

A method for computing multicomponent chemical equilibria based on equilibrium constants

DAVID A. CRERAR

Department of Geological and Geophysical Sciences, Princeton University,
Princeton, N.J. 08540, U.S.A.

(Received 21 November 1974; accepted in revised form 10 March 1975)

Abstract—The equilibrium activities and concentrations of N chemical species in a multicomponent system may be calculated given M independent equilibrium constants relating these species and $N-M$ mass balances. These N equations are solved by Newton-Raphson iteration. Where initial concentration estimates are poor or the number of species large, an additional curve crawler technique introduces components by stepwise infinitesimal increments.

INTRODUCTION

MANY AVAILABLE techniques for the computation of chemical equilibria in complex systems have been reviewed by VAN ZEGGEREN and STOREY (1970), who recognized two main methods: (1) the solution of a generalized set of simultaneous non-linear equations which usually incorporate equilibrium constants (e.g. FELDMAN *et al.*, 1969), and (2) optimization techniques, which normally minimize the total Gibbs free energy function (e.g. REESE, 1973; KARPOV and KAZ'MIN, 1972). Such techniques are typically generalized and apply to arbitrary systems for which suitable thermodynamic data are available.

Two additional methods often used within the geosciences, could be added to this list. Method (3), developed by HELGESON (1968, 1970), determines compositional changes, mass transfers, and the order of appearance of stable and metastable phases in tracing irreversible reaction paths from an initial set of non-equilibrium conditions to a final state of equilibrium.

The fourth method entails specific, as opposed to generalized, calculations. Here, a set of equations describing a given system is reduced to one or more equations amenable to simple numerical solution. Typical procedures are described by BUTLER (1964), BLACKBURN (1969), and FREISER and FERNANDO (1966). Various geochemical examples are given by HELGESON (1964, p. 56), who calculates galena solubility in the system NaCl-HCl-H₂O, and by CRERAR and ANDERSON (1971), who calculate quartz solubility in the systems H₂O-NaOH and H₂O-NaOH-NaHS. On a larger scale, TRUESDELL and JONES (1974) have now developed the program WATEQ, which computes the equilibrium distribution of inorganic species

in natural waters, given total element concentrations, pH, and Eh.

This paper introduces a method of the first type for computing generalized chemical equilibria. Equilibrium concentrations or activities are derived from simple mass and charge balances and arbitrary independent equilibrium constants. Non-ideality corrections may be included in the computation. The resultant non-linear equations are solved by combining Newton-Raphson iteration and supportive curve crawler techniques. Because it uses arbitrary equilibrium constants, the method can be particularly appropriate to geochemical systems lacking complete free energy data.

GLOSSARY OF SYMBOLS

a_{ij}	number of atoms of the i th element in 1 molecule of the j th component.
b_{ei}	number of atoms of element e in 1 molecule of species i .
B_e	total molal concentration of the e th element in the system.
C	total number of independent chemical components in the system.
C_{ah}^i	molarity of the i th species corrected for association and hydration.
f_e^i	mole-fractional specific ion activity coefficient correcting for electrostatic interaction.
$\Delta G_{f,i}^0$	Gibbs free energy of formation of the i th species.
h_i	average moles of solvent hydrating 1 mole of solute species i .
I	true ionic strength.
K_i	i th equilibrium constant.
m_i	molal concentration of the i th species.
m_a^i	molality of the i th species corrected for association.

m_{ah}^i	molality of the i th species corrected for association and hydration.
M	total number of independent equilibrium constants.
n	total number of moles of all components in the system.
N	total number of chemical species in the system.
q_j	total number of moles of the j th component in the system.
Q_l	total number of moles of the l th element in the system.
R	total number of components in the system.
S	total number of constituent species formed from 2 or more components.
x_j	mole-fraction of the j th component in the system.
X_j	j th component species.
y_i	mole-fraction of the i th constituent in the system.
Y_i	i th constituent species formed from 2 or more components.
Z_i	signed valence of the i th species.
γ_i	true molal activity coefficient of the i th species.
γ_e^i	molal activity coefficient of the i th species correcting for electrostatic interaction.
γ_h^i	molal activity coefficient of the i th species correcting for hydration.
γ_{eh}^i	molal activity coefficient of the i th species correcting for electrostatic interaction and hydration.
v_{ij}	number of moles of the j th component in 1 mole of the i th constituent species.
v_{ki}	signed stoichiometric coefficient representing the number of formulae of the i th species written in the k th reaction; sign is negative for reactants and positive for products.
ρ	solution density (g/ml).
ψ_i	i th mass balance, charge balance, or equilibrium constant equation.

STATEMENT OF THE PROBLEM

Most simpler geochemical applications are satisfied by the fourth, or specific, type of equilibrium calculation cited above. In other words, a system-defining set of specific charge and mass balances and mass action expressions is solved by algebraic manipulation. However, as the number of components or species increases, the defining equations more frequently reduce to difficult non-linear expressions. With the simpler systems, the alternative generalized routines can be time-saving; for more complex problems, they may often provide the only practical solution.

As a case in point, generalized routines have now been applied to geochemical systems so complex that they could not be solved by simple algebraic manipulation. For example, HOLLOWAY and REESE (1974) have used free-energy minimization programs to solve for the equilibrium fugacities of over 40 species in

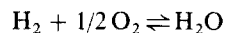
the system C—O—H—N at elevated temperatures. Similarly, KARPOV and KAZ'MIN (1972) have determined the equilibrium activities of 21 species in seawater using an alternative minimization algorithm. Where Gibbs free energies of all chemical species are available, optimization methods are convenient and reliable.

Unfortunately, free-energy data are often frustratingly incomplete for systems of practical interest. This is particularly true, for example, with the high temperature mineral-water systems crucial to the current demand for alternative geothermal power (BARNES, *in press*). Note, however, that equilibrium constants may be available for such systems even when free-energy data are not—see, for example, SILLÉN and MARTELL (1964), BARNES *et al.* (1966), HELGESON (1969), and TRUESDELL and JONES (1974). Although any equilibrium constants can be calculated given formation free-energies of all reacting species, the converse is not necessarily true. Accordingly, there is a growing demand for computational methods based exclusively on equilibrium constants, which represent a minimal set of free-energy information.

Using one such method, FELDMAN *et al.* (1969) have now computed equilibrium compositions of high temperature coal combustion mixtures containing up to 65 species including gases, liquids, free electrons, and ions. Their basic method was originally described by BRINKLEY (1947) and KANDINER and BRINKLEY (1950) (see also VAN ZEGGEREN and STOREY, 1970, Chap. 4). Typically, all N chemical species of a given system are divided into R components, and S constituents, defined by the following set of formation reactions:

$$\sum_{j=1}^R v_{ij} X_j \rightleftharpoons Y_i \quad (i = 1, \dots, S), \quad (1)$$

where each v_{ij} is a stoichiometric coefficient representing formation of the i th constituent, Y_i , from the j th component, X_j . For example, choosing H_2O as a constituent formed from the components H_2 and O_2 , then reaction (1) would be written:



and the stoichiometric coefficients v_{H_2} and v_{O_2} would be 1 and 1/2, respectively. Reactions (1) can be described by S mass action expressions:

$$y_i = K_i \prod_{j=1}^R x_j^{v_{ij}} \quad (i = 1, \dots, S), \quad (2)$$

where y_i and x_j represent mole-fractional compositions of constituents Y_i and components X_j , respectively, and each K_i is a conventional equilibrium constant.

Assume now that the total number of moles, Q_l , of each element in the system is known, and that the number of components equals the number of elements ($l = 1, \dots, R$). Then mass balances on each component give

$$Q_l = \sum_{j=1}^R a_{lj} q_j \quad (l = 1, \dots, R), \quad (3)$$

where q_j is the total moles of j th component in the system, and each a_{lj} represents the stoichiometry, or number of atoms of element l in component j . Thus, with the component CO_2 , a_{lj} is 1 for the element carbon, 2 for oxygen, and 0 for any other element.

Constituent mass balances now may be expressed in terms of the concentrations of each pure component, and of those components tied up in each constituent species of the system:

$$q_j = x_j n + \sum_{i=1}^S v_{ij} y_i n \quad (j = 1, \dots, R), \quad (4)$$

where n represents the total moles of all components in the system

$$\left(n = \sum_{j=1}^R q_j \right).$$

Finally, the mole fraction identity condition may be expressed by the single equation

$$1 = \sum_{j=1}^R x_j + \sum_{i=1}^S y_i. \quad (5)$$

The above equations (1)–(5) may be solved for the equilibrium concentrations x_j and y_i by numerical methods such as the following: (i) estimate an initial or k th set of all R component concentrations $x_j^{(k)}$. (ii) Using these $x_j^{(k)}$ and equations (2), calculate the corresponding S constituent concentrations $y_i^{(k)}$. (iii) With these $y_i^{(k)}$ estimates, solve the R mass balance equations (4) [possibly substituting expression (5) for one of these] for new estimates, $x_j^{(k+1)}$, of all R component compositions. The q_j term in equations (4) is given by expression (3), and is constant throughout. (iv) Return to step (1) and repeat to convergence, each time setting $x_j^{(k+1)} = x_j^{(k)}$.

The revised Brinkley method used by FELDMAN *et al.* (1969) includes terms for multiple phases. While omitted here for clarity, the mass balances (4) then become non-linear in x_j , y_i , and $n^{(\phi)}$, where $n^{(\phi)}$ is the total moles of all components in the ϕ th phase. The mass balances must then be solved by Newton–Raphson iteration, rather than by simple matrix algebra.

The Brinkley method has proven effective in handling multicomponent, multiphase problems of considerable complexity. However, the use of mass action

expressions (1) and (2) requires that equilibrium constants be known for the formation of all S constituents from all R components. These specific constants may not be available unless free energies are known for all N species. For example, the equilibrium constants K_i would usually be obtained from the relationship

$$\ln K_i = \frac{1}{RT} \left[-\Delta G_{f,i}^0 + \sum_{j=1}^R v_{ij} \Delta G_{f,j}^0 \right], \quad (6)$$

where $\Delta G_{f,i}^0$ and $\Delta G_{f,j}^0$ are the standard Gibbs free energies of formation from the elements of the i th constituent and j th component, respectively. Because the method typically requires prior knowledge of formation free-energies for all $R + S = N$ species within the system, free energy minimization techniques apply equally well in such cases; thus, the goal of a generalized method using arbitrary equilibrium constants is no closer at hand. Therefore, in order to permit the use of arbitrary equilibrium constants relating any two or more species of the system, the method outlined below does not distinguish so-called component species from constituents.

COMPUTING ROUTINE

Consider an arbitrary system of C components containing N chemical species. Assume that equilibrium constants are known for M independent reactions relating some or all of these species.

If the system is ionic, a charge balance may be written:

$$\Psi_1 = 0 = \sum_{i=1}^N Z_i m_i, \quad (7)$$

for which

$$\frac{\partial \Psi_1}{\partial m_i} = Z_i \quad (i = 1, \dots, N). \quad (8)$$

Z_i is the signed valence of the i th species, and m_i is its concentration (here arbitrarily considered as molality).

Assume next that the total molal concentrations B_e of $N-M-1$ elements or atomic species are specified for the system. Simple mass balances on these elements give,

$$\Psi_j = 0 = -B_e + \sum_{i=1}^N b_{ei} m_i \quad (j = 2, 3, \dots, N-M, \text{ as } e = j - 1) \quad (9)$$

and

$$\frac{\partial \Psi_j}{\partial m_i} = b_{ei} \quad \begin{matrix} (i = 1, \dots, N) \\ (j = 2, 3, \dots, N-M). \end{matrix} \quad (10)$$

Here B_e is the total molal concentration of the e th element in the system, and b_{ei} describes the elemental composition of the i th species according to the formula vector $\beta_i = [b_{i1}, \dots, b_{ie}, \dots, b_{i,N-M-1}]^T$. For example, if the elements H, C, O, and N are assigned the row positions 1, 2, 3,

and 4 in β_i , respectively, then the formula vector for the species H_2CO_3 is $[2\ 1\ 3\ 0]^T$. If the total number of elements in the system is E , then the scalar quantities b_{ei} define an $E \times N$ system composition matrix of rank C (see VAN ZEGGEREN and STOREY, 1970, p. 16).

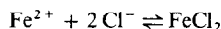
Finally, the M mass action expressions may be written in the form:

$$\psi_k = 0 = \frac{-K_k}{N} + \prod_{i=1}^N m_i^{v_{ki}} \quad (k = N - M + 1, \dots, N) \quad (11)$$

and

$$\begin{aligned} \frac{\partial \psi_k}{\partial m_i} &= v_{ki} m_i^{v_{ki}-1} \prod_{i \neq l}^N m_i^{v_{li}} \quad (l = 1, \dots, N) \\ &= v_{ki} m_i^{-1} \prod_{i=1}^N m_i^{v_{ki}} \quad (k = N - M + 1, \dots, N). \end{aligned} \quad (12)$$

Here, K_k is the k th equilibrium constant. Each v_{ki} is a signed stoichiometric coefficient representing the number of formulae of the i th species involved in the k th reaction; it is negative for reactants, and positive for products. Thus, for the reaction



v_{ki} is -1 , -2 , and 1 for the species Fe^{2+} , Cl^- , and FeCl_2 , respectively, and is 0 for any other species. γ_i is an activity coefficient correcting the i th species concentration for non-ideality.

Equations (7), (9), and (11) constitute a system of N non-linear equations in N unknowns (m_i , or $\gamma_i m_i$). Note that the charge balance (7) does not apply to nonionic systems where the number of mass balance or mass action expressions must be increased by one. The above system of equations may be solved by combining the Newton-Raphson method with so-called curve crawler techniques.

For a complete description of the Newton-Raphson method, the reader is referred to CARNAHAN and WILKES (1973, p. 368), ACTON (1970, p. 367) or HILDEBRAND (1956, p. 447). First, equations (7), (9), and (11) are approximated by the linear system:

$$\begin{bmatrix} Z_1 & \dots & Z_N \\ b_{1,1} & \dots & b_{1,N} \\ \vdots & \ddots & \vdots \\ b_{N-M+1,1} & \dots & b_{N-M+1,N} \\ v_{11} m_1^{-1} \prod_{i=1}^N m_i^{v_{1i}} & \dots & v_{1N} m_N^{-1} \prod_{i=1}^N m_i^{v_{1i}} \\ \vdots & \ddots & \vdots \\ v_{M1} m_1^{-1} \prod_{i=1}^N m_i^{v_{M1}} & \dots & v_{MN} m_N^{-1} \prod_{i=1}^N m_i^{v_{Mi}} \end{bmatrix} \begin{bmatrix} \delta m_1 \\ \delta m_2 \\ \vdots \\ \delta m_{N-M} \\ \delta m_{N-M+1} \\ \vdots \\ \delta m_N \end{bmatrix} = \begin{bmatrix} -\psi_1 \\ -\psi_2 \\ \vdots \\ -\psi_{N-M} \\ -\psi_{N-M+1} \\ \vdots \\ -\psi_N \end{bmatrix} \quad (13)$$

Equation (13) can be expressed more succinctly by,

$$\bar{\Psi}_m \bar{\Delta} = -\bar{\Psi}, \quad (14)$$

where $\bar{\Psi}_m$ is the Jacobian coefficient matrix given by equa-

tions (8), (10), and (12):

$$\bar{\Psi}_m = \frac{\partial(\Psi_1, \dots, \Psi_N)}{\partial(m_1, \dots, m_N)}.$$

$\bar{\Psi}$ is the right-hand side vector in (13),

$$\bar{\Psi} = [\Psi_1, \dots, \Psi_N]^T$$

and $\bar{\Delta}$ is the solution vector,

$$\bar{\Delta} = [\delta m_1, \dots, \delta m_N]^T.$$

Note that all Ψ_i scalars are concentration-dependent; thus, if $\bar{m} = [m_1, \dots, m_N]^T$, then $\bar{\Psi} = \bar{\Psi}(\bar{m})$ and $\bar{\Psi}_m = \bar{\Psi}_m(\bar{m})$.

In practice, the linear system of equations (13) is solved for the vector $\bar{\Delta}$ using an initial, or k th, estimate of the concentrations $m_i^{(k)}$. At this stage, activity coefficients, γ_i , are set equal to unity. An improved estimate of the concentrations is given by

$$\bar{m}^{(k+1)} = \bar{m}^{(k)} + \bar{\Delta}$$

or

$$m_i^{(k+1)} = m_i^{(k)} + \delta m_i \quad (i = 1, \dots, N). \quad (15)$$

With $\bar{m}^{(k+1)}$ as a new initial guess, the process is repeated to satisfactory convergence in all m_i .

Note that system (13) will not possess a unique solution when the Jacobian determinant

$$J \equiv \left| \frac{\partial(\Psi_1[m_i^{(k)}], \dots, \Psi_N[m_i^{(k)}])}{\partial(m_1, \dots, m_N)} \right|$$

of the coefficient matrix $\bar{\Psi}_m$ approaches zero. For this reason, it is advisable to write all mass action expressions (11) with the least concentrated species as reactants. Because $v_{ki} < 0$ for reactants, the partials (12) are thereby maximized (see the following example). A test on the magnitude of J is recommended at each iteration.

As a rule of thumb, when initial guesses are accurate to a rough order of magnitude, successful convergence may usually be expected for $N < 10$. For systems containing 10 or more species, the following

curve crawler technique is recommended (see ACTON, 1970, pp. 379-386):

(i) Choose a subset of the total chemical system con-

taining fewer than C components and fewer than 10 chemical species. Solve for the equilibrium concentrations of these species using the Newton–Raphson method.

(ii) Consider an increment of one omitted component so small that concentrations of the above species are not significantly changed. Compute the concentrations of any new species appearing with this increment of new component.

(iii) With these new concentrations as initial guesses, solve the expanded system by the Newton–Raphson method.

(iv) Repeat step (iii), each time adding an increment of the new component, up to the desired concentration of this component.

(v) Repeat steps (ii)–(iv), each time adding a new component, until all C components are present at their specified concentrations.

Up to this point in the calculation, all activity coefficients have been set equal to unity. If required, these may now be computed from empirical or *a priori* functions relating each γ_i to species concentrations:

$$\gamma_i = f(m_1, \dots, m_N) \quad (i = 1, \dots, N). \quad (16)$$

Various approaches to this problem have been considered, for example, by THOMPSON (1967), HELGESON (1969), HELGESON and JAMES (1968), TRUESDELL and JONES (1969), and CRERAR and BARNES (in preparation). Important uncertainties currently inherent in the *a priori* estimation of single ion activity coefficients are discussed in the latter two papers.

For the present purposes, functions (16) predict initial $\gamma_i^{(k)}$ estimates, given a first set of concentrations $m_i^{(k)}$. System (13) is then solved by Newton–Raphson iteration [using these initial $\gamma_i^{(k)}$, $m_i^{(k)}$ values] for an improved set of concentrations $m_i^{(k+1)}$. Functions (16) then predict corresponding $\gamma_i^{(k+1)}$, and the process is repeated to satisfactory convergence in all γ_i , m_i . In practice, the change in various γ_i from one iteration to the next may be so large that the process diverges. In such cases, successive γ_i are changed by some small fraction δ , of this step by step difference:

$$\gamma_i^{(k)} = \gamma_i^{(k-1)} + \{f_i[m_1^{(k)}, \dots, m_N^{(k)}] - \gamma_i^{(k-1)}\} \delta, \quad (17)$$

where f_i is the function (16).

While molal units have been used in the above discussion, the method applies equally well to other concentration scales. Note that when mole-fractional units are used, the identity condition (5) may be substituted for any of the charge and mass balances, or mass action expressions (7), (9), and (11).

While the Newton–Raphson method with supportive curve crawlers has been applied exclusively in the foregoing, it should be mentioned that the original

equations (7), (9), and (11) may also be solved by standard false position, secant, and interval halving procedures (e.g. CARNAHAN and WILKES, 1973, Chap. 5; ACTON, 1970, Chap. 2, 14). Additional numerical methods specific to the Brinkley approach are cited in VAN ZEGGEREN and STOREY (1970, Chap. 4). The simple method of successive substitution is not recommended here for general use because of its overly restrictive convergence criteria (CARNAHAN and WILKES, 1973, p. 368).

Of all applicable root-solvers, the Newton–Raphson approach offers fastest (quadratic) convergence. The false position, interval halving, and secant methods can be somewhat unwieldy for the present purposes, and converge at a slower (first order) rate. All four procedures require initial estimates, and all four can hang up on undesired multiple roots. In addition, the false position and interval halving procedures require a second set of input points straddling the desired root.

Because the Newton–Raphson method projects derivatives in its search for roots, there is always a danger that it might be led astray along functional slopes and extrema; under such circumstances, it will typically diverge or oscillate indefinitely. For this reason, initial estimates can be crucial with this method, and should always lie as close as possible to the true roots. Fortunately, the simple Newton–Raphson procedure can be enhanced considerably by the addition of so-called fine tuners or curve crawlers of the type introduced above. These have the general effect of improving initial estimates to any desired degree of precision.

Should the Newton–Raphson method fail to converge, even with the addition of supportive curve crawlers, several options remain. As a first approach, initial estimates can be adjusted and the method tried again. Alternatively, the curve crawler step interval may be decreased. Should the method still fail, then a less sensitive algorithm such as interval halving or false position can be invoked. Under some circumstances, the modified, more rapidly converging Newton's methods derived by BROWN (1969) or BOGGS (1971) may improve both computation time and the prospects of convergence. Brown's method is now available in FORTRAN IV through the IMSL Library, Houston, Texas.

NUMERICAL EXAMPLE

As an example, consider a problem requiring equilibrium activities or concentrations of all significant species in the system 0.25 m NH_4Cl –0.25 m NaCl –0.25 m KCl –0.25 m NaHSO_4 – H_2O at 300°C and at vapor saturated pressure. The aqueous species NH_4^+ , NH_4OH , H^+ , HCl ,

NH_4Cl , Cl^- , Na^+ , NaCl , K^+ , KCl , HSO_4^- , KSO_4^- , NaSO_4^- , NH_4SO_4^- , KHSO_4^- , NaHSO_4^- , and $\text{NH}_4\text{HSO}_4^-$ are considered. Relative activities of the species H_2SO_4 , SO_4^{2-} , OH^- , NaOH , and KOH are assumed to be negligible.

The complete system is described by the following equations, analogous to (7), (9), and (11) above:

$$\begin{aligned} &[\text{NH}_4^+] + [\text{H}^+] + [\text{Na}^+] + [\text{K}^+] = [\text{Cl}^-] \\ &+ [\text{HSO}_4^-] + [\text{KSO}_4^-] + [\text{NaSO}_4^-] \\ &+ [\text{NH}_4\text{SO}_4^-] \end{aligned} \quad (18)$$

$$\begin{aligned} \sum \text{NH}_3 = 0.25 = &[\text{NH}_4^+] + [\text{NH}_4\text{OH}] + [\text{NH}_4\text{Cl}] \\ &+ [\text{NH}_4\text{SO}_4^-] + [\text{NH}_4\text{HSO}_4^-] \end{aligned} \quad (19)$$

$$\begin{aligned} \sum \text{Cl} = 0.75 = &[\text{HCl}] + [\text{NH}_4\text{Cl}] + [\text{Cl}^-] \\ &+ [\text{NaCl}] + [\text{KCl}] \end{aligned} \quad (20)$$

$$\begin{aligned} \sum \text{Na} = 0.50 = &[\text{Na}^+] + [\text{NaCl}] + [\text{NaSO}_4^-] \\ &+ [\text{NaHSO}_4^-] \end{aligned} \quad (21)$$

$$\begin{aligned} \sum \text{K} = 0.25 = &[\text{K}^+] + [\text{KCl}] + [\text{KSO}_4^-] + [\text{KHSO}_4^-] \end{aligned} \quad (22)$$

$$\begin{aligned} \sum \text{S} = 0.25 = &[\text{HSO}_4^-] + [\text{KSO}_4^-] + [\text{NaSO}_4^-] \\ &+ [\text{NH}_4\text{SO}_4^-] + [\text{KHSO}_4^-] + [\text{NaHSO}_4^-] \\ &+ [\text{NH}_4\text{HSO}_4^-] \end{aligned} \quad (23)$$

$$\frac{K_{\text{NH}_4\text{OH}}}{K_{\text{H}_2\text{O}}} = \frac{(\text{NH}_4^+)}{(\text{NH}_4\text{OH})(\text{H}^+)} = 10^{4.57} \quad (24)$$

$$K_{\text{NH}_4\text{Cl}} = \frac{(\text{NH}_4^+)(\text{Cl}^-)}{(\text{NH}_4\text{Cl})} = 10^{-0.82} \quad (25)$$

$$K_{\text{NaCl}} = \frac{(\text{Na}^+)(\text{Cl}^-)}{(\text{NaCl})} = 10^{-0.82} \quad (26)$$

$$K_{\text{HCl}}^{-1} = \frac{(\text{HCl})}{(\text{H}^+)(\text{Cl}^-)} = 10^{1.24} \quad (27)$$

$$K_{\text{KCl}} = \frac{(\text{K}^+)(\text{Cl}^-)}{(\text{KCl})} = 10^{-0.6} \quad (28)$$

$$\frac{K_{\text{KSO}_4^-}}{K_{\text{HSO}_4^-}} = \frac{(\text{K}^+)(\text{HSO}_4^-)}{(\text{KSO}_4^-)(\text{H}^+)} = 10^{4.06} \quad (29)$$

$$\frac{K_{\text{NaSO}_4^-}}{K_{\text{HSO}_4^-}} = \frac{(\text{Na}^+)(\text{HSO}_4^-)}{(\text{NaSO}_4^-)(\text{H}^+)} = 10^{4.06} \quad (30)$$

$$\frac{K_{\text{NH}_4\text{SO}_4^-}}{K_{\text{HSO}_4^-}} = \frac{(\text{NH}_4^+)(\text{HSO}_4^-)}{(\text{NH}_4\text{SO}_4^-)(\text{H}^+)} = 10^{4.06} \quad (31)$$

$$K_{\text{KHSO}_4^-} = \frac{(\text{K}^+)(\text{HSO}_4^-)}{(\text{KHSO}_4^-)} = 10^{-0.3} \quad (32)$$

$$K_{\text{NaHSO}_4^-} = \frac{(\text{Na}^+)(\text{HSO}_4^-)}{(\text{NaHSO}_4^-)} = 10^{-0.3} \quad (33)$$

$$K_{\text{NH}_4\text{HSO}_4^-} = \frac{(\text{NH}_4^+)(\text{HSO}_4^-)}{(\text{NH}_4\text{HSO}_4^-)} = 10^{-0.3} \quad (34)$$

In equations (18)–(34), square brackets denote molal concentrations (m_i) and parentheses denote activities ($\gamma_i m_i$). Note that all mass action equations (24)–(34) are written with smallest expected activities in the denominator, as previously discussed.

Table 1 lists appropriate values of the constants Z_i , b_{ei} , B_e , v_{ki} , and K_k used in matrix equations (13). In this table, the rows labeled ψ_1 – ψ_{17} represent equations (18)–(34), arranged in the same order as in the text. Numerical values of the equilibrium constants $K_{\text{H}_2\text{O}}$, $K_{\text{NH}_4\text{OH}}$, and $K_{\text{KSO}_4^-}$ were obtained from SWEETON *et al.* (1974). FISHER and BARNES (1972), and OHMOTO (1972), respectively; K_{NaCl} , K_{HCl} , K_{KCl} , $K_{\text{HSO}_4^-}$, and $K_{\text{KHSO}_4^-}$ were taken from HELGESON (1969). For present purposes, $K_{\text{NH}_4\text{Cl}}$ was approximated by

Table 1. Data for the system 0.25 m NH_4Cl –0.25 m NaCl –0.25 m KCl –0.25 m NaHSO_4 – H_2O at 300°C

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
		NH_4^+	NH_4OH	H^+	HCl	NH_4Cl	Cl^-	Na^+	NaCl	K^+	KCl	HSO_4^-	KSO_4^-	NaSO_4^-	NH_4SO_4^-	KHSO_4^-	NaHSO_4^-	$\text{NH}_4\text{HSO}_4^-$
ψ_1	Z_1	1	0	1	0	0	-1	1	0	1	0	-1	-1	-1	-1	0	0	0
ψ_2	$b_{\text{NH}_3,1}$	1	1	0	0	1	0	0	0	0	0	0	0	0	1	0	0	1 $B_{\text{NH}_3} = 0.25$
ψ_3	$b_{\text{Cl},1}$	0	0	0	1	1	1	0	1	0	1	0	0	0	0	0	0	0 $B_{\text{Cl}} = 0.75$
ψ_4	$b_{\text{Na},1}$	0	0	0	0	0	0	1	1	0	0	0	0	1	0	0	1	0 $B_{\text{Na}} = 0.50$
ψ_5	$b_{\text{K},1}$	0	0	0	0	0	0	0	0	1	1	0	1	0	0	1	0	0 $B_{\text{K}} = 0.25$
ψ_6	$b_{\text{S},1}$	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1 $B_{\text{S}} = 0.25$
ψ_7	$v_{1,1}$	1	-1	-1	0	0	0	0	0	0	0	0	0	0	0	0	0	0 $K_1 = 10^{4.57}$
ψ_8	$v_{2,1}$	1	0	0	0	-1	1	0	0	0	0	0	0	0	0	0	0	0 $K_2 = 10^{-0.82}$
ψ_9	$v_{3,1}$	0	0	0	0	0	1	1	-1	0	0	0	0	0	0	0	0	0 $K_3 = 10^{-0.82}$
ψ_{10}	$v_{4,1}$	0	0	-1	1	0	-1	0	0	0	0	0	0	0	0	0	0	0 $K_4 = 10^{1.24}$
ψ_{11}	$v_{5,1}$	0	0	0	0	0	1	0	0	1	-1	0	0	0	0	0	0	0 $K_5 = 10^{-0.6}$
ψ_{12}	$v_{6,1}$	0	0	-1	0	0	0	0	0	1	0	1	-1	0	0	0	0	0 $K_6 = 10^{4.06}$
ψ_{13}	$v_{7,1}$	0	0	-1	0	0	0	1	0	0	0	1	0	-1	0	0	0	0 $K_7 = 10^{4.06}$
ψ_{14}	$v_{8,1}$	1	0	-1	0	0	0	0	0	0	0	1	0	0	-1	0	0	0 $K_8 = 10^{4.06}$
ψ_{15}	$v_{9,1}$	0	0	0	0	0	0	0	0	1	0	1	0	0	0	-1	0	0 $K_9 = 10^{-0.3}$
ψ_{16}	$v_{10,1}$	0	0	0	0	0	1	0	0	0	0	1	0	0	0	0	-1	0 $K_{10} = 10^{-0.3}$
ψ_{17}	$v_{11,1}$	1	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	-1 $K_{11} = 10^{-0.3}$

Table 2. Computed equilibria in the system NH_4Cl – NaCl – KCl – NaHSO_4 – H_2O at 300°C

	A	B	C	D	E	F
NH_4^+	0.105	8.48×10^{-2}	---	8.75×10^{-2}	1.83×10^{-1}	0.326
NH_4OH	1.61×10^{-3}	3.70×10^{-3}	---	2.01×10^{-3}	1.29×10^{-3}	1.21
H^+	1.76×10^{-3}	6.17×10^{-4}	---	1.17×10^{-3}	3.18×10^{-3}	0.326
HCl	6.40×10^{-3}	3.09×10^{-3}	---	4.76×10^{-3}	2.60×10^{-3}	1.21
NH_4Cl	0.145	1.61×10^{-1}	---	1.35×10^{-1}	5.72×10^{-2}	1.21
Cl^-	0.210	2.88×10^{-1}	---	2.33×10^{-1}	5.37×10^{-1}	0.326
Na^+	0.105	8.61×10^{-2}	---	1.76×10^{-1}	3.69×10^{-1}	0.326
NaCl	0.146	1.64×10^{-1}	---	2.72×10^{-1}	1.15×10^{-1}	1.21
K^+	0.105	1.16×10^{-1}	---	1.13×10^{-1}	2.03×10^{-1}	0.326
KCl	0.146	1.33×10^{-1}	---	1.05×10^{-1}	3.81×10^{-2}	1.21
HSO_4^-	---	---	6.20×10^{-4}	1.40×10^{-1}	2.17×10^{-1}	0.326
KSO_4^-	---	---	1.02×10^{-5}	1.17×10^{-3}	1.21×10^{-3}	0.326
NaSO_4^-	---	---	7.54×10^{-6}	1.84×10^{-3}	2.19×10^{-3}	0.326
NH_4SO_4^-	---	---	7.42×10^{-6}	9.13×10^{-4}	1.09×10^{-3}	0.326
KHSO_4	---	---	1.44×10^{-4}	3.16×10^{-2}	7.71×10^{-3}	1.21
NaHSO_4	---	---	1.06×10^{-4}	4.95×10^{-2}	1.40×10^{-2}	1.21
NH_4HSO_4	---	---	1.05×10^{-4}	2.45×10^{-2}	6.97×10^{-3}	1.21

A and B: Initial estimates and equilibrium molalities respectively, in the system 0.25 m NH_4Cl –0.25 m NaCl –0.25 m KCl – H_2O at 300°C , assuming all $\gamma_i = 1.0$.

C: Equilibrium molalities of sulfur species in the system 0.25 m NH_4Cl –0.25 m NaCl –0.25 m KCl –0.001 m NaHSO_4 – H_2O at 300°C assuming all $\gamma_i = 1.0$.

D: Equilibrium molalities in the system 0.25 m NH_4Cl –0.25 m NaCl –0.25 m KCl –0.25 m NaHSO_4 – H_2O at 300°C , assuming all $\gamma_i = 1.0$.

E and F: Equilibrium molalities and molal activity coefficients, respectively, in the system 0.25 m NH_4Cl –0.25 m NaCl –0.25 m KCl –0.25 m NaHSO_4 – H_2O at 300°C .

K_{NaCl} ; $K_{\text{NaSO}_4^-}$ and $K_{\text{NH}_4\text{SO}_4^-}$ by $K_{\text{KSO}_4^-}$; and K_{NaHSO_4} and $K_{\text{NH}_4\text{HSO}_4}$ by K_{KHSO_4} .

It is unlikely that initial estimates of all 17 species concentrations would be sufficiently accurate to permit a simple Newton–Raphson solution to this problem. Selecting instead the subsystem 0.25 m NH_4Cl –0.25 m NaCl –0.25 m KCl – H_2O eliminates equations (23), (29)–(34), and all sulfur-bearing terms from the remaining 10 equations. Note that the mass balance on total sodium falls to $B_{\text{Na}} = 0.25$ m. The resultant 10 equations can now be solved by Newton–Raphson iteration and a reasonable initial guess. Initial guesses and calculated equilibrium concentrations are listed in Table 2, columns A and B, respectively. Convergence to 0.1% precision required 6 iterations. For this calculation, all activity coefficients, γ_i , were set equal to unity.

The next step uses the curve crawler technique to solve for all concentrations in the full 5-component system. First, concentrations of all sulfur species in the system 0.25 m NH_4Cl –0.25 m NaCl –0.25 m KCl –0.001 m NaHSO_4 – H_2O are estimated from equilibrium molalities in the reduced

4-component system (Table 2, column B):

$$(\text{KSO}_4^-) = \frac{(\text{K}^+)(\text{HSO}_4^-)}{10^{4.06}(\text{H}^+)} \quad (35)$$

$$(\text{NaSO}_4^-) = \frac{(\text{Na}^+)(\text{HSO}_4^-)}{10^{4.06}(\text{H}^+)} \quad (36)$$

$$(\text{NH}_4\text{SO}_4^-) = \frac{(\text{NH}_4^+)(\text{HSO}_4^-)}{10^{4.06}(\text{H}^+)} \quad (37)$$

$$(\text{KHSO}_4) = \frac{(\text{K}^+)(\text{HSO}_4^-)}{10^{-0.3}} \quad (38)$$

$$(\text{NaHSO}_4) = \frac{(\text{Na}^+)(\text{HSO}_4^-)}{10^{-0.3}} \quad (39)$$

$$(\text{NH}_4\text{HSO}_4) = \frac{(\text{NH}_4^+)(\text{HSO}_4^-)}{10^{-0.3}} \quad (40)$$

$$[\text{HSO}_4^-] = 0.001 - [\text{KSO}_4^-] - [\text{NaSO}_4^-] - [\text{NH}_4\text{SO}_4^-] - [\text{KHSO}_4] - [\text{NaHSO}_4] - [\text{NH}_4\text{HSO}_4]. \quad (41)$$

Again, activities are set equal to concentrations. Equations (35)–(41) may be solved by Gauss–Seidel iteration on (HSO_4^-) . Results for the 7 sulfur species considered are listed in Table 2, column C; concentrations of the other original species (Table 2, column B) remain essentially unchanged.

The next step adds successive 0.001 m increments of the NaHSO_4 component to the system. All 17 equations (18)–(34) may now be solved by Newton–Raphson iteration, using calculated molalities at one increment as initial guesses for the next. Thus, concentrations in Table 2, columns B and C, are used to compute a new set of molalities at $[\text{NaHSO}_4] = 0.002$ m. These, in turn, predict new concentrations of all species at $[\text{NaHSO}_4] = 0.003$ m, and so on to $[\text{NaHSO}_4] = 0.25$ m. Activity coefficients are again set equal to unity. Final concentrations are listed in Table 2, column D.

The final step in the calculation imposes an activity coefficient correction on the computed molalities. The subject of *a priori* activity corrections for electrolyte solutions is treated at length in CRERAR and BARNES (in preparation). The model introduced for illustrative purposes here is derived and tested by Crerar and Barnes, and represents one among many possible approaches to the problem. Because of the assumptions required in its present application, it should be considered only a first approximation.

First, the uncorrected molalities in Table 2, column C, are used to estimate specific ion activity coefficients. These molalities may first be corrected for the loss of free solvent molecules to ion hydration spheres:

$$m_{ah}^i = \frac{55.51 m_i}{55.51 - \sum h_i m_i}, \quad (42)$$

where m_i^i is the molality of the i th species corrected for ion association as listed in Table 2, column D; m_{ah}^i is the molality of the same species corrected for both hydration and ion association; and h_i represents the average moles of solvent hydrating one mole of solute species i . Next, each m_{ah}^i is converted to an association- and hydration-corrected molarity, C_{ah}^i :

$$C_{ah}^i = m_{ah}^i \left[\frac{1000 \rho}{1000 + \sum G^* m^*} \right]. \quad (43)$$

Here, ρ is solution density (g/ml), and $\sum G^* m^*$ is the summed products of gram molecular weights and stoichiometric molalities for all solute components.

A mole-fraction specific-ion activity coefficient may now be computed from the complete Debye–Hückel equation:

$$\log f_e^i = \frac{-C(Z_i)^2 \sqrt{I}}{(DT)^{3/2} \left[1 + \frac{E\tilde{a}\sqrt{I}}{(DT)^{1/2}} \right]}, \quad (44)$$

where Z_i is species valence, D is the dielectric constant of water at temperature (AKERLOF and OSHRY, 1950); \tilde{a} is the empirical Debye–Hückel ‘distance of closest approach’; $E = 50.29158$, and $C = 1.8248 \times 10^6$ (HAMER,

1968). I is the conventional ionic strength,

$$I = \frac{1}{2} \sum_i (Z_i)^2 C_{ah}^i.$$

The mole-fractional activity coefficient f_e^i corrects for long-range electrostatic ion–ion interactions. It is converted to molal units by the relation

$$\log \gamma_e^i = \log f_e^i - \log \left[\frac{1000 + G_{\text{H}_2\text{O}} \sum m_{ah}^i}{1000} \right], \quad (44a)$$

where $G_{\text{H}_2\text{O}}$ is the gram molecular weight of the solvent, water, and γ_e^i is the molal specific ion activity coefficient correcting for electrostatic interaction. It may be converted to a complete molal activity coefficient, γ_{eh}^i , correcting for both hydration and electrostatic interaction by the relation,

$$\gamma_{eh}^i = \frac{\gamma_e^i m_{ah}^i}{m_a^i}. \quad (45)$$

The corresponding coefficient, γ_h^i , correcting the i th species for hydration alone is given by

$$\gamma_h^i = \frac{\gamma_{eh}^i}{\gamma_e^i} = \frac{m_{ah}^i}{m_a^i}. \quad (46)$$

With uncharged molecular species, it is assumed that electrostatic interactions are negligible ($\gamma_e^i = 1.0$), and that the complete activity coefficient is given by γ_h^i alone.

For illustrative purposes, the system density ρ and Debye–Hückel \tilde{a} parameter are here approximated by the corresponding values for 1.0 m NaCl at 300°C (0.772 g/ml, HAAS, 1970; and 3.0 Å, LIU and LINDSAY, 1972, respectively). The hydration number, h_i , of neutral molecules is approximated by the value 2.0 for NaCl^0 (QUIST and MARSHALL, 1968), and the hydration number of cations and anions, grouped as pairs, is approximated by 10.0—the total hydration of $\text{Na}^+ + \text{Cl}^-$ at 300°C (YEATTS and MARSHALL, 1972).

The molalities in Table 2, column D, were calculated on the assumption that all $\gamma_i = 1.0$. These concentrations may now be used in equations (42)–(46) for first estimates of γ_{eh}^i and γ_h^i —the activity coefficients of ions and neutral species, respectively. Using these γ_i and m_i as initial estimates, the complete system of equations (18)–(34) may be solved by Newton–Raphson iteration for a new set of concentrations. A corresponding set of new activity coefficients is then calculated from equations (42)–(46) and the process is repeated to satisfactory convergence in all γ_i and m_i . Because successive γ_i change considerably during the first few iterations, and might otherwise diverge, each γ_i is changed by stepwise increments using relationship (17), and setting $\delta = 0.1$; in other words, only 10% of the predicted change in γ_i is used at each step.

Final molalities, m_i , and molal activity coefficients, γ_i , are listed in Table 2, column E, for the full 5-component system. Activities of the less important species H_2SO_4 , SO_4^{2-} , OH^- , NaOH , and KOH may be computed using the above γ_i , m_i values and appropriate equilibrium constants. The inclusion of these additional species has negligible effect on the initial charge and mass balances (18)–(23), justifying the original assumption.

SUMMARY

The equilibrium activities and concentrations of species in multicomponent systems may be calculated

given (1) total concentrations of each component or of selected elements, and (2) the appropriate minimum number of independent equilibrium constants. Because the method does not require complete free-energy data for all species, it may often apply where optimization techniques cannot. Although free-energy data are currently incomplete for many rock-water systems of geochemical interest, equilibrium constants are often either known, or may be estimated for important reactions within many such systems. Indeed, much of modern experimental geochemistry has been concerned, either directly or indirectly, with the compilation and measurement of such equilibrium constants. As interest turns toward multicomponent equilibria of ever increasing complexity, computer-based techniques such as those considered here should find important applications within the geosciences.

Acknowledgements—It is a pleasure to thank N. FRAZER, S. MACRAE, P. MALIN, R. PHINNEY, and R. STRELITZ for their kind assistance. Research supported by the Earth Sciences Section, National Science Foundation, NSF Grant DES75-14929.

REFERENCES

- ACTON F. S. (1970) *Numerical Methods that Work*, 541 pp. Harper & Row.
- AKERLOF G. C. and OSHRY H. I. (1950) The dielectric constant of water at high temperatures and in equilibrium with its vapor. *J. Amer. Chem. Soc.* **72**, 2844–2847.
- BARNES H. L. (in press) Applied hydrothermal geochemistry. In *International Conference on High-Temperature High-Pressure Electrochemistry in Aqueous Solutions*, Vol. 4. Natl. Assoc. Corrosion Engineers, D.S.A.
- BARNES H. L., HELGESON H. C. and ELLIS A. J. (1966) Ionization constants in aqueous solutions. In *Handbook of Physical Constants*, (editor S. P. Clark, Jr.), pp. 401–413. *Geol. Soc. Amer. Mem.* **97**.
- BLACKBURN T. R. (1969) *A Chemistry of Solutions*, 220 pp. Holt, Rinehart & Winston.
- BOGGS P. T. (1971) The solution of nonlinear systems of equations by A-stable integration techniques. *SIAM J. Numer. Anal.* **8**, 767–785.
- BRINKLEY S. R. (1947) Calculation of the equilibrium composition of systems of many constituents. *J. Chem. Phys.* **15**, 107–110.
- BROWN K. M. (1969) A quadratically convergent Newton-like method based upon Gaussian elimination. *SIAM J. Numer. Anal.* **6**, 560–569.
- BUTLER J. N. (1964) *Ionic Equilibrium. A Mathematical Approach*, 547 pp. Addison-Wesley.
- CARNAHAN B. and WILKES J. O. (1973) *Digital Computing and Numerical Methods*, 477 pp. Wiley.
- CRERAR D. A. and ANDERSON G. M. (1971) Solubility and solvation reactions of quartz in dilute hydrothermal solutions. *Chem. Geol.* **8**, 107–122.
- CRERAR D. A. and BARNES H. L. (in preparation) *The Estimation of Activity Coefficients of Electrolyte Solutions and Related Thermodynamic Models*. Penn. State Studies Monograph Series, Penn. State Univ. Press.
- FELDMAN H. F., SIMONS W. H. and BIENSTOCK D. (1969) Calculating equilibrium compositions of multicomponent, multiphase, chemical reacting systems. *U.S. Bur. Mines Rep. Invest.* **7257**, 22 pp.
- FISHER J. R. and BARNES H. L. (1972) The ion-product constant of water to 350°. *J. Phys. Chem.* **76**, 90–99.
- FREISER H. and FERNANDO Q. (1966) *Ionic Equilibria in Analytical Chemistry*, 338 pp. Wiley.
- HAAS J. L., JR. (1970) An equation for the density of vapor-saturated NaCl–H₂O solutions from 75° to 325°C. *Amer. J. Sci.* **269**, 489–493.
- HAMER W. J. (1968) Theoretical mean activity coefficients of strong electrolytes in aqueous solutions from 0 to 100°C. *National Standard Reference Data Series—Nat. Bur. Std.* **24**, 271 pp. U.S. Government Printing Office.
- HELGESON H. C. (1964) *Complexing and Hydrothermal Ore Deposition*, pp. 56–64. Macmillan.
- HELGESON H. C. (1968) Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solutions—I. Thermodynamic relations. *Geochim. Cosmochim. Acta* **32**, 853–877.
- HELGESON H. C. (1969) Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *Amer. J. Sci.* **267**, 729–804.
- HELGESON H. C. (1970) A chemical and thermodynamic model of ore deposition in hydrothermal systems. *Mineral. Soc. Amer. Spec. Paper* **3**, 155–186.
- HELGESON H. C. and JAMES W. R. (1968) Activity coefficients in concentrated electrolyte solutions at elevated temperatures. *Abstracts of Papers, 155th Nat. Meeting, Amer. Chem. Soc.*, April, 1968, San Francisco, California, S-130.
- HILDEBRAND F. B. (1956) *Introduction to Numerical Methods*, pp. 447–453. McGraw-Hill.
- HOLLOWAY J. R. and REESE R. L. (1974) The generation of N₂–CO₂–H₂O fluids for use in hydrothermal experimentation I. Experimental method and equilibrium calculations in the C–O–H–N system. *Amer. Mineral.* **59**, 587–597.
- KANDINER H. J. and BRINKLEY S. R. (1950) Calculation of complex equilibrium relations. *Ind. Eng. Chem.* **42**, 850–855.
- KARPOV I. K. and KAZ'MIN L. A. (1972) Calculation of geochemical equilibria in heterogeneous multicomponent systems. *Geochem. Int.* **9**, 252–262.
- LIU C. T. and LINDSAY W. T. (1972) Thermodynamics of sodium chloride solutions at high temperatures. *J. Solution Chem.* **1**, 45–69.
- OHMOTO H. (1972) Systematics of sulfur and carbon isotopes in hydrothermal ore deposits. *Econ. Geol.* **67**, 551–578.
- QUIST A. S. and MARSHALL W. L. (1968) Electrical conductances of aqueous sodium chloride solutions from 0 to 800° and at pressures to 4000 bars. *J. Phys. Chem.* **72**, 684–703.
- REESE R. L. (1973) Computed solid-vapor equilibria in multicomponent systems. M.S. Thesis, Arizona State University, Tempe, Arizona.
- SILLÉN L. G. and MARTELL A. E. (1964) *Stability Constants of Metal-Ion Complexes*, 2nd edition, *Chem. Soc. London Spec. Publ.* **17**, 754 pp.
- SWEETON F. H., MESMER R. E. and BAES C. F., JR. (1974) Acidity measurements at elevated temperatures. VII. Dissociation of water. *J. Solution Chem.* **3**, 191–214.
- THOMPSON J. B., JR. (1967) Thermodynamic properties of simple solutions. In *Researches in Geochemistry*, (editor P. ABELSON), Vol. 2, pp. 340–361. Wiley.

- TRUEDELL A. H. and JONES B. F. (1969) Ion association in natural brines. *Chem. Geol.* **4**, 51–62.
- TRUEDELL A. H. and JONES B. F. (1974) WATEQ, a computer program for calculating chemical equilibria of natural waters. *J. Res. U.S. Geol. Surv.*, **2**, 233–248.
- VAN ZEGGEREN F. and STOREY S. H. (1970) *The Computation of Chemical Equilibria*, 176 pp. Cambridge University Press.
- YEATTS L. B. and MARSHALL W. L. (1972) Electrical conductance and ionization behaviour of sodium chloride in dioxane–water solutions at 300° and pressures to 4000 bars. *J. Phys. Chem.* **76**, 1053–1062.