2 in hydrothermal solutions are exceedingly small. In most hydrothermal environments, the chemical potentials of oxygen and sulfur are functions of equilibrium states in the system, which may consist of homogeneous equilibria in the aqueous phase. Nevertheless, it is not uncommon for these components to be treated as independent variables in hydrothermal studies. By choosing an alternate set of components, all the disadvantages connected with using the fugacities of elemental components can be avoided, and phase relations among sulfides, silicates, and other minerals in geochemical processes can be represented together in terms of a single set of variables.

As in the case of silicates the thermodynamic components chosen to describe hydrothermal sulfide systems should include provision for the composition of the aqueous phase, which in many instances consists of a chloride-rich electrolyte solution. Hydrothermal systems involving such solutions can be described in terms of various alternate sets of thermodynamic components. If we confine our attention for the moment to sulfides and sulfates of the ore-forming metals we can write three of these as

Cu	Cu_2S	CuCl
Fe	FeS	$FeCl_2$
Zn	ZnS	$ZnCl_2$
Pb	PbS	$PbCl_2$
Ag	Ag_2S	AgCl
S	H_2S	H_2S
O	H_2SO_4	H_2SO_4
H_2O	H_2O	H_2O
HCl	HCl	HCl

Each of these sets of components includes provision for all the oxidation states of the elements considered. This provision is explicit with respect to the most important oxidation states in the second and third sets, which are analogous to those discussed earlier for silicate systems. The compositions of sulfide minerals and a coexisting aqueous chloride solution described by elemental components in the first set can be represented in terms of corresponding components in the other two sets. As in the analogous silicate system, the number of components required for this will always be equal to the minimum number required in any of the sets to describe the composition of the aqueous phase.

A given elemental metal component can be represented in terms of corresponding components in the other two sets listed above by writing oxidation-reduction reactions such as

$$4\nu_+ M + H_2SO_4 + 3H_2S \rightleftarrows 4M\nu_+ S + 4H_2O \tag{12}$$

and

$$\frac{8}{\nu_-} M + H_2SO_4 + 8HCl \rightleftarrows \frac{8}{\nu_-} MCl\nu_- + H_2S + 4H_2O \tag{13}$$

for which

$$\frac{a_{M_{\nu_+}S}\ a_{H_2O}{}^4}{a_M{}^{4\nu_+}\ a_{H_2SO_4}\ a_{H_2S}{}^3} = K_{12} \tag{14}$$

and

$$\frac{a_{MCl}{}^{8/\nu_-}\ a_{H_2S}\ a_{H_2O}{}^4}{a_M{}^{8/\nu_-}\ a_{H_2SO_4}\ a_{HCl}{}^8} = K_{13} \tag{15}$$

where M stands for the elemental metal component, $M\nu_+S$ and $MCl\nu_-$ refer to the sulfide and chloride components corresponding to the elemental components, ν_+ and ν_- are the number of moles of the cation and ligand in the sulfide and chloride components, respectively, and K_{12} and K_{13} represent the equilibrium constants for reactions (12) and (13). As before, if we assume constant activity of H_2O and combine the logarithmic derivatives of equations (14) and (15) with appropriate statements of equation (6) we can write (for constant temperature and pressure)

$$\frac{d\mu_M}{d\mu_{M_{\nu_+}S}} = \frac{d \ln a_M}{d \ln a_{M_{\nu_+}S}} = \frac{1}{4\nu_+}\left(1 - \frac{d \ln a_{H_2SO_4}}{d \ln a_{M_{\nu_+}S}} - 3\frac{d \ln a_{H_2S}}{d \ln a_{M_{\nu_+}S}}\right) \tag{16}$$

and

$$\frac{d\mu_M}{d\mu_{MCl_{\nu_-}}} = \frac{d \ln a_M}{d \ln a_{MCl_{\nu_-}}} =$$

$$1 + \frac{\nu_-}{8}\left(\frac{d \ln (a_{H_2S}/a_{H_2SO_4})}{d \ln a_{MCl_{\nu_-}}}\right) - \nu_-\left(\frac{d \ln a_{HCl}}{d \ln a_{MCl_{\nu_-}}}\right). \tag{17}$$

It can be deduced from equations (16) and (17) that the relative change in the chemical potentials of components in alternate sets of components selected to describe hydrothermal sulfide systems involving an aqueous chloride solution depends (among other things) on the change in the oxidation state of the system, which is defined by

$$\frac{d \ln f_{O_2}}{d\xi} = -\frac{1}{2}\frac{d \ln (a_{H_2S}/a_{H_2SO_4})}{d\xi}, \tag{18}$$

where f_{O_2} is the fugacity of oxygen. For systems in which the chemical potential of a given metal chloride component is constant, we can write

$$\frac{d\mu_M}{d\xi} = \frac{RT\ d\ \ln a_M}{d\xi} =$$

$$RT\left(\frac{\nu_-}{8}\left(\frac{d\ \ln\ (a_{H_2S}/a_{H_2SO_4})}{d\xi}\right) - \nu_-\left(\frac{d\ \ln a_{HCl}}{d\xi}\right)\right) \cdot \quad (19)$$

It follows from equations (18) and (19) and the discussion presented below that if the activity of the chloride ion in solution is also constant, then the change in the chemical potential of an elemental metal component depends only on the change in the oxidation potential and pH of the aqueous phase. It will be shown in later discussion that in many hydrothermal processes (such as ore deposition), the change in the chemical potential of the component HCl is proportional to the change in the pH of the aqueous phase, owing to the constant activity of the chloride ion in solution. In many instances the pH change in the aqueous phase is controlled by reaction of the solution with silicates, which may cause isothermal precipitation of sulfides (Helgeson, 1964, 1970c; Helgeson and Garrels, 1968; Helgeson, Garrels, and Mackenzie, 1969).

Hydrothermal systems.—Perhaps because of the limitations imposed by having only two dimensions available for diagrammatic description of equilibrium phase relations, complicated geologic systems are commonly represented by idealized models of but a few components. Recent advances in computer technology have largely obviated this approach by making it possible to represent mathematically (and quantitatively) equilibrium phase relations in geochemical processes involving as many components and phases as we find in natural systems (Helgeson, 1968b; Helgeson, Garrels, and Mackenzie, 1969; Helgeson, Brown, and Leeper, 1969; Helgeson and others, 1970). Sufficient thermodynamic data are now available (Robie and Waldbaum, 1968; Wagman and others, 1968, 1969; Helgeson, 1969) to permit comprehensive description of equilibrium and mass transfer in systems involving aqueous chloride solutions and silicate, oxide, hydroxide, sulfide, sulfate, and carbonate minerals. This can be done simultaneously by the computer within a unified frame of reference if we describe the system with sets of components such as

Na_2O	Na_2O	NaCl
K_2O	K_2O	KCl
CaO	CaO	$CaCl_2$
MgO	MgO	$MgCl_2$
FeO	FeS	$FeCl_2$
Cu_2O	Cu_2S	CuCl
ZnO	ZnS	$ZnCl_2$
PbO	PbS	$PbCl_2$
Ag_2O	Ag_2S	AgCl

Al_2O_3	Al_2O_3	Al_2O_3
SiO_2	SiO_2	SiO_2
H_2O	H_2O	H_2O
CO_2	CO_2	CO_2
H_2SO_4	H_2SO_4	H_2SO_4
HCl	HCl	HCl
H_2S	H_2S	H_2S

None of these sets of components is suitable for diagrammatic description of all phase compositions and compatibilities in the system represented by the sets of components. On the other hand, the computer supersedes most of the advantages of the topological approach used in phase equilibrium studies. For example, both reversible and irreversible chemical reactions written in terms of components in any one of these sets can be represented by differential equations programmed for simultaneous machine evaluation (Helgeson, 1968b; Helgeson, Garrels, and Mackenzie, 1969; Helgeson and others, 1970). The chemical potentials of the components are cast in terms of the activities of species in the aqueous phase, which can then be converted to molalities with the aid of activity coefficients (Helgeson and James, 1968; Helgeson, 1969) and compared with the compositions of natural aqueous solutions. Regardless of the number of components, the thermodynamic data used in the machine calculations permit diagrammatic depiction by the computer of phase relations at any stage of a geochemical process (for example, Helgeson, Brown, and Leeper, 1969; Helgeson, 1970c).

Interpretation of chemical potential.—Because at equilibrium the chemical potential of a given component of a phase is equal to that of the component in all other phases, it suffices to characterize the chemical potentials of components in the aqueous phase to describe equilibrium among all phases in the system. Oxide, hydroxide, chloride, sulfide, sulfate, and carbonate components can be represented in terms of aqueous species by writing the general reaction (Helgeson, 1967a, 1968b),

$$M_{\nu_+}L_{\nu_-} + \nu_+ Z_+ H^+ \rightleftarrows \nu_+ M^{Z_+} + \nu_- H_{Z_-} L \tag{20}$$

for which

$$\frac{a_{M^{Z_+}}^{\nu_+} \; a_{H_{Z_-}L}^{\nu_-}}{a_{M_{\nu_+}L_{\nu_-}}^{\nu_+ Z_+} \; a_{H^+}^{Z_+}} = K_{20}, \tag{21}$$

where ν_+ and ν_- stand for the number of moles of the cation (M) and anion (L), respectively, in one mole of the component represented by $M_{\nu_+}L_{\nu_-}$, H refers to hydrogen, Z_+ and Z_- are the charges on the cation and anion, and K_{20} is the equilibrium constant for reaction (20). The derivative of equation (21) with respect to ξ, the progress variable used

above to describe geochemical processes, can be combined with an appropriate statement of equation (6) to give

$$\frac{d\mu_{M_{\nu_+}L_{\nu_-}}}{d\xi} = \frac{RT\, d \ln a_{M_{\nu_+}L_{\nu_-}}}{d\xi} = \frac{\nu_+ RT\, d \ln\left(a_{M_{Z_+}}/a_{H^+}^{Z_+}\right)}{d\xi} + \frac{\nu_- RT\, d \ln a_{H_{Z_-}L}}{d\xi} \quad (22)$$

For two such components (designated by the subscripts 1 and 2) having the same ligand we can now write

$$\frac{d\mu_1}{d\mu_2} = \frac{d \ln a_1}{d \ln a_2} = \frac{\nu_{+(1)}\, d \ln \left(a_{M(1)}/a_{H^+}^{Z_{+(1)}}\right) + \nu_{-(1)}\, d \ln a_{H_{Z_-}L}}{\nu_{+(2)}\, d \ln \left(a_{M(2)}/a_{H^+}^{Z_{+(2)}}\right) + \nu_{-(2)}\, d \ln a_{H_{Z_-}L}}. \quad (23)$$

The representation of changes in the chemical potentials of thermodynamic components in terms of changes in the activities of corresponding aqueous species afforded by equations (22) and (23) provides a single frame of reference for describing phase equilibrium and mass transfer in geochemical processes. All equilibrium states in such processes can be described by independent reversible chemical reactions written in terms of minerals and aqueous species. Although equilibrium states are normally described in terms of the ratios of the activities of individual ions in solution, it is often advantageous to represent simultaneously equilibrium and mass transfer among phases in terms of the actual predominant species (which usually include complexes) in the aqueous phase. When this is done, reaction paths for geochemical processes can be deduced directly from theoretical logarithmic activity diagrams.

Mass transfer of a component to or from the aqueous phase reacting with a mineral can be expressed in terms of the change in its chemical potential and the change in the concentrations of aqueous species by an alternate statement of equation (22); that is

$$\frac{d\mu_{M_{\nu_+}L_{\nu_-}}}{d\xi} = RT\left(\frac{\nu_+ \bar{n}_{M_{Z_+}}}{m_{M_{Z_+}}} - \frac{\nu_+ Z_+ \bar{n}_{H^+}}{m_{H^+}} + \frac{\nu_- \bar{n}_{H_{Z_-}L}}{m_{H_{Z_-}L}}\right) + RT\left(\frac{\nu_+ d \ln \gamma_{M^{Z_+}}}{d\xi} - \frac{\nu_+ Z_+ d \ln \gamma_{H^+}}{d\xi} + \frac{\nu_- d \ln \gamma_{H_{Z_-}L}}{d\xi}\right), \quad (24)$$

where m_{H^+} and γ_{H^+} denote the molality and activity coefficient of the subscripted species, and $\bar{n}_{H^+}$ is the reaction coefficient (kg H_2O)$^{-1}$ for the subscripted species in the overall irreversible chemical reaction describing the geochemical process (Helgeson, 1967a, 1968b). The activity

coefficient and reaction coefficient of the ith aqueous species are defined, respectively, by

$$\gamma_i = \frac{a_i}{m_i}, \tag{25}$$

and

$$\bar{n}_i = \frac{\mathrm{d}m_i}{\mathrm{d}\xi}. \tag{26}$$

It can be seen in equation (24) that if the chemical potential of a given in the aqueous phase related to that component are not necessarily constant.

Activity coefficients in the aqueous phase can be represented as a function of the ionic strength of the solution at a given temperature. Because ionic strength changes only slightly in geochemical processes involving relatively concentrated electrolyte solutions, the second parenthetical term in equation (24) is often negligible in magnitude compared with the first. In processes involving such solutions, if the molalities of M^+ and H_Z_L are large compared to that of the hydrogen ion, equation (24) can be closely approximated by

$$\frac{\mathrm{d}\mu_{\mathrm{M}_{\nu_+}\mathrm{L}_{\nu_-}}}{\mathrm{d}\xi} \approx -\frac{\mathrm{RT}\,\nu_+ Z_+\,\bar{n}_{\mathrm{H}^+}}{m_{\mathrm{H}^+}}, \tag{27}$$

and thus for two components (denoted by the subscripts 1 and 2) containing the same ligand,

$$\frac{\mathrm{d}\mu_1}{\mathrm{d}\mu_2} \approx \frac{\nu_{+(1)}Z_{+(1)}}{\nu_{+(2)}Z_{+(2)}}. \tag{28}$$

Expressions of equations (27) and (28) for oxide components are applicable to many geochemical processes.

COMPOSITIONAL CONSTRAINTS

The gross compositional characteristics of natural electrolyte solutions are much the same the world over; that is, the solute consists predominantly of NaCl, $CaCl_2$, KCl, $MgCl_2$, and/or $NaHCO_3$ and Na_2SO_4 et cetera. The relative molalities of these components vary from place to place, but the concentration of total dissolved solids is commonly high with NaCl and other alkali and alkaline earth chlorides accounting for the bulk of the solute.

The initial composition of electrolyte solutions such as sea water, interstitial waters in sediments, and hydrothermal vein solutions is the major discriminant factor responsible for the sequence of minerals produced and the extent of mass transfer caused by reaction of such solutions with their mineralogic environments (Korzhinskii, 1964, 1967b, 1968; Helgeson, 1967a, 1968b, 1970c). Because the concentration of the chloride ion as well as the concentrations of cations common to rock-forming minerals are relatively high in many of these solutions, systems involved in geochemical processes are commonly open with respect to alkali and alkaline earth chloride components; that is, their chemical potentials are

constant during reaction progress. Theoretical calculations (Helgeson, 1967a and b, 1970a and c; Helgeson, Garrels, and Mackenzie, 1969) and experimental studies (Wollast, 1967; Lagache, Wyart, and Sabatier, 1961; Althaus and Johannes, 1969) indicate that the total mole transfer of material to the aqueous phase resulting from reaction of silicate rocks with aqueous electrolye solutions is of the order of 10^{-4} moles (kg of $H_2O)^{-1}$ at 25°C, increasing to 10^{-2} or $>10^{-1}$ moles (kg of $H_2O)^{-1}$ at 300°C, depending on the pH of the solution. Where these reactions involve alkali and alkaline earth chloride solutions in which the initial concentrations of Na^+, Ca^{++}, Mg^{++}, and/or K^+ exceed the mole transfer of these ions to or from the aqueous phase, the activities and activity coefficients of these ions remain essentially constant throughout the reaction process.

As a general rule the activity of the chloride ion changes negligibly during reaction of an alkali-alkaline earth chloride solution with its mineralogic environment. Accordingly, the geochemical process takes place with constant chemical potentials of the chloride components corresponding to the alkali and alkaline earth cations present in large concentrations. This observation can be stated formally by first writing

$$MCl_{\nu_-} \rightleftarrows M^{z_+} + \nu_- Cl^- \tag{29}$$

for which

$$a_{MCl_{\nu_-}} = \frac{a_{M^{z_+}} \, a_{Cl^-}^{\nu_-}}{K_{29}} \tag{30}$$

where MCl_{ν_-} is a chloride component consisting of cation M^{z_+} and ν_- moles of Cl^-, and K_{29} is the equilibrium constant for reaction (29). The logarithmic derivative of equation (30) with respect to the progress variable, ξ, appears as

$$\frac{d \ln a_{MCl_{\nu_-}}}{d\xi} = \frac{d \ln a_{M^{z_+}}}{d\xi} + \frac{\nu_- d \ln a_{Cl^-}}{d\xi}. \tag{31}$$

Because both the activity of the chloride ion and the activity coefficients of aqueous species are essentially constant in geochemical processes involving concentrated electrolyte solutions, we can abridge equation (31) for such processes; that is, taking account of equation (26) we can write

$$\frac{d \ln a_{MCl_{\nu_-}}}{d\xi} \approx \frac{d \ln a_{M^{z_+}}}{d\xi} \approx \frac{d \ln m_{M^{z_+}}}{d\xi} = \frac{\bar{n}_{M^{z_+}}}{m_{M^{z_+}}}. \tag{32}$$

For a process in which the initial concentration of M^{z+} is much larger than the change in the concentration of this ion, it follows that

$$\frac{d\mu_{MCl_{\nu_-}}}{d\xi} = \frac{RT \, d \ln a_{MCl_{\nu_-}}}{d\xi} \approx \frac{d \ln a_{Cl^-}}{d\xi} \approx \frac{d \ln a_{M^{z_+}}}{d\xi} \approx 0. \tag{33}$$

The concentration of the hydrogen ion in the aqueous phase is commonly several orders of magnitude smaller than the concentrations of the alkali and alkaline earth chlorides in natural electrolyte solutions, but the activity of the hydrogen ion is rarely constant in geochemical processes. Consequently, the chemical potential of HCl varies with reaction progress. Because the activity of the chloride ion and activity coefficients are essentially constant in most such processes, it follows that

$$\frac{d \ln a_{HCl}}{d\xi} \approx \frac{d \ln a_{H^+}}{d\xi} \approx \frac{\bar{n}_{H^+}}{m_{H^+}} \tag{34}$$

and thus (from eq 6)

$$\frac{d\mu_{HCl}}{d\xi} \approx \frac{RT\, d \ln a_{H^+}}{d\xi} \approx \frac{RT\, \bar{n}_{H^+}}{m_{H^+}}. \tag{35}$$

Equation (34) can also be written as

$$\frac{\bar{n}_{H^+}}{m_{H^+}} \approx \frac{\bar{n}_{HCl}}{m_{HCl}} \tag{36}$$

which is consistent with equation (24) because $\nu_+ = 1$ and $Z_+ = \nu_-$ for chloride components. Note that equation (35) can be integrated to give

$$\mu_{HCl} = \mu^\circ_{HCl} + RT \ln a_{H^+} + \mathfrak{C} \tag{37}$$

where $\mathfrak{C}$ is the constant of integration defined by

$$\mathfrak{C} = RT(\ln a_{Cl^-} - \ln K_{29}). \tag{38}$$

At elevated temperatures, the chloride ion associates to a considerable extent with cations in natural electrolyte solutions. The bulk of the ore-forming metals in hydrothermal solutions are distributed in a variety of chloride complexes, and above 300°C acids, bases, and alkali chlorides are present in solution primarily as neutral molecules corresponding to components in the sets discussed above; for example, HCl, KOH, NaCl, KCl, et cetera (Franck, 1961; Helgeson, 1964, 1969; Marshall, 1968, 1969; Quist and Marshall, 1969). It should be emphasized that the compositional constraints discussed above may still be present in a geochemical process under such conditions as long as the *total* concentration of a given cation exceeds the mole transfer of the corresponding component to or from the aqueous phase.

As indicated in the derivation of equation (11), if the chemical potential of an alkali chloride component is constant in a geochemical process, the chemical potential of the corresponding oxide component is *not* constant; it changes as a function of the activity of the hydrogen ion in the aqueous phase. For processes in which the ionic strength of the solution remains essentially constant this relation is described in general nota-

tion by equation (27), which can be derived for an oxide component by combining equations (11) and (35). The resulting expression can be written as

$$\frac{d\mu_{M_{\nu_+}O_{\nu_-}}}{d\xi} \approx -\frac{RT\,\nu_+Z_+\,d\ln a_{H^+}}{d\xi} \approx -\frac{RT\,\nu_+Z_+\,\bar{n}_{H^+}}{m_{H^+}}$$

$$\approx 2.303RT\,\nu_+Z_+\,\frac{d(pH)}{d\xi}. \qquad (39)$$

If the chemical potentials of two alkali chloride components are constant, the relative change in the chemical potentials of the corresponding oxide components is defined by equations (23) and (28), which can be combined (for two oxide components represented by the subscripts 1 and 2) to give

$$\frac{d\mu_1}{d\mu_2} = \frac{\nu_{+(1)}\,d\ln\left(a_{M(1)}/a_{H^+}^{Z_{+(1)}}\right)}{\nu_{+(2)}\,d\ln\left(a_{M(2)}/a_{H^+}^{Z_{+(2)}}\right)} = \frac{\nu_{+(1)}Z_{+(1)}}{\nu_{+(2)}Z_{+(2)}}. \qquad (40)$$

It can be seen in equation (39) that the change in the chemical potential of the oxide component is proportional to the change in the pH of the aqueous phase, and the *relative* change in the chemical potentials of the two oxide components is constant (eq 40) under the constraint represented by equation (33). Each expression of equation (39) thus refers to a degree of freedom (in the phase rule) corresponding to a constant chemical potential of a chloride component.

The phase rule.—Phase rule interpretation of mineral assemblages has received considerable attention in recent years (for example, Korzhinskii, 1959, 1965; Thompson, 1955, 1959; Zen, 1963), and much discussion has been devoted to open systems with little specific regard for the composition of the aqueous phase (Korzhinskii, 1963). If an aqueous solution is involved in the formation of a mineral assemblage, it is rarely preserved in the rock, and the mineral assemblage seldom contains all of the components that were present in the aqueous phase. Both valid and invalid criticism of Korzhinskii's methods (Weill and Fyfe, 1964, 1967) as well as the ensuing rebuttal (Korzhinskii, 1966, 1967) have tended to confuse and obscure application and interpretation of the phase rule in petrology. This is particularly true with respect to recognition of the ways in which chemical potentials of components become fixed constants in geologic systems, and determination of their identity and the extent to which they control equilibrium phase relations in actual geochemical processes. The chemical potential of a component may be constant throughout a geochemical process, or it may be constant initially and vary at later stages of reaction progress (Korzhinskii, 1959; Zen, 1963; Helgeson, 1968b).

The concept of osmotic equilibrium is commonly used to illustrate the thermodynamic principles of open systems (Thompson, 1955, 1959;

Weill and Fyfe, 1964, 1967; Korzhinskii, 1959, 1966). As emphasized by Korzhinskii (1962, 1964, 1967b, 1968), such models have limited application to geologic systems and are not realistic illustrations of open systems in many geochemical processes. Because these processes commonly involve aqueous alkali-alkaline earth chloride solutions, the chemical potential of one or another chloride component in the system may be constant during the process simply because the initial concentration of the component in the aqueous phase is large relative to the mass transfer of the cation in the component to or from the aqueous phase as it reacts with its environment. The system is then open to such a component; that is, the chemical potential of the component is constant during the process. Taking into account the general compositional characteristics of natural waters, the components NaCl, $CaCl_2$, and to a lesser extent, KCl, and $MgCl_2$ appear to be common members of this category of components.

The chemical potential of CO_2 in a geochemical process may also be constant as a result of a large initial concentration of the component in the aqueous phase. However, this condition not only requires the initial concentration of CO_2 to exceed the change in the concentration of the component, but the pH of the solution must remain low enough so that no other aqueous species involving CO_2 forms to an appreciable degree. In most cases, the chemical potentials of SiO_2, Al_2O_3, O_2, and S_2 appear to be functions of equilibrium states in geochemical processes, but the chemical potentials of HCl, and to a lesser extent H_2SO_4 and H_2S are commonly controlled by the activity of the hydrogen ion in the aqueous phase. The activity of the hydrogen ion (or alternatively, the hydroxyl ion) is the most important single variable (other than temperature and pressure) in many geochemical processes (Korzhinskii, 1964, 1967a, 1968; Helgeson, 1967a, 1968b, 1970c).

Although the chemical potential of H_2O is often regarded as an independent variable in geochemical processes, more often than not it is a dependent variable in systems involving aqueous electrolyte solutions. This is true despite the fact that the concentration of H_2O in such solutions is much larger than either the concentration of the solute or the mass transfer of H_2O to or from the aqueous phase. Although the activity of H_2O in most natural aqueous electrolyte solutions can be regarded as unity without introducing serious error (Helgeson, 1967a, 1969), H_2O should not be regarded as a component with a fixed chemical potential corresponding to a degree of freedom in the phase rule. The activity of H_2O is related to the concentration of dissolved solids in the aqueous phase by the Gibbs-Duhem equation, which can be written for a given temperature and pressure as

$$d\mu_{H_2O} = -\frac{1}{55.5}\sum_{i}^{j} m_i d\mu_i \qquad (41)$$

where i refers to independent actual components other than H_2O in the aqueous phase. Obviously, if the chemical potentials of all components

other than H_2O in the aqueous solution are fixed, the chemical potential of H_2O is also fixed, but the maximum number of degrees of freedom (in addition to temperature and pressure) required to describe equilibrium between the solution and a mineral is equal to f. Because the chemical potential of H_2O in an electrolyte solution depends on the composition and total concentration of the solute, the chemical potential of H_2O is a function of homogeneous equilibrium; as such it is not a candidate for a degree of freedom in the phase rule.

The phase rule is commonly invoked to analyze mineral assemblages to determine the number of degrees of freedom required to account for observed phase relations in terms of equilibrium models. As observed above, constraints in nature represented by degrees of freedom are usually assumed to consist of temperature, pressure, and/or constant chemical potentials of components in the set chosen by the petrologist to describe the system, which is usually a set of oxide components. Because HCl is rarely included as a component, and because the activity of the hydrogen ion is seldom constant in geochemical processes, *at least one less than the maximum number of degrees of freedom is commonly calculated from the phase rule for systems in which an aqueous chloride solution was present at the time the mineral assemblage formed.* It has been demon-

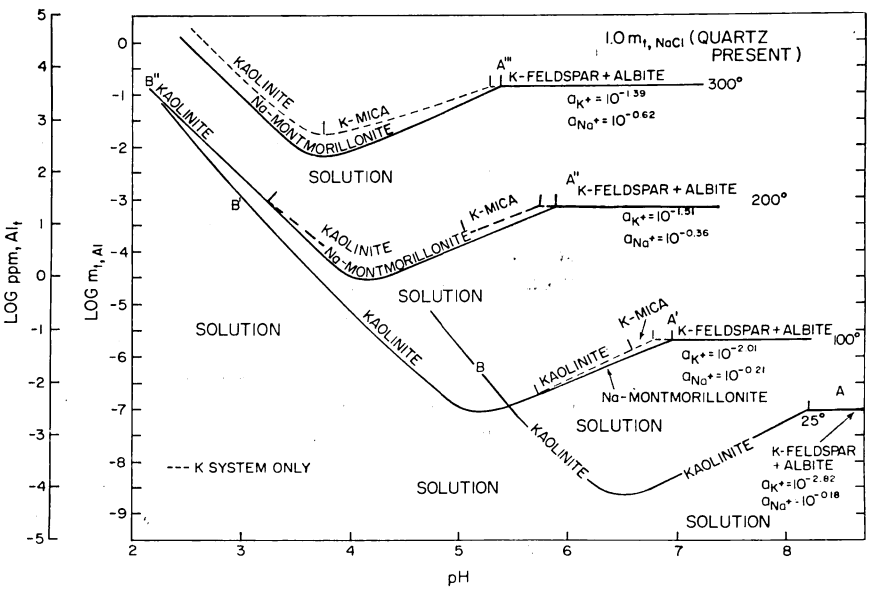

Fig. 1. Computed solubilities of silicates in the system NaCl–KCl–Al_2O_3–SiO_2–H_2O–HCl at 25°, 100°, 200°, and 300°C in the presence of quartz. The aqueous phase is a one molal NaCl solution consistent with curves AB, A′B′, A″B″, and A‴B‴ in figure 2.. The solubilities were computed for unit activity of H_2O and one atmosphere pressure, but they are appropriate for (liquid) hydrothermal solutions up to ~300 atmospheres. The calculations include provision for complexes and activity coefficients in the aqueous phase; the equations and data used in the calculations have been summarized elsewhere Helgeson, 1969).[1]

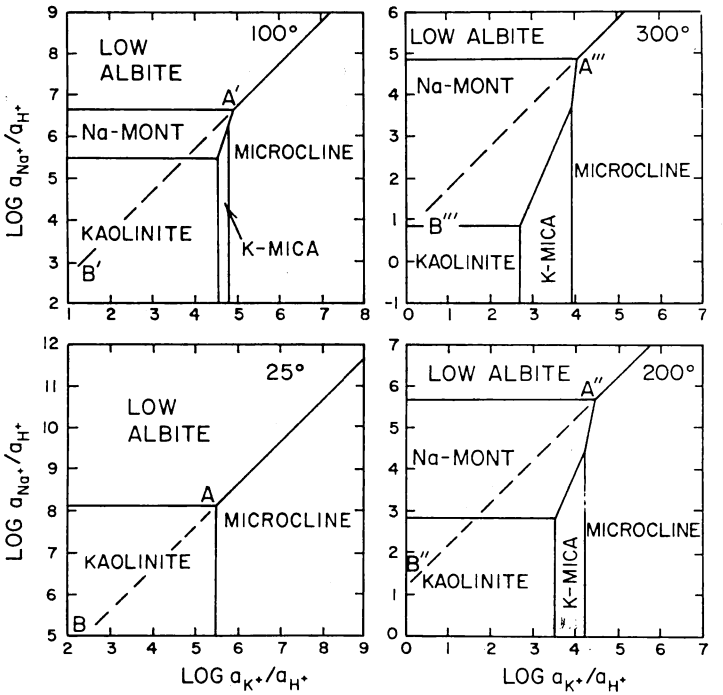

Fig. 2. Computed phase relations in the system NaCl–KCl–Al_2O_3–SiO_2–H_2O–HCl at 25°, 100°, 200°, and 300°C and one atmosphere in the presence of quartz and an aqueous phase with unit activity of H_2O. The thermodynamic data and equations used in the calculations have been summarized elsewhere (Helgeson, 1969).

strated above that two degrees of freedom computed from the phase rule may not represent fixed chemical potentials of two oxide components, but rather their pedendence on the activity of the hydrogen ion, which is consistent with constant chemical potentials of two corresponding chloride components.

The chemical potentials of components such as Na_2O, K_2O, MgO, CaO, FeO, and Fe_2O_3 are constant in geochemical processes involving aqueous solutions (at a given temperature and pressure) only when the aqueous phase is highly acid or highly alkaline. Constant chemical potentials of these components not only require relatively large concentrations of the corresponding ions in the aqueous phase but also an invariant solution pH. The pH of the solution is essentially constant only when the activity of *either* H^+ or OH^- is much larger than the change in these activities, which occurs under natural conditions below ~pH 3 and above ~pH 9.

Because the chloride counterparts of oxide components are seldom considered by petrologists, degrees of freedom calculated from the phase rule are rarely ascribed to constant chemical potentials of chloride components. Nevertheless, as indicated above, it appears that the chemical

potentials of the components NaCl, $CaCl_2$, and less commonly KCl and $MgCl_2$ are constant in many geochemical processes. It perhaps should be emphasized that the chemical potentials of *both* oxide and chloride components involving alkali and alkaline earth cations may be constant in the initial stages of a process involving highly acid or alkaline solutions, but later when the solution pH begins to change (in response to continued reaction of the solution with its environment) the chemical potentials of the oxide components change in proportion to the change in the activity of the hydrogen ion; in contrast, the chemical potentials of the corresponding chloride components continue to be constant as long as the activities of the chloride ion and the alkali and alkaline earth cations in solution remain essentially constant. Note that in hydrothermal solutions the chemical potentials of components such as $ZnCl_2$, CuCl, $PbCl_2$, and AgCl are constant (at a given temperature and pressure) until a solid phase containing one or more of these components begins to precipitate. At that point, if precipitation proceeds as a reversible reaction, the chemical potentials of the metal chloride components involved in the depositional process become functions of equilibrium between the mineral and the aqueous phase.

DISCUSSION

The concentrations of dissolved electrolytes in the aqueous phase involved in geochemical processes determines the identities of minerals produced or destroyed as the solution reacts with its environment (Helgeson, 1967a, 1968, 1970c; Helgeson, Garrels, and Mackenzie, 1969). In most cases the initial chemical potential of HCl in the aqueous solution determines the extent to which other components are redistributed among the phases in the system. The chemical potentials of HCl and oxide components corresponding to chloride components with fixed chemical potentials are controlled by the activity of the hydrogen ion, which changes with reaction progress. As emphasized by Korzhinskii (1967a) hydrogen ion metasomatism is responsible for most isothermal changes caused by geochemical processes, and metasomatic zoning can be viewed as a product of acid-base differentiation. Hydrogen ion may be produced (and hydroxyl ion consumed) by reaction of electrolyte solutions with clay minerals, congruent precipitation of silicates, deposition of iron and copper oxides and sulfides, and adiabatic expansion of high temperature solutions. In contrast, hydrogen ion is consumed by reaction of most natural electrolyte solutions with framework silicates and other rock forming minerals (Helgeson, Garrels, and Mackenzie, 1969; Helgeson, 1967a and b, 1970c).

Chemical reactions responsible for metamorphism almost invariably involve an aqueous electrolyte solution, which may be present only as a surface phase along grain boundaries in the rock. The mass transfer involved in metamorphic reactions takes place by diffusional flux of material through the aqueous phase, which may or may not be moving through the rock (Korzhinskii, 1968). The thermodynamic relations

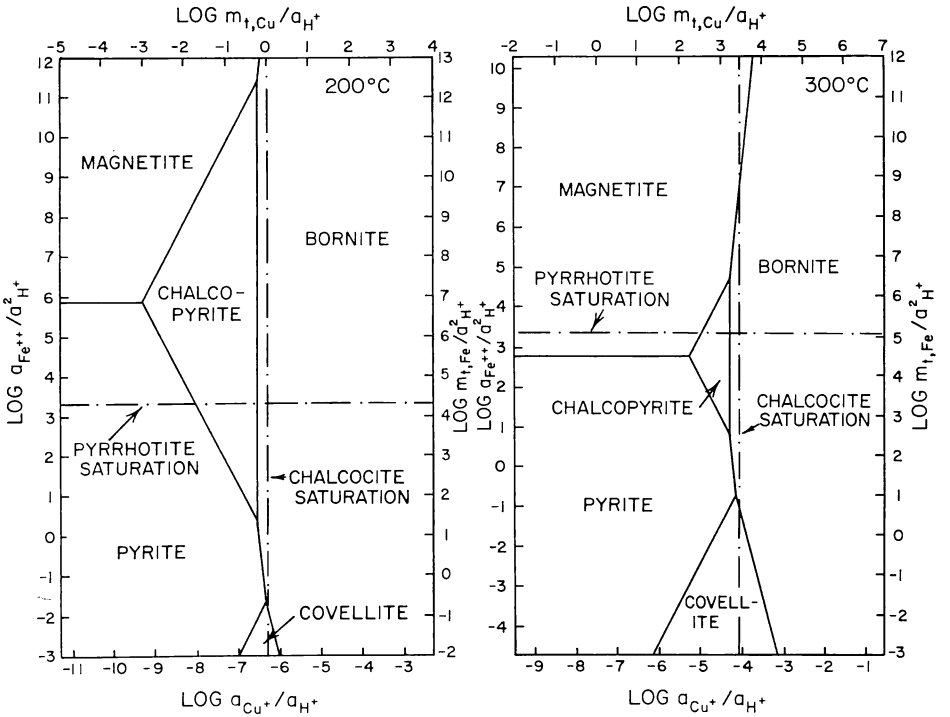

Fig. 3. Predicted phase relations in the system NaCl–$FeCl_2$–CuCl–H_2S–H_2SO_4–HCl–H_2O at 200° and 300°C and one atmosphere with $a_{H_2O} = 1$ and $a_{H_2S} = 10^{-2.5}$. Calculated solubilities of the minerals in a 3.0 molal NaCl solution are represented by the ratios of the total molalities of the metal ions to the activity of the hydrogen ion shown on the top and on the right of each diagram. The thermodynamic data and equations used in the calculations have been summarized elsewhere (Helgeson, 1969).

described above are as applicable to static systems and diffusional mass transfer (Helgeson, 1970b) as they are to those involving bulk transport of the aqueous solution. The chemistry of the process in both cases is one of rock-solution interaction.

Recognition of thermodynamic constraints imposed by the compositional nature of the aqueous phase in a geochemical process permits diagrammatic representation of the mutual solubilities of minerals. For example, computed solubilities of silicates in the system NaCl–KCl–HCl–Al_2O_3–SiO_2–H_2O in the presence of quartz are shown in figure 1, which depicts the total molality of the aluminum ion in solution as a function of solution pH. The solubilities shown in figure 1 are those in a one molal NaCl solution corresponding to that represented by curves AB, A′B′, A″B″, and A‴B‴ in figure 2. At a given temperature, the chemical potentials of the components NaCl and KCl are constant along these curves, and the chemical potential of SiO_2 is fixed by the presence of quartz. These constraints, together with the stipulation that pressure

and the activities of Cl^- and H_2O are constant at each temperature permits phase relations in the system to be depicted solely in terms of temperature and the chemical potential of Al_2O_3, which can be represented by log $a_{Al^{+++}}/a_{H^+}{}^3$ in the aqueous phase (eq 21). Taking into account complexing in the solution and activity coefficients for aqueous species (Helgeson, 1969), $a_{Al^{+++}}$ can be recast in terms of the total molality of aluminum in solution, which can then be employed together with pH to describe phase relations in the system (fig. 1). The resulting diagram represents an approximation of the actual chemical environ-

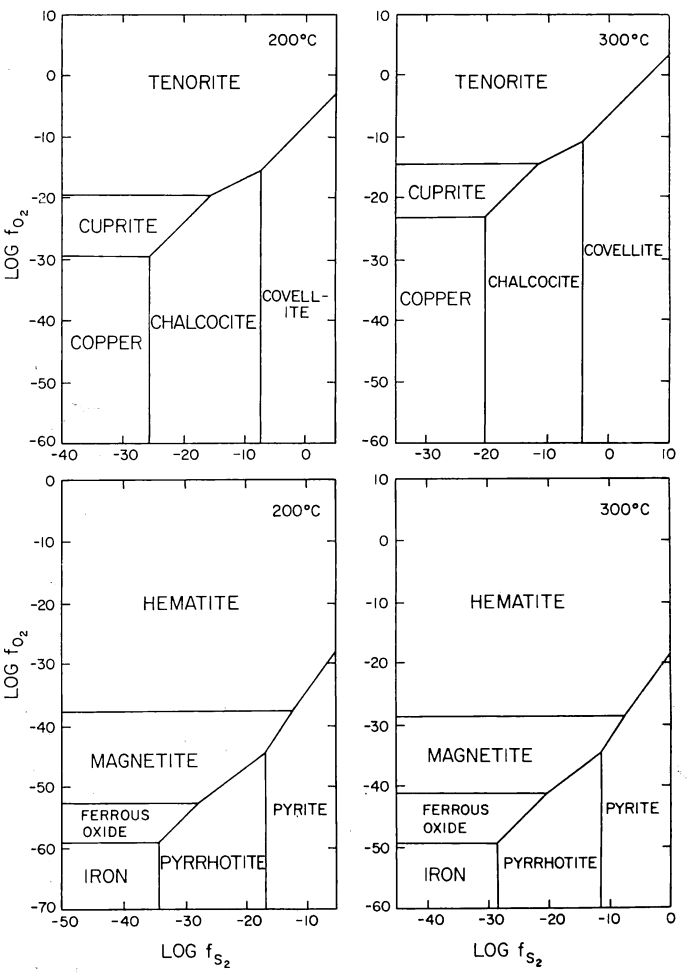

Fig. 4. Fugacity diagrams depicting phase relations at 200° and 300°C in the systems Cu–S–O and Fe–S–O. The thermodynamic data used in the calculations were taken from Helgeson (1969).

ment in an hydrothermal vein system involving a concentrated alkali chloride solution.[1]

Hydrothermal sulfide systems can be represented diagrammatically in a similar fashion to that described above for silicate systems. An example is shown in figure 3, which depicts phase relations in the system $NaCl–FeCl_2–CuCl–H_2S–H_2SO_4–HCl–H_2O$ at two temperatures in terms of the activities and total molalities of species in the aqueous phase. The chemical potentials of NaCl, H_2S, and H_2O are constants for each diagram, and the chemical potential of H_2SO_4 is a function of the equilibrium states corresponding to the stability field boundaries. The solubilities represented by the ratios of the total molalities of the metal ions to the activity of the hydrogen ion shown at the top and on the right side of each diagram are for a 3.0 molal NaCl solution; they were computed from the activity ratios using equilibrium constants and activity coefficients presented elsewhere (Helgeson, 1969). The metal ions in the aqueous phase are predominantly present as chloride complexes; the degrees of formation of these species are essentially independent of solution pH (Helgeson, 1969).

The diagrams shown in figure 3 represent approximations of the actual chemical environment in an hydrothermal system in terms of the composition of the aqueous phase. They can be correlated and integrated with diagrams depicting silicate equilibria such as those in figures 1 and 2 (Helgeson, 1970c). In practice such diagrams (particularly those cast in terms of activity ratios involving cations common to sulfides and silicates like $a_{Fe^{++}}/a_{H^+}{}^2$) are far more useful in the study of geologic problems than are corresponding fugacity diagrams such as those shown in figure 4.

CONCLUDING REMARKS

The history of a natural aqueous electrolyte solution largely dictates the subsequent chemical behavior of the solution as it travels through the Earth's crust (Helgeson and Mackenzie, 1970). Once its gross compositional characteristics have been achieved, later chemical interaction of the solution with its environment is largely controlled by constant chemical potentials of the components present in relatively large concentrations in solution. Explicit provision for the compositional characteristics of these solutions in thermodynamic calculations enables prediction of their chemical behavior in terms of relatively few variables, even though the systems involve many components. Owing to the sophisti-

[1] The computed solubilities of silicates shown in figure 1 for 300°C are considerably higher than those reported by Fyfe and McKay (1961) at 330°C. However, the experimental determinations were done by weight loss measurements of single crystals, which is ambiguous with respect to reaction products that may have formed on the surface of the reactant mineral. Also, evidence of equilibrium in the experiments is lacking. On the other hand, the theoretical solubilities shown in figure 1 are based on extrapolated values of dissociation constants of aluminum hydroxide complexes, which may be in error. The diagram is presented here primarily to illustrate the advantages of the theoretical approach discussed above rather than the verities of the phase relations in the system.

cation of modern computers, both reversible and irreversible reactions in n-dimensional multicomponent systems can be evaluated simultaneously and quantiatively. Hydrothermal ore deposition is but one of the many geochemical processes that can be approached in this way (Helgeson, 1964, 1967a and b, 1970c; Helgeson and Garrels, 1968; Helgeson, Garrels and Mackenzie, 1969; Helgeson and Mackenzie, 1970; Helgeson and others, 1970). Many of the requisite thermodynamic data are now available (Criss and Cobble, 1964; Wagman and others, 1968, 1969; Robie and Waldbaum, 1968; Helgeson, 1967c, 1969), and modern computers make it possible to model geologic reality with considerable confidence (Helgeson, 1968b; Helgeson, Brown, and Leeper, 1970).

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